

PREFACE

I would like to thank my co-advisor Prof. Dr. Ayşe Erdem-Şenatalar and Prof. Dr. Ferdi Schüth; to Prof. Erdem-Şenatalar for her unlimited encouragement, motivation, patience and help, and to Prof. Schüth for providing me with the opportunity to work at Mülheim, and his continuous support.

**SYNTHESIS AND CATALYTIC APPLICATIONS OF
CROSSLINKED COLLOIDAL ZEOLITE
CATALYSTS**

I would also like to thank Dr. Wolfgang Schmidt, Dr. Bodo Zbrowius, Dr. Chia-min Yang, Dr. Sobyun Park, Dr. Claudia Weidenbaler and Dipl. Chem. Ing. Stefan Olejnik for their support, in expanding my knowledge and finding practical solutions to my equipment problems.

Very special thanks go to Dipl. Chem. Inga Ritzkopf and Dr. Mika Linden, for their help, friendship and unlimited support.

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Demirbaş No: 115.363

Küt. Giriş No : ...

Ph.D. Thesis by

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Date of submission : 25 June 2004

Date of defence examination: 6 October 2004

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001153630014

OCTOBER 2004

PREFACE

I would like to thank my co-advisors; Prof. Dr. Ayşe Erdem-Şenatalar and Prof. Dr. Ferdi Schüth; to Prof. Erdem-Şenatalar for her unlimited encouragement, motivation, patience and help, and to Prof. Schüth for providing me with the opportunity of working at the laboratories of the Max-Planck Institute at Mülheim, and his continuous support and guidance.

I would also like to thank Dr. Wolfgang Schmidt, Dr. Bodo Zibrowius, Dr. Chia-min Yang, Dr. Sohyun Park, Dr. Claudia Weidenthaler and Dipl. Chem. Eng. Stefan Olejnik for their support, in expanding my knowledge and finding practical solutions to my equipment problems.

Very special thanks go to Dipl. Chem. Alberto Martinez-Joaristi, Dipl. Chem. Inga Ritzkopf and Dr. Mika Linden, for editing this thesis, for their help, friendship and unlimited support.

All friends in our group especially, Dr. Özlem Weiss, Dipl. Chem. Sascha Vukojevic, Dipl. Chem. Mamatha Mayanna, Dipl. Chem. Piotr Krawiec, Dipl. Chem. Pablo Arnal, Dipl. Chem. Seher Yalçın, deserve a special word of thanks for pleasant memories and for helping me enjoy life and learn German. I also want to thank my friends in İstanbul Technical University, Dr. Çiğdem Atalay-Oral, Chem. Eng. Özlem Andaç, Chem. Eng. Serhat Şen for their support.

Şahin-Sevim Söylemez have been like a family to me and deserve special acknowledgement. I will always treasure their help and friendship. Special thanks go to Helga Wasilewski for her help, attention and friendship.

I am grateful to my parents and sisters for their love, understanding and continuous support. Their many sacrifices will not be forgotten. A very special thanks goes to my little daughter Zeynep, for her support, existence and her patience during my work.

I am grateful to the Max-Planck Institute für Kohlenforschung, Mülheim, for the financial support provided to make this study possible.

Finally, my deepest thanks go to my husband and my best friend, Tahsin İlhan. I could not have done it without his support.

Yasemin İlhan

October, 2004

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X-ray diffraction, TEM, ^{13}C MAS NMR, and ^{29}Si MAS NMR techniques. Crosslinked catalysts were compared with a commercial ZSM-5 sample, and with crosslinked Aerosil, for their performances in the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam.

All solid products recovered from the colloidal solutions without crosslinking were X-ray amorphous with the exception of silicalite-1 aged at 363 K. Samples were also analysed by using ^{13}C MAS NMR and TEM techniques, however, none of the ZSM-5 samples showed any crystallinity. On the other hand, it was documented by XRD and TEM analyses that the Silicalite-1 samples aged at 363 K for 24 hours were crystalline. Since the ZSM-5 samples did not exhibit any crystallinity, they are called ZSM-5 (prep.) indicating that they were prepared from a solution, which would result in the formation of ZSM-5 crystals under suitable conditions.

SYNTHESIS AND CATALYTIC APPLICATIONS OF CROSSLINKED COLLOIDAL ZEOLITE CATALYSTS

SUMMARY

Colloidal zeolites, with particle sizes in the range of about 10 to 100 nm, which have very high external surface areas, have been extensively investigated in the last decade. It has been suggested that even smaller entities of several nanometers in size exist in synthesis solutions under certain conditions.

Small particle sized catalysts are known to be advantageous for some reactions due to their high external surface areas. Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam can be given as an example for these reactions. If catalyst samples prepared by crosslinking the smallest entities are used, it might be possible to have an extremely high surface area catalyst, which might be useful for the Beckmann rearrangement reaction.

In this study, it is aimed to synthesize colloidal sized zeolite catalysts, crosslinked with a silicone linker, and to characterize and test these catalysts in the Beckmann rearrangement reaction. Investigation of the synthesis parameters such as aging time, aging temperature, linker amount and their effects on the catalyst characteristics are also within the scope of this study.

Thus, in this study, colloidal Silicalite-1, TS-1, and ZSM-5 samples were synthesized and crosslinked with 1,7-dichloro-octamethyl-tetrasiloxane. The effects of preparation parameters such as aging time, aging temperature and linker amount on the characteristics of the samples were investigated by N_2 adsorption, X-ray Diffraction, TEM, ^{13}C MAS NMR, and ^{29}Si MAS NMR techniques. Crosslinked catalysts were compared with a commercial ZSM-5 sample, and with crosslinked Aerosil, for their performances in the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam.

All solid products recovered from the colloidal solutions without crosslinking were X-ray amorphous with the exception of silicalite-1 aged at 363 K. Samples were also analysed by using ^{13}C MAS NMR and TEM techniques, however, none of the ZSM-5 samples showed any crystallinity. On the other hand, it was documented by XRD and TEM analyses that the Silicalite-1 samples aged at 363 K for 24 hours were crystalline. Since the ZSM-5 samples did not exhibit any crystallinity, they are called ZSM-5 (prep.) indicating that they were prepared from a solution, which would result in the formation of ZSM-5 crystals under suitable conditions.

It was possible to observe that crosslinking was indeed achieved by using N_2 adsorption analysis. Crosslinking invariably produced a higher porosity, with the additional pores forming predominantly in the mesopore range as was shown by N_2 adsorption. Spacer molecules with different lengths were also tried but any pronounced effect on pore size distribution could not be observed.

^{29}Si MAS NMR analyses also provided significant evidence on the interaction of the crosslinker with the silanols on the zeolite surfaces. After crosslinking, the concentration of Q^2 and Q^3 groups decreased, while the intensity of the Q^4 group increased. This was ascribed to the reaction between the silanol groups of the zeolite and the silicone crosslinker. ^{29}Si MAS NMR results made it possible to follow the extent of consumption during the crosslinking reaction, of the silanols on the zeolite surfaces, which are desirable for the Beckmann rearrangement reaction.

In all cases, these crosslinked materials were found to have substantially better catalytic performance than the non-crosslinked samples and than a commercial ZSM-5 catalyst (ALSI-PENTA® SH-27, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23\text{-}27$). About tenfold increase of the caprolactam yield was typical for many of the crosslinked colloidal zeolites, and typically, the crosslinked materials performed better than the commercial ZSM-5.

It was observed that, aging temperature had a positive effect on the catalytic performances of all materials. Although increasing the linker amount above a certain level did not increase the reaction rates of ZSM-5 (prep.) samples further, the stabilities of the samples crosslinked with large amounts of linker were higher resulting in slower deactivation rates.

The best performance was obtained by the catalysts prepared by crosslinking of Silicalite-1 aged at 363 K. A strong relationship was observed to exist between the reaction rates and mesopore areas of the crosslinked Silicalite-1 samples aged at this temperature. Reaction rate increased parallel to the increase in the mesopore area. Reaction rates were related to the mesopore areas for the samples aged at room temperature too. The only difference between the samples aged at 363 K and room temperature was in their behaviour when linked with high amounts of linker. For the samples aged at 363 K, mesopore areas and the reaction rates of the samples continued to increase at high linker amounts, while for those aged at room temperature, mesopore area and reaction rate started to decrease when a certain level of linker amount was exceeded.

There was no clear relation between the reaction rates and mesopore areas for ZSM-5 (prep.) samples, if they were calcined and acid treated (CAT) or calcined and ion exchanged (CIE) before the catalytic tests. On the other hand, for the samples, which were acid treated without calcination (UAT), the reaction rates and the mesopore areas increased after crosslinking up to a certain amount of linker usage. Further increase in linker amount did not improve the reaction rate while it decreased the mesoporosity.

Aerosil crosslinked using the same linker did not exhibit any activity in the Beckmann reaction, indicating that the crosslinker had no catalytic activity on its own and that all catalytic activity originated from the zeolite surfaces.

Effect of crosslinking was also studied for TS-1 samples. Very high mesopore area was detected for the TS-1 samples crosslinked with large amounts of linker. Crosslinked TS-1 samples were tested both in the Beckmann rearrangement and the epoxidation of propene reactions. Although these samples, in general, did not exhibit a significant catalytic activity in the epoxidation reaction, the TS-1 sample crosslinked with a large amount of linker had a high catalytic activity in the Beckmann rearrangement reaction. Another advantage of crosslinked TS-1 was its long lifetime in the Beckmann rearrangement reaction. The catalyst life was longer in case of TS-1 samples crosslinked with large amounts of linker. After 4 h of TOS, almost no decrease in the reaction rate was observed for these catalysts, whereas the rates obtained with ZSM-5 and Silicalite-1 samples decreased by 49 % and 48 %, respectively, under similar conditions.

The selectivity toward caprolactam varied for the different materials, but was mostly above 65 %. The higher reactivity of the crosslinked materials was attributed to improved mass transfer and a high concentration of readily accessible catalytic sites on or close to the external surfaces of the colloidal zeolite particles.

Tanecik boyutları küçük, dolayısıyla dış yüzey alanları geniş olan kolloidal boyuttaki katalizörlerin kullanımına, dış yüzeylerindeki yaygın asit merkezlerinde yürüten bazı reaksiyonlarda etkin olduğu bilinmektedir. Sikloheksanon oksim'in Beckmann reaksiyonu ile ϵ -kaprolaktama dönüştürülmesi bunlara örnektir. Zeolit sentez çözeltilerinde bulunduğu öngörülen küçük zeolit parçacıklarının bir bağlayıcı yardımıyla çapraz bağlanması durumunda elde edilecek dış yüzey alanı çok geniş olan katalizörlerin Beckmann reaksiyonunda etkin olması beklenmektedir.

Bu çalışmada, kolloidal zeolit taneciklerinin çapraz bağlanmasıyla hazırlanan katalizörlerin Beckmann reaksiyonu gibi geniş dış yüzey alanı gerektiren reaksiyonlarda kullanılabilirliği incelenmiştir. Bu kapsamda, bağlayıcı miktarı, yaşlandırma süresi, ve yaşlandırma sıcaklığının katalizörün özellikleri üzerindeki etkilerinin incelenmesi de hedeflenmiştir.

Kolloidal ZSM-5, Silikalit-1 ve TS-1 örnekleri bilinen prosedürlere göre sentezlenmiş ve 1,7-dikloro-oktametil-adenasikolan ile çapraz bağlanmıştır. Bağlayıcı miktarı, yaşlandırma süresi ve yaşlandırma sıcaklığının katalizör özellikleri üzerine etkileri incelenmiştir. Örnekler N_2 adsorpsiyonu, X-ışın kırınımı, TEM, ^{13}C MAS NMR, ^{29}Si MAS NMR teknikleri ve Beckmann reaksiyonu ile karakterize edilmiştir. Çapraz bağlanmış örnekler, Beckmann reaksiyonundaki performansları açısından ticari bir ZSM-5 örneği ile ve çapraz bağlanmış Aerosil ile karşılaştırılmıştır.

Yapılan XRD analizleri ile ZSM-5 ve oda sıcaklığında yaşlandırılan Silikalit-1 örneklerinde kristallinite görülenmemiştir. Örnekler, XRD analizinin yanı sıra, TEM ve ^{29}Si MAS NMR teknikleri ile de incelenmiş, ancak ZSM-5 örneklerinin hiçbirinde kristalin oluşumlar gözlemlenmemiştir. Buna karşın, 363 K'da 24 saat yaşlandırılan Silikalit-1 örneklerinin kristalin bir yapıya sahip olduğu gerek XRD, gerekse TEM analizleri yardımıyla belirlenmiştir. ZSM-5 örneklerinin hiçbirinde kristal yapı

ÇAPRAZ BAĞLI KOLLOİDAL ZEOLİT KATALİZÖRLERİN SENTEZİ VE KATALİTİK UYGULAMALARI

ÖZET

Kolloidal zeolitler yaklaşık on nanometreden yüz nanometreye kadar değişen boyutları ve sahip oldukları geniş dış yüzey alanlarıyla son on yılın ilginç bir araştırma konusudur. Konuyla ilgili literatürde belirli koşullarda hazırlanan zeolit sentez çözeltisinin içinde birkaç nanometre boyutunda zeolit parçacıklarının dahi bulunabileceği belirtilmektedir.

Tanecik boyutları küçük, dolayısıyla dış yüzey alanları geniş olan kolloidal boyuttaki katalizörlerin kullanımının, dış yüzeylerdeki zayıf asit merkezlerde yürüyen bazı reaksiyonlarda etkin olduğu bilinmektedir. Sikloheksanon oksim'in Beckmann reaksiyonu ile ϵ -kaprolaktama dönüşümü bunlara örnektir. Zeolit sentez çözeltisinde bulunduğu öngörülen küçük zeolit parçacıklarının bir bağlayıcı yardımıyla çapraz bağlanması durumunda elde edilecek dış yüzey alanı çok geniş olan katalizörlerin Beckmann reaksiyonunda etkin olması beklenmektedir.

Bu çalışmada, kolloidal zeolit taneciklerinin çapraz bağlanmasıyla hazırlanan katalizörlerin Beckmann reaksiyonu gibi geniş dış yüzey alanı gerektiren reaksiyonlarda kullanılabilirliği incelenmiştir. Bu kapsamda, bağlayıcı miktarı, yaşlandırma süresi, ve yaşlandırma sıcaklığının katalizörün özellikleri üzerindeki etkilerinin incelenmesi de hedeflenmiştir.

Kolloidal ZSM-5, Silikalit-1 ve TS-1 örnekleri bilinen prosedürlere göre sentezlenmiş ve 1,7-dikloro-oktametil-tetrasiloksan ile çapraz bağlanmıştır. Bağlayıcı miktarı, yaşlandırma süresi ve yaşlandırma sıcaklığının katalizör özellikleri üzerine etkileri incelenmiştir. Örnekler N_2 adsorpsiyonu, X-ışını kırınımı, TEM, ^{13}C MAS NMR, ^{29}Si MAS NMR teknikleri ve Beckmann reaksiyonu ile karakterize edilmiştir. Çapraz bağlanmış örnekler, Beckmann reaksiyonundaki performansları açısından ticari bir ZSM-5 örneği ile ve çapraz bağlanmış Aerosil ile karşılaştırılmıştır.

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gözlenemediğinden, bu örnekler ZSM-5 (prep.) olarak adlandırılmıştır. Bu terim söz konusu sentez çözeltisinden uygun koşullarda ZSM-5 kristallerinin hazırlanabildiğini, ancak bu çalışma koşullarında kristalin örnekler elde edilemediğini ifade etmektedir.

Çapraz bağlanmanın gerçekleştiği adsorpsiyon izotermelerindeki değişimlerden izlenebilmiştir. Söz konusu izotermeler, çapraz bağlamanın mikrogözenek yapısına ek olarak bir de mezogözenek yapı oluşturduğunu göstermiştir. Kullanılan bağlayıcının zincir uzunluğunun etkisi de incelenmiş, ancak gözenek boyut dağılımı üzerinde belirgin bir etki gözlenmemiştir.

Silikalit-1 örnekleri için yapılan ^{29}Si MAS NMR analizleri yardımıyla çapraz bağlama sırasında bağlayıcının zeolit yüzeylerindeki silanol gruplarıyla etkileşimi izlenebilmiştir. Bağlayıcının Q^2 ve Q^3 gruplarıyla tepkimeye girdiği ve bu grupların konsantrasyonlarının azaldığı, buna karşın Q^4 grup konsantrasyonunun arttığı görülmüştür. Q^2 ve Q^3 gruplarındaki azalma ile Q^4 grubundaki artış çapraz bağlamanın gerçekleştiğinin kanıtıdır ve çapraz bağlama işleminin Beckmann dönüşümü tepkimesinde etkin olduğu düşünülen silanol gruplarının ne kadarını tükettiğinin izlenebilmesini sağlamıştır.

Reaksiyon sonuçları değerlendirildiğinde, her durumda, çapraz bağlı örneklerin bağlanmamış olanlara ve ticari ZSM-5 örneğine (ALSI PENTA ®SH-27, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23-27$) göre belirgin olarak daha iyi katalitik performans gösterdikleri gözlenmiştir. Çoğu bağlanmış örnek için kaprolaktam veriminde yaklaşık on kata varan artışlar saptanmıştır.

Tüm örnekler için yaşlandırma sıcaklığının katalitik aktiviteyi olumlu etkilediği gözlenmiştir. ZSM-5 (prep.) örneklerinde bağlayıcı miktarının belli bir değerin üzerinde artırılması sonucunda reaksiyon hızında bir artış kaydedilmemiş, ancak bu örneklerin deaktivasyon hızlarının diğerlerine göre daha az olduğu belirlenmiştir.

En iyi performans 363 K'de yaşlandırılmış Silikalit-1 örneğinin bağlanmasıyla elde edilmiştir. Bu sıcaklıkta bağlanmış Silikalit-1 örneklerinde mezogözenek alanı ve katalitik aktivite arasında kuvvetli bir ilişki olduğu görülmüştür. Mezogözenek alanındaki artışa paralel olarak reaksiyon hızı da artmıştır. Oda sıcaklığında yaşlandırılan örneklerde de mezogözenek alanları ve reaksiyon hızları paralellik göstermiştir. 363 K'de ve oda sıcaklığında yaşlandırılan örnekler arasındaki fark yalnızca yüksek miktarda bağlayıcı kullanıldığında ortaya çıkmıştır. 363 K'de yaşlandırılan örneklerde bağlayıcı miktarının artmasıyla mezogözenek alanı ve reaksiyon hızı artmaya devam etmiş, oda sıcaklığında yaşlandırılan örneklerde ise belli bir bağlayıcı miktarının üzerinde mezogözenek alanının ve reaksiyon hızının düşmeye başladığı gözlenmiştir.

ZSM-5 (prep.) örneklerinde ise örneklerin kalsine edildiği ve asitle işlem yapıldığı (CAT) veya kalsine edilerek iyon değiştirildiği (CIE) durumlarda reaksiyon hızları ve mezogözenek alanları arasındaki ilişkinin çok belirgin olmadığı gözlenmiştir. Buna karşın, kalsine edilmeksizin asitle işlem yapılan örnekler (UAT) için çapraz bağlama sonucunda reaksiyon hızı ve mezogözenek alanı belirli bir bağlayıcı miktarına kadar artmıştır. Yüksek miktarda bağlayıcı kullanımı ise reaksiyon hızını artırmamış, mezogözenekliliği azaltmıştır.

Aynı bağlayıcı kullanılarak çapraz bağlanmış olan Aerosil örneğinin Beckmann reaksiyonunda aktivite göstermemiş olmasından, bağlayıcının aktif olmadığı, katalitik aktivitenin tümüyle zeolit yüzeylerinden kaynaklandığı anlaşılmıştır.

1. IN TS-1 örneklerinde de çapraz bağlamanın etkisi incelenmiş, yapılan adsorpsiyon ölçümlerinde yüksek miktarda bağlayıcı kullanılarak hazırlanan TS-1 örneklerinde çok geniş mezogözenek alanı belirlenmiştir. Bu örnekler hem Beckmann reaksiyonunda, hem de propenin propen oksite epoksidasyonunda denenmiştir. TS-1 örnekleri epoksidasyon reaksiyonunda yüksek bir aktivite göstermemiş, ancak Beckmann reaksiyonunda, çapraz bağlı örneğin aktivitesinin yüksek olduğu belirlenmiştir. TS-1 örnekleri için gözlenen önemli bir üstünlük, ZSM-5 ve Silikalit-1 örneklerine kıyasla katalizör ömrünün daha uzun olmasıdır. Yüksek bağlayıcı miktarlarında katalizör ömrü daha da artmıştır. TS-1 örneklerinde 4 saatlik reaksiyon sonucunda hiç deaktivasyon gözlenmezken, aynı koşullarda hazırlanan ZSM-5 ve Silikalit-1 örneklerinin reaksiyon hızlarında sırasıyla % 49 ve % 48 oranında düşüşler gözlenmiştir.

Kaprolaktam seçiciliği değişkenlik göstermekle birlikte, çoğunlukla % 65'in üzerinde bulunmuştur. Çapraz bağlanmış örneklerin yüksek aktiviteleri, kütle transferinin iyileşmiş olması ve zeolit yüzeylerindeki yüksek konsantrasyonlardaki aktif merkezlerin rahatça ulaşılabilir olması ile açıklanmıştır.

In this respect, the preparation and applications of colloidal zeolites have gained significant attention recently (1-3). Synthesis of colloidal zeolites, which conventionally have sizes in the range of 10-100 nanometers, has been accomplished for a limited number of zeolite types up to date. Syntheses of high-silica zeolite ZSM-5 and its pure silica analog Silicalite-1 with colloidal sizes are well known examples (4-6). They are synthesized from clear solutions of tetraethylorthosilicate (TEOS), and tetrapropylammonium hydroxide (TPAOH) in water at low temperatures. Schoeman et al. were the first to report the synthesis of colloidal zeolites under such conditions (7). The authors evidenced that colloidal sized zeolitic structures can be synthesized at RT and aging of solutions at low temperature cause an increase in nucleation rate.

Martens et al. (8) have reported the formation of "nanoslabs" or "nanoblocks" as the product of the polycondensation process at RT, which are supposed to be highly uniform and well-defined units with a very specific geometry. In this study, it was claimed that nanoslabs, which are supposed to have a zeolite structure, can be extracted from the synthesis solution. The evidences presented in Marten's study were highly disputed by Knight (9) and Tsapatsis (10).

1. INTRODUCTION

1.1. Foreword

Zeolites are microporous crystalline aluminosilicates, which are used in a broad range of applications, mainly as catalysts, adsorbents and ion exchangers. The prospect of synthesizing novel zeolitic materials for new applications is a continuing driving force for research.

In this respect, the preparation and applications of colloidal zeolites have gained significant attention recently (1-3). Synthesis of colloidal zeolites, which conventionally have sizes in the range of 10-100 nanometers, has been accomplished for a limited number of zeolite types up to date. Syntheses of high-silica zeolite ZSM-5 and its pure silica analog Silicalite-1 with colloidal sizes are well known examples (4-6). They are synthesized from clear solutions of tetraethylorthosilicate (TEOS), and tetrapropylammonium hydroxide (TPAOH) in water at low temperatures. Schoeman et al. were the first to report the synthesis of colloidal zeolites under such conditions (7). The authors evidenced that colloidal sized zeolitic structures can be synthesized at RT and aging of solutions at low temperature cause an increase in nucleation rate.

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The reduction of the particle size is known to decrease the mass and heat transfer resistances and to increase the effectiveness factor of the zeolite crystallites in some catalytic processes. Zeolites with small particle sizes and high external surface areas also have additional advantages for some catalytic applications. A number of reactions are proposed to preferably occur on the outer surfaces of the catalysts. The vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam is an example of these reactions (11).

Commercially, the Beckmann rearrangement proceeds in the liquid phase, with sulfuric acid as the catalyst. The reaction pathway is given in Figure 1.1.

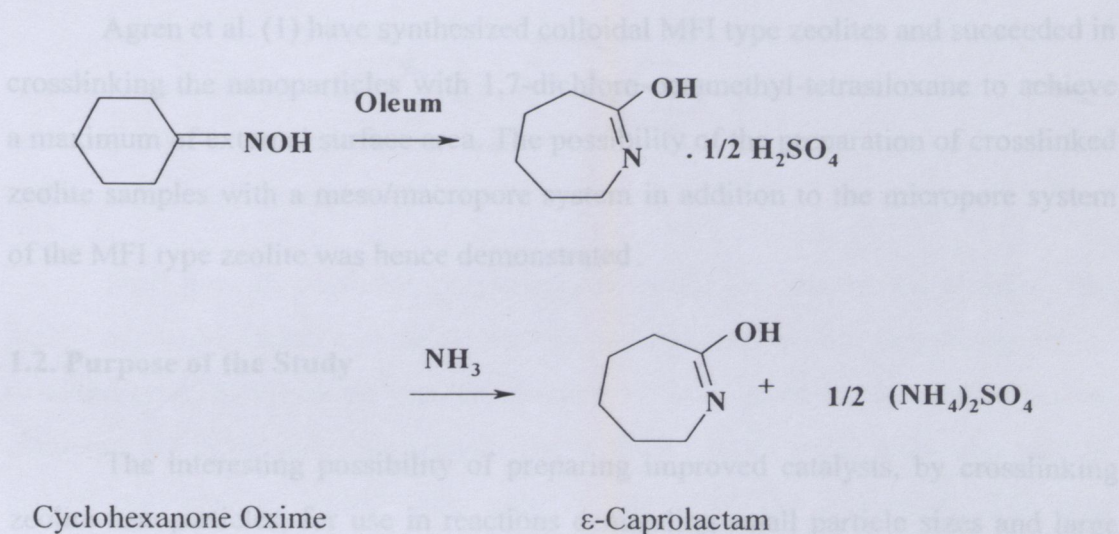


Figure 1.1. Classical reaction pathway for the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam.

The disadvantages of the use of sulfuric acid as the catalyst are the production of high amounts of ammonium sulfate as by-product and the corrosion of the equipment due to the acid. Since ϵ -caprolactam is an important intermediate in some industrial applications, its production via heterogeneous catalysis has been the subject of significant research for some years (11-13).

Zeolite catalysts have been investigated for this purpose. High silica MFI type zeolites were found to be active for the reaction (11). It has been proposed (11,14-16)

that the gas phase reaction takes place on the outer surface of the zeolite catalysts, although there are also claims on the contrary (17) relating the improvement in activity to the increased effectiveness factor. In any case, zeolite catalysts having small particle sizes with increased external surface areas and effectiveness factors may be expected to be more suitable for such reactions.

If small zeolitic crystallites could be used as catalysts in these reactions, in the form that exist in the synthesis solutions, this would establish the limit of maximizing the external surface area. However, loss of external surface area due to agglomeration occurs upon recovery of the small particles.

Agren et al. (1) have synthesized colloidal MFI type zeolites and succeeded in crosslinking the nanoparticles with 1,7-dichloro-octamethyl-tetrasiloxane to achieve a maximum of external surface area. The possibility of the preparation of crosslinked zeolite samples with a meso/macropore system in addition to the micropore system of the MFI type zeolite was hence demonstrated.

1.2. Purpose of the Study

The interesting possibility of preparing improved catalysts, by crosslinking zeolite nanoparticles, for use in reactions demanding small particle sizes and large external surface areas, such as the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam, is investigated in this study.

Silicalite-1, Ti-Silicalite-1, and ZSM-5 samples of small particle sizes are synthesized and crosslinked with 1,7-dichloro-octamethyl-tetrasiloxane. The effects of zeolite synthesis and crosslinking conditions on the properties of the catalysts are investigated. Aging temperature, aging time and the amount of linker are the parameters varied in the preparation of the catalysts. Aging time and temperature are expected to affect the particle size of the zeolite samples, and the extent of aluminum incorporation into the framework in the case of ZSM-5. The amount of linker above the minimum necessary to link a certain amount of zeolite particles, on the other hand, may change the fraction of surface silanols used for crosslinking and those used for the reaction, and may also affect the pore system.

2. STATE OF THE ART

2.1. Zeolites

Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimensions. Many occur as natural minerals, but it is the synthetic varieties, which are among the most widely used sorbents, catalysts and ion exchange materials in the world (18-20).

Their three-dimensional, polyanionic networks are constructed of $\text{SiO}_{4/2}$ and $\text{AlO}_{4/2}$ tetrahedra linked via the corners through oxygen atoms. Depending on the structure type, they contain regular channels or interlinked voids whose aperture diameters are in the micropore range. These pores contain water molecules and the cations necessary to balance the negative charge of the framework. The pore structures of mordenite and ZSM-5 zeolites are shown in Figure 2.1

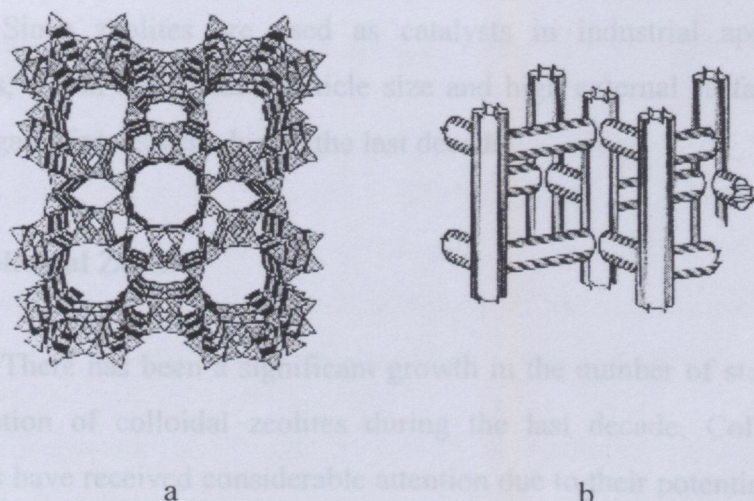
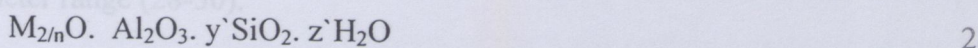
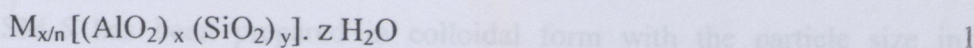


Figure 2.1. The pore structure of a) Mordenite, b) ZSM-5 zeolites.

The cations, which are mobile and can be exchanged, are mainly alkali metal or alkaline earth metal ions. Formula 1 describes these characteristics. The expression enclosed in the square brackets shows the composition of the anionic framework in the crystallographic unit cell. M represents the nonframework metal cation, and n its charge. Formula 2 occurs frequently in the literature and, unlike Formula 1, simply represents the overall chemical composition.



Zeolites are also important as adsorbents for separating and purifying substances and as catalysts in a number of important processes in the chemical and petrochemical industries.

The wide range of commercial applications has stimulated intensive investigations of the chemistry and physics of zeolites (19). Current research is focused on zeolite-like molecular sieves, which has expanded the field of zeolites enormously during the last two decades (20-22).

Since zeolites are used as catalysts in industrial applications, colloidal zeolites, which have small particle size and high external surface areas, have been investigated intensively during the last decade.

2.2. Colloidal Zeolites

There has been a significant growth in the number of studies concerning the preparation of colloidal zeolites during the last decade. Colloidal or nanosized zeolites have received considerable attention due to their potential applications in the areas of separation and catalysis, as well as in the preparation of new and advanced materials. Their potential uses in the preparation of zeolite membranes of sub-micron thickness (23), hollow zeolite fibers (24), films, monoliths (25) and catalysts in

general (26), and in the development of optic, electronic, and optoelectronic materials (27), for example, are some of the major reasons for the interest in colloidal zeolites.

2.2.2. Colloidal Zeolite Syntheses

Colloidal zeolites are typically synthesized from clear solutions. The synthesis starts with the hydrolysis of TEOS in a concentrated aqueous TPAOH solution at RT. Some zeolites, including A, Y, X, β , Hydroxysodalite, Silicalite-1 and ZSM-5 has been prepared in colloidal form with the particle size in the nanometer range (28-30).

The synthesis and properties of colloidal zeolites have been investigated by several research groups and most of them are focused on the TPA-Silicalite-1 systems.

Persson *et al.* (31) synthesized colloidal TPA-Silicalite-1 with a narrow size distribution and an average particle size of less than 100 nm. The effects of alkalinity, silica source, silica content and temperature were investigated. They concluded that high silica contents with high alkalinities favor the synthesis of colloidal silicalites. They also showed that polymeric silica sources resulted in larger particles compared to TEOS. It was noted that the conversion of SiO_2 to TPA-Silicalite-1 increased with temperature and the particle size decreased from 95 nm to 79 nm when the temperature was reduced from 371 K to 353 K.

The same research group investigated the effects of the synthesis parameters on the preparation of colloidal H-ZSM-5 (32). The effects of the Si/Al ratio, alkalinity and temperature were investigated. They concluded that an increase in the aluminum content of the synthesis solutions results in a reduced number of crystals, smaller product yields and an increase in the ultimate particle size.

Decreasing the TPAOH content in this synthesis led to large increases in the product yield, particle concentration and crystal growth rate in contradiction to the results obtained for Silicalite-1. The same researchers showed that there is a value of the alkalinity below which the crystal growth rate is essentially independent of the

alkalinity of the synthesis mixture, whereas above this value the crystal growth rate decreases with increasing alkalinity.

Schoeman *et al.* (7) reported in a study on the synthesis of colloidal A type zeolites the effect of the sodium content of the synthesis mixture on the crystalline phase and on the ultimate particle size of the colloidal zeolite particles. They determined that high sodium content favors the formation of zeolite A, and results in shorter crystallization times and a higher ultimate crystallinity. It was shown that the zeolite yield increases with increasing sodium content.

The effect of the water content of the synthesis mixture was also investigated by the same research group (32). Increasing the water content in a series of synthesis mixtures resulted in an increased crystal growth rate and a larger particle size. Decreasing the water content while keeping the alkalinity constant resulted in smaller ZSM-5 crystals, in combination with higher conversions.

It was also shown (32) that the introduction of sodium in the form of sodium hydroxide into the synthesis mixture increases the crystal growth rate when compared with the growth rate in the sodium-free mixture.

Moor *et al.* (33) synthesized TPA-Silicalite-1 and monitored the process of the nucleation and crystal growth by using several techniques such as SAXS (Small Angle X-ray Scattering)-WAXS (Wide Angle X-ray Scattering) and HREM (High-Resolution Electron Microscopy). They followed Schoeman's procedure (7) to prepare clear synthesis solutions. Small species around 2.8 nm were detected by in situ measurements. IR spectra of these isolated species were measured and a band around 560 cm^{-1} was detected which is attributed to the five membered silicate rings.

In 1999, Mintova and Bein published a study (34) about a colloidal solution, in which zeolite crystals are formed even at RT aging. Zeolite A was synthesized according to Schoeman's procedure and aged at RT. One could observe spherical objects that have a particle size around 5-10 nm. Although X-Ray diffraction patterns of the samples showed an amorphous phase, these samples were crystalline after hydrothermal treatment for 3-7 days. After aging at RT for 3 days, small particles of around 10-30 nm particle sizes could be observed. During further aging tiny little

zeolite A crystallites grew up to a size of 80 nm. In the case that this solution had been aged at 373 K for 1 day, much larger particles (200-400 nm) could be obtained. A nucleation mechanism is proposed in this study, which is given in Figure 2.2.

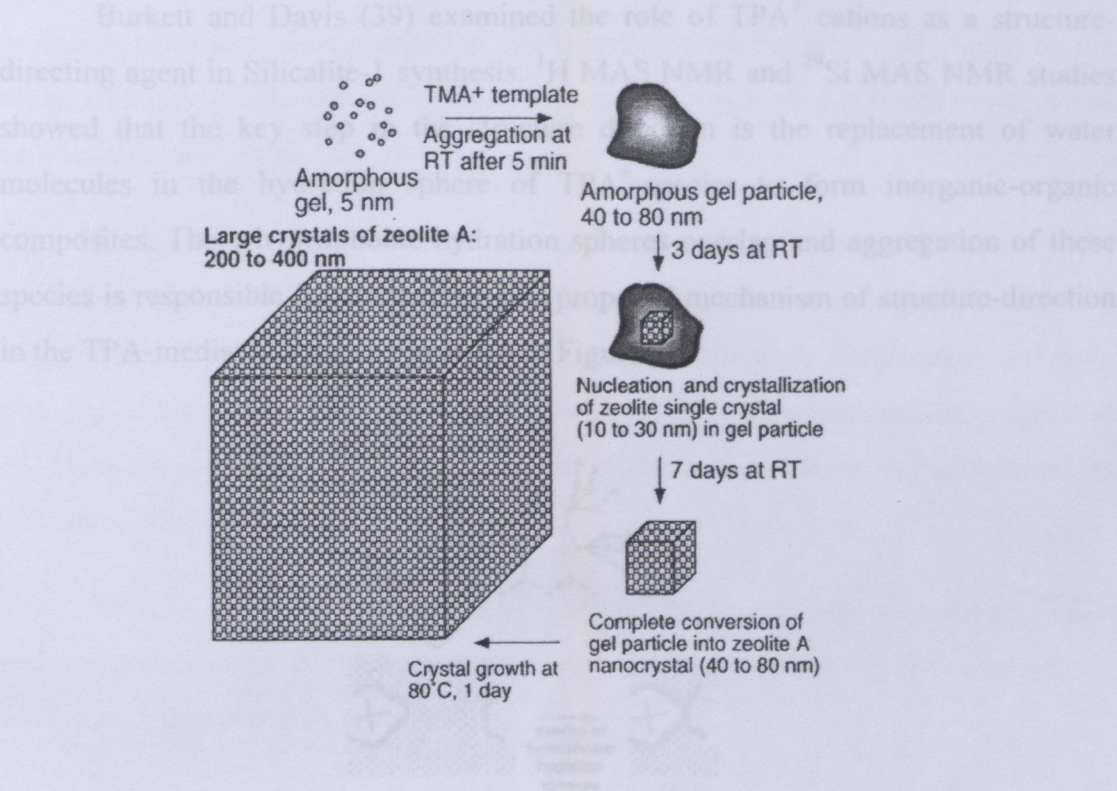


Figure 2.2. Schematic representation of the proposed zeolite growth mechanism (34).

The same group has also synthesized other colloidal zeolites, such as FAU type (35), MEL type (36), and MFI type (37). They examined the influence of different parameters, such as silica source (38) and aging time (35,37), on the formation and crystallization of particles. Crystal growth of Silicalite-1 is investigated in one of the studies of the same group (37). In this study, aging time was extended up to 30 days with stirring. After 30 days of aging at RT, small sub-colloidal particles in the range of about 1-10 nm were detected by Dynamic Light Scattering, although the samples were amorphous according to XRD. Upon hydrothermal treatment times between 4 min and 6 h, the crystalline phase could be detected due to the secondary generation of particles with a mean radius of 15 nm.

By increasing the treatment time, the small particle phase vanished. This strongly suggests that the aging period in zeolite synthesis leads to the formation of nanoscale crystalline particles.

Burkett and Davis (39) examined the role of TPA^+ cations as a structure-directing agent in Silicalite-1 synthesis. ^1H MAS NMR and ^{29}Si MAS NMR studies showed that the key step in the structure direction is the replacement of water molecules in the hydration sphere of TPA^+ -species to form inorganic-organic composites. These hydrophobic hydration spheres overlap and aggregation of these species is responsible for nucleation. The proposed mechanism of structure-direction in the TPA-mediated synthesis is given in Figure 2.3.

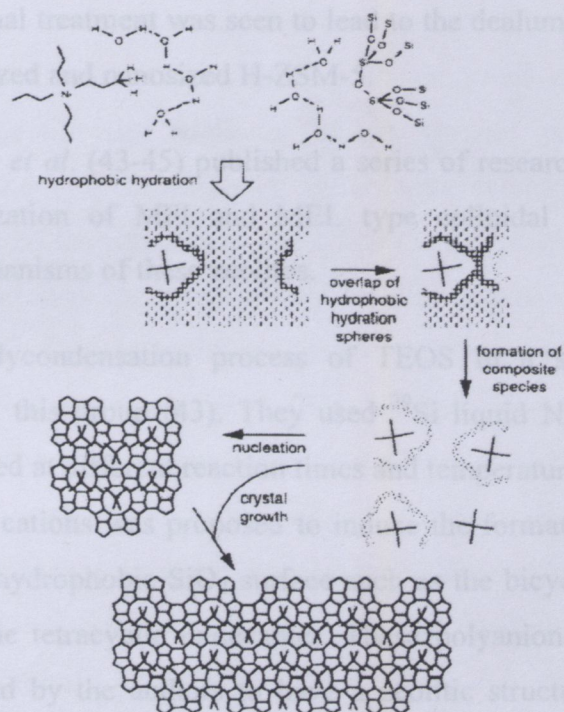


Figure 2.3. Mechanism of structure directing in the TPA-mediated synthesis of Silicalite-1 (40).

Tsay and coworkers (41) synthesized colloidal TPA-Silicalite-1. A relation was determined between the particle number density, the silica concentration and the TPAOH/TEOS ratio, x . It was predicted that an x value of 0.25 might be an optimum ratio to produce a large number of small zeolite particles at high yield. Considering

the linear growth rates of colloidal zeolites it was concluded that the growth rate is independent of x , but it varies with the $H_2O/TEOS$ ratio. One of the interesting results was that the number density of the zeolite particles increased with the 3.4th power of silica concentration. In this study, the authors believed that collecting the zeolite by centrifuge always ended in yields less than the amounts determined by the initial amount of silica present in the system, which might be due to the existence of sub-colloidal particles.

Zhang *et al.* (42) performed a high-resolution solid-state NMR study for micro-sized (1000 nm) and nano-sized (70 nm) H-ZSM-5 by varying the calcination temperature. They observed that increasing the calcination temperature led to a decrease of both the amounts of the framework Al and the nonframework octahedral Al. Thus, thermal treatment was seen to lead to the dealumination of the frameworks of both micro-sized and nano-sized H-ZSM-5.

Martens *et al.* (43-45) published a series of research papers on the synthesis and characterization of MFI and MEL type colloidal zeolites and studied the formation mechanisms of these zeolites.

The polycondensation process of TEOS in a solution of TPAOH was investigated by this group (43). They used ^{29}Si liquid NMR and FTIR spectra of samples recorded at different reaction times and temperatures. The structure directing action of TPA cations was proposed to induce the formation of silicate polyanions with a curved hydrophobic SiO_2 surface such as the bicyclic pentamer, pentacyclic octamer and the tetracyclic undecamer. These polyanionic species in the solution were interpreted by the authors to have a zeolitic structure. This assumption was argued (9) by Knight *et al.* claiming that even though the polyanionic species exist in the solution, this could not be an evidence of zeolitic formation. The authors also suggested that some other polyanionic species like the cubic octamer should have been mentioned in Marten's study since TPA and TBA containing solutions produce high proportions of the cubic octamer.

Martens *et al.* (45) suggested that it could be possible to realize the topology of MFI at the very early stages of the synthesis, when the slab's dimension is $1.3 \times 4 \times 4$ nm in the a , b and c directions, respectively. They claimed that the rectangular

shape of the nanoslabs can be seen from TEM pictures, and with this assumption, they calculated the size of the nanoslabs as $4 \times 4 \text{ nm}^2$. On the other hand, this conclusion was disputed by Tsapatsis *et al.* (10). They repeated the synthesis according to Martens *et al.* and claimed that the sharp Bragg reflections, which are suggested to be characteristic for MFI type materials, are due to NaCl, which is not sufficiently washed out. Nevertheless, Thermo Gravimetric Analysis (TGA) results, micropore areas and volumes determined by adsorption analysis are in agreement with Martens results.

In a recent study, a colloidal ZSM-5 sample was synthesized (1) and the nanoparticles in the solution were crosslinked with 1,7-dichloro-octamethyl-tetrasiloxane. The samples were characterized by using ^{29}Si and ^{27}Al MAS NMR and IR techniques as well as adsorption experiments. NMR data indicated that the reaction of the silicone with the surface silanols proceeded smoothly and went to completion. The nitrogen isotherms of the samples provided evidence for the formation of an additional mesopore system after calcination. The IR band around 563 cm^{-1} indicated the presence of ZSM-5 in the crosslinked material, and the bands at 806 , 1263 and 2962 cm^{-1} were assigned to the vibrations of the silicone linker. IR spectroscopy of adsorbed pyridine pointed to differences in acidity characteristics when compared to a commercial H-ZSM-5 sample. This was attributed to the high concentration of moderately acidic terminal silanol groups corresponding to the high external surface area, and to the lack of aluminum incorporation into the framework. The presence of silanol groups originating from the crosslinker, with differing acidity compared to the silanols in zeolites, is also indicated as a possible reason for the observed differences.

Colloidal sized zeolites, their formation and their crystallization have been investigated intensively during the last decade. Most of the studies were focused on the synthesis and the nucleation and formation mechanism. All studies agreed in that nanoscale species with the size about $3\text{-}4 \text{ nm}$ are formed at low temperatures. However, the exact nature of these species is highly disputed. The authors called these entities subcolloidal particles (34) or nanoslabs, assuming that they have rectangular geometry (43). Irrespective of the exact nature of the species, if these small entities in the synthesis solutions could be extracted from the solution they

could be advantageous in catalytic applications due to their high external surface area.

2.2.3. Catalytic Applications of Nanosized Zeolites

Aguado *et al.* (46) used nanosized H-ZSM-5 for the catalytic conversion of polyolefin mixtures, consisting of polypropylene and polyethylene. They investigated the effects of the polymer/catalyst mass ratio and the temperature on the reaction mentioned above. They determined that the cracking reactions took place on the external surface of the nanosized H-ZSM-5 particles, yielding mainly light olefins as the primary product. Nanosized H-ZSM-5 samples have better catalytic activity in comparison to the H-MCM-41.

The olefin selectivity was very high for this catalyst. The researchers concluded that the presence of a high external surface area was the reason for the increased catalytic activities of the nanosized H-ZSM-5. In the case of nano H-ZSM-5 the cracking reaction is assumed to take place on the outer surface of the crystals, yielding mainly light olefins as the primary products coming from the end-chain scission mechanism. On the other hand, polyolefin cracking over H-MCM-41 catalyst occurs mainly within the mesopores yielding waxes as the primary products.

Ravishankar *et al.* (2) synthesized and characterized nano Silicalite-1 and nano TS-1 molecular sieves, isolated as powders. The IR spectra of nano Silicalite-1 and nano TS-1 samples exhibited a characteristic band at 550-590 cm⁻¹. After partial calcination, this band shifted from 590-570 cm⁻¹ to 570-550 cm⁻¹, indicating some increase in the particle size. It was noted that the calcination performed at 823 K to remove TPA⁺ might lead to a structural collapse of the Silicalite-1 samples. TS-1 type zeolites were tested in the hydroxylation of phenol and the epoxidation of 1-hexene using hydrogen peroxide as the oxidant. Partly and fully calcined TS-1 samples were tested and compared with commercial TS-1 as well as with blank experiment without catalyst. Reaction results are given in Table 2.1.

Table 2.1. Catalytic partial oxidation reactions over partly calcined nano TS-1 (2).

Catalyst	Hydroxylation of phenol ^a		Epoxidation of 1-hexene ^b	
	Conversion, %	Selectivity to hydroquinon, %	Conversion, %	Selectivity to epoxide, %
Blank	2	25	0	0
Partly calcined nanopowder	39	40	1.2	100
TS-1	53	58	3.5	100

Catalyst:10 wt %; Solvent/substrate: 10; Substrate :1 mmol;
a, Solvent: H₂O; Temperature: 338 K; Reaction Time: 1 h; Phenol/H₂O: 5
b, Solvent: Methanol; Temperature: 293 K; Reaction Time: 10 min.; 1-hexene/H₂O: 3.

Fully calcined and as-synthesized nano TS-1 samples were found to be inactive where partly calcined samples had quite good performance. The authors claimed that although the conventional catalyst has higher catalytic activity, the catalytic turnovers per accessible Ti atoms in partly calcined samples are much higher.

The Leuven group has published a study (47) about the synthesis and catalytic activity of “Zeogrids” which are obtained by precipitation of so called “nanoslabs” in presence of cetyltrimethylammoniumbromide (CTAB) or decyltrimethyl ammoniumbromide (DTAB) and calcination of the precipitate. They claim that “Zeogrids” have a layered structure with some open places between the tablets. The void volumes of these zeogrids are supposed to have a characteristic height of 1.5 nm in the radial direction, and they are extended with multiples of 1.3 and 2 nm in the other directions. Samples were characterized by several techniques such as X-ray diffraction, ²⁷Al MAS NMR, nitrogen adsorption, and IR spectroscopy. The samples were tested in the decane hydroisomerization reaction, which was performed using a high throughput reactor with 15 parallel micro reactor tubes. Zeogrid samples were compared to the commercial ZSM-5 catalysts as well as to aluminum doped nano Silicalite-1 catalyst, which had been prepared in stainless steel autoclaves at 393 K.

Samples were impregnated with an aqueous Pt (NH₃)₄Cl₂ solution. Nano-zeolite samples gave high yields of total isomers around 70 %. The zeogrid samples exhibited a low yield up to a maximum at around 45 %. The commercial ZSM-5 favored the formation of 2-methylnonane isomers more than 3-, 4- and 5-methylnonane while nano-ZSM-5 and zeogrid samples did not show this preference for 2-methylnonane. On the other hand, the formation of other isomers like 3- and 4-methylnonane is higher for zeogrids. In addition, ethyloctane could also be obtained when zeogrid samples were used. Because of these reasons, the authors claimed that zeogrid samples behaved like a large pore material.

2.3. Beckmann Rearrangement of Cyclohexanone Oxime to ε-Caprolactam

2.3.1. ε-Caprolactam; Commercial Importance and Producers

ε-Caprolactam (aminocaproic lactam; 2-oxo-hexamethylene imine) is an important intermediate in the manufacture of synthetic fibers, engineering plastics and for the preparation of L-lysine, which is an essential ingredient in animal food.

Today, ε-caprolactam annually accounts for over \$ 45 billion in global sales and the production amounted to 4.4 million tons in 1999 (48). The breakdown of the worldwide production capacity of ε-caprolactam is given in Figure 2.4.

North America	Allied Signal, BASF, DSM, DuPont-Alpek	855
Europe	BASF, Bayer, Domogroup, EniChem, DSM, UBE, Tarnow, Palawy, Spolana, Zilana, Fibrex, Stara Zagora,	1780
Asia / Pacific	Ube Kosan, Mitsubishi Kagaku, Ube Sumitomo, Tokai, CPC, Hankook Caprolactam, Thai Caprolactam	1984

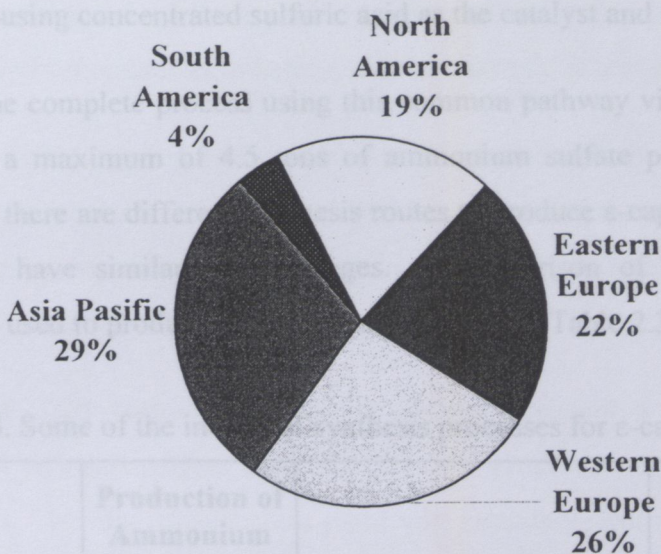


Figure 2.4. Worldwide production capacity of ε-caprolactam (48).

Since caprolactam is a monomer for the versatile Nylon-6 polyamide, the demand for caprolactam depends on the demand for the Nylon-6 fibers. Nylon-6 is widely used in the manufacture of fishing nets, sewing threads, industrial drive belts, and other applications. Producers and the production capacities worldwide are presented in Table 2.2.

Table 2.2. Producers of and capacities for nylon-6 (48).

Region	Company	Capacity (in 10 ³ m.t./year)
North America	Allied Signal, BASF, DSM, DuPont-Alpek	855
Europe	BASF, Bayer, Domogroup, EniChem, DSM, UBE, Tarnow, Pulawy, Spolana, Zilana, Fibrex, Stara Zagora,	1780
Asia / Pacific	Ube Kosan, Mitsubishi Kagaku, Ube Sumitomo, Tokai, CPC, Hankook Caprolactam, Thai Caprolactam	1984

ϵ -Caprolactam is produced commercially in a large scale from cyclohexanone oxime by using concentrated sulfuric acid as the catalyst and solvent.

The complete process using this common pathway via cyclohexanone oxime produces a maximum of 4.5 tons of ammonium sulfate per ton of product (49). Although there are different synthesis routes to produce ϵ -caprolactam, most of these processes have similar disadvantages. A comparison of some of the industrial processes used to produce ϵ -caprolactam is given in Table 2.3.

Table 2.3. Some of the industrial synthesis processes for ϵ -caprolactam (49).

Process	Production of Ammonium Sulfate (tons/ton of product)	Advantages	Disadvantages
Classical processes	4.5	Optimized processes possible	High (NH ₄) ₂ SO ₄ formation, Low conversion in ammoxidation step
BASF/Inventa	1.9	Low (NH ₄) ₂ SO ₄ formation	Classical rearrangement step
HPO	1.8	Low (NH ₄) ₂ SO ₄ formation	Classical rearrangement step
PNC	1.55	One step reaction to the oxime	High material costs, High energy consumption
SNIA	0	No (NH ₄) ₂ SO ₄ formation, toluene less expensive than cyclohexane, destruction of by-products	High fuel costs due to thermal cracking
H ₂ O ₂ process	0	No (NH ₄) ₂ SO ₄ formation	Hydrogen peroxide costs, zeolite costs

Besides those mentioned in Table 2.3, another common problem encountered in the production of ϵ -caprolactam is related to handling a large amount of fuming

sulfuric acid, which leads to environmental problems and corrosion of the equipment. In order to eliminate all these problems, attempts have been made for many years to switch from homogeneous to heterogeneous catalytic processes.

In 2001, two big companies, Sumitomo and EniChem, have co-developed a manufacturing process to produce caprolactam, the key material for nylon-6, without co-generating ammonium sulfate. The firms plan to build a 90,000 metric tones /year plant to produce caprolactam (50).

The two companies have developed proprietary catalysts that provide significant cost advantages over conventional processes, according to Tokyo-based Sumitomo. The new caprolactam plant will essentially combine the technologies of Sumitomo's gas-phase Beckmann rearrangement with EniChem's direct ammoximation process, which involves the direct ammoximation of cyclohexanone from ammonia and hydrogen peroxide with the use of TS-1 catalysts (51). Details of the technology were not disclosed.

2.3.2. Beckmann Rearrangement of Cyclohexanone Oxime to ϵ -Caprolactam – Classical Synthesis Routes

The classical production of ϵ -caprolactam is based on cyclohexanone oxime and consists of the following steps

- The synthesis of cyclohexanone
- The ammoximation of cyclohexanone to cyclohexanone oxime with hydroxylamine
- The Beckmann rearrangement of cyclohexanone oxime to caprolactam.

• The Synthesis of Cyclohexanone

The production of cyclohexanone is primarily done with cyclohexane as the starting material, which is obtained by the hydrogenation of benzene (52). The cyclohexane is oxidized to a mixture of cyclohexanol/cyclohexanone, separated by distillation. Cyclohexane oxidation is the most important as well as a potentially

hazardous reaction in the caprolactam process. The reaction is usually carried out by bubbling air through liquid cyclohexane at temperatures of 413-444 K and pressures of 0.1-2.5 MPa. Conversion of cyclohexane is usually limited to 3-5% to avoid potential hazards. The cyclohexanol is catalytically dehydrogenated to cyclohexanone at 673-723 K over Cu-Zn catalysts. The synthesis pathway of cyclohexanone is given in Figure 2.5.

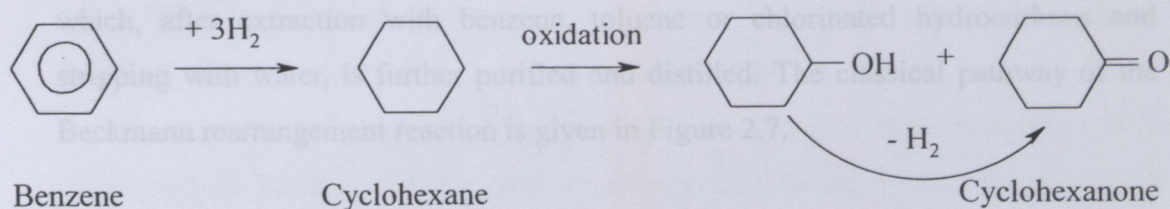


Figure 2.5. Synthesis of cyclohexanone from cyclohexane.

- **The Ammoximation of Cyclohexanone to Cyclohexanone Oxime**

Oxime formation with cyclohexanone is done with a hydroxylamine salt, usually the sulfate, at 388 K. The synthesis pathway is given in Figure 2.6.

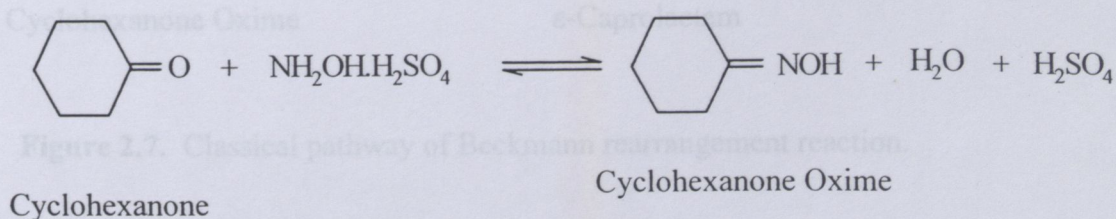


Figure 2.6. The ammoximation of cyclohexanone to cyclohexanone oxime.

In order to shift the equilibrium, NH_3 must be continuously introduced to maintain a pH of 7. The first ammonium sulfate formation takes place at this stage in the process. This formation of ammonium sulfate is a big ecological and economical concern. Therefore, much effort was put into preventing the formation of the salt during the ammoximation.

- **Beckmann Rearrangement of Cyclohexanone Oxime to Caprolactam**

The Beckmann rearrangement of cyclohexanone oxime to caprolactam is a very well known reaction. Commercial development of this process was done by BASF (53). In the continuous process, the oxime solution, acidified with sulfuric acid, is passed through the reaction zone, which is kept at the reaction temperature (363-393 K). The rearrangement is complete within a few minutes, and the resulting lactam sulfate solution is converted into free lactam with NH_3 in a neutralization vessel. It separates from the saturated ammonium sulfate solution as an oily layer, which, after extraction with benzene, toluene or chlorinated hydrocarbons and stripping with water, is further purified and distilled. The classical pathway of the Beckmann rearrangement reaction is given in Figure 2.7.

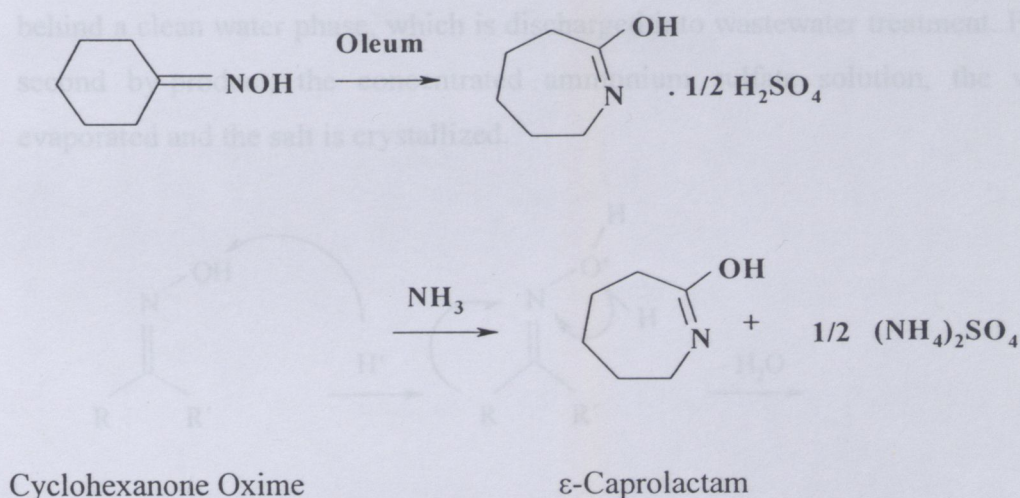


Figure 2.7. Classical pathway of Beckmann rearrangement reaction.

The mechanism of the Beckmann rearrangement reaction is given in Figure 2.8. First, the proton from an employed acid attacks a lone pair of electrons on either the nitrogen or oxygen atom of the ketoxime, and generates an iminium or an oxonium ion.

The loss of the water molecule causes a deficiency of electrons. The R migrates as an anion with a pair of electrons to the nitrogen atom, thus generating a carbenium ion in the process. A water acting as a nucleophile attaches itself to this carbenium atom, giving rise to an N-substituted carboxylic acid amide or anilide.

The Beckmann rearrangement includes the exothermic insertion of nitrogen into the cyclohexyl ring. To control the temperature of the reaction the rearrangement of cyclohexanone oxime to caprolactam is done in large amounts of already rearranged products using molar ratios of oxime to sulfuric acid around 1. The added sulfur trioxide is able to bind the water in the moisturized cyclohexanone oxime melt and thus forms sulfuric acid, which further catalyzes the rearrangement. The product of this reaction step is the sulfate of cyclohexanone oxime, which is converted with ammonia and water, preventing the precipitation of solid ammonium sulfate.

The reaction product is then separated from the lighter phase, which forms over the heavy saturated ammonium sulfate phase as 70 % aqueous crude caprolactam. After separation of the crude caprolactam in a separation drum, it is extracted with benzene, toluene, and sometimes, chlorinated hydrocarbons, leaving behind a clean water phase, which is discharged into wastewater treatment. From the second by-product, the concentrated ammonium sulfate solution, the water is evaporated and the salt is crystallized.

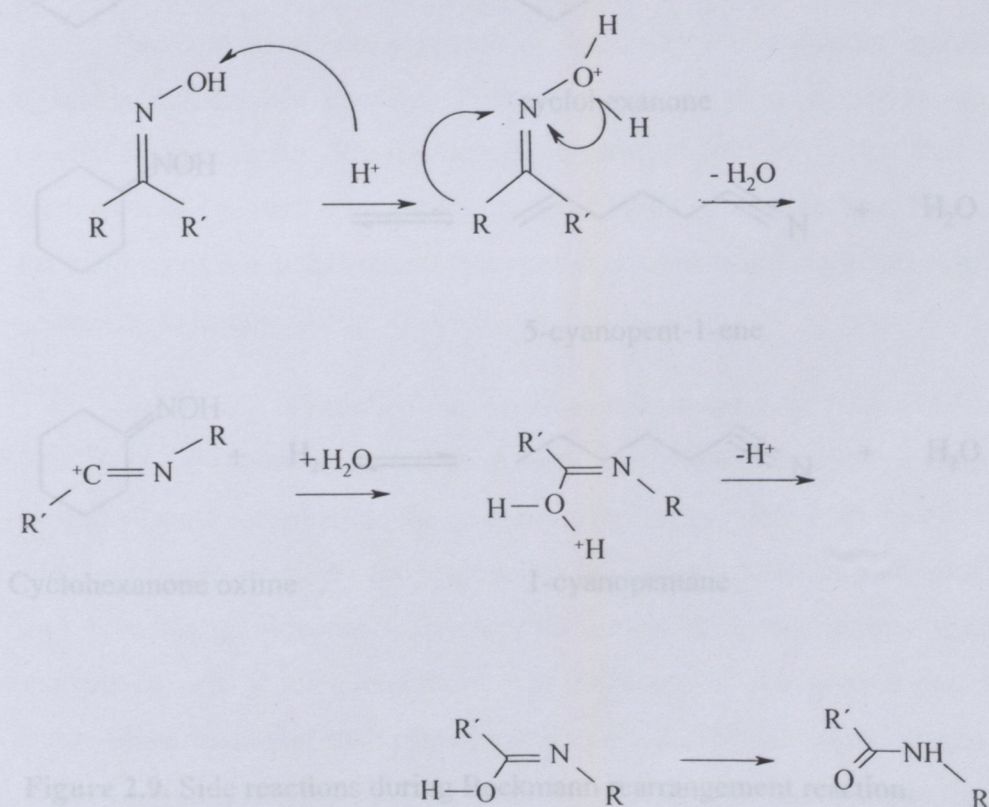
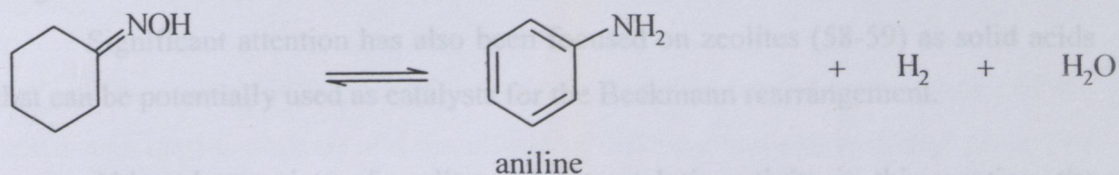


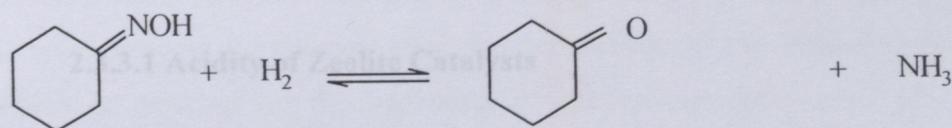
Figure 2.8. The mechanism of the Beckmann rearrangement reaction.

2.3.3. During Beckmann rearrangement, various reactions to by-products occur as well. General by-products of Beckmann rearrangement reactions are given in Figure 2.9.

The vapor phase Beckmann rearrangement of cyclohexanone oxime over solid catalysts has been the subject of intense research for several years. Beckmann rearrangement has been investigated over various solid-acid catalysts, such as tungsten oxide (54), tantalum oxide (55), titanium oxide (56) and borosilicate (57).



Although a variety of zeolites exhibit catalytic activity in this reaction, the properties of the zeolite catalysts need to be improved further for industrial applications since the performances of amorphous materials still are much better for this reaction. Zeolite catalysts have been mainly investigated with respect to several parameters, such as Si/Al ratio, types of acid centers, location of the reaction sites and the solvent, which are believed to affect catalytic performance.



2.3.3.1 Acidic Zeolite Catalysts

The Beckmann rearrangement of cyclohexanone oxime to caprolactam is a typical acid catalyzed reaction. Types of acid centers are therefore crucial parameters for this reaction. Early studies (60) suggested that strong and medium acid sites are effective for this reaction. However, today the majority of researchers claim that neutral or weak acid sites affect conversion and selectivity to lactam.

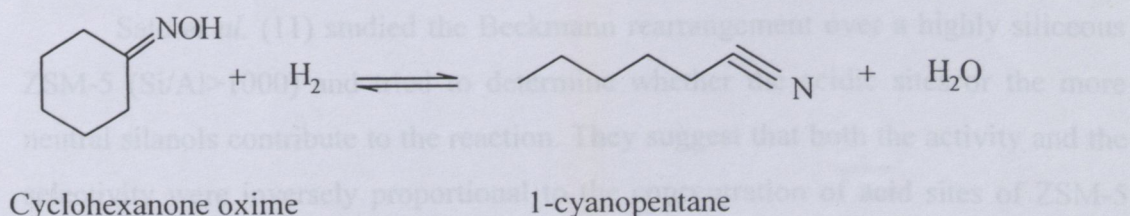
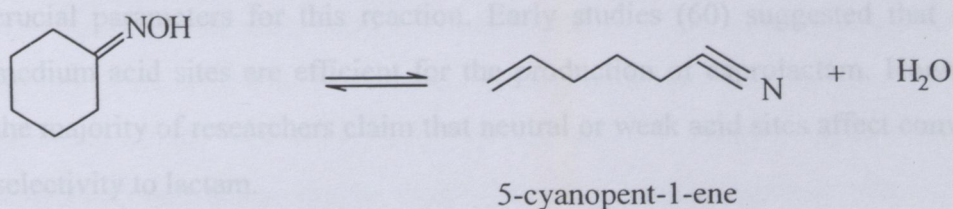


Figure 2.9. Side reactions during Beckmann rearrangement reaction.

2.3.3. Heterogeneous Catalysis on Beckmann Rearrangement Reaction

The vapor phase Beckmann rearrangement of cyclohexanone oxime over solid catalysts has been the subject of intense research for several years. Beckmann rearrangement has been investigated over various solid-acid catalysts, such as tungsten oxide (54), tantalum oxide (55), titanium oxide (56) and borosilicate (57).

Significant attention has also been focused on zeolites (58-59) as solid acids that can be potentially used as catalysts for the Beckmann rearrangement.

Although a variety of zeolites exhibit catalytic activity in this reaction, the properties of the zeolite catalysts need to be improved further for industrial applications since the performances of amorphous materials still seem to be better for the reaction. Zeolite catalysts have been mainly investigated with respect to several parameters, such as Si/Al ratio, types of acid centers, location of the reaction sites and the solvent, which are believed to affect catalytic performance.

2.3.3.1 Acidity of Zeolite Catalysts

The Beckmann rearrangement of cyclohexanone oxime to caprolactam is a typical acid catalyzed reaction. Types and strength of acid centers are therefore crucial parameters for this reaction. Early studies (60) suggested that strong and medium acid sites are efficient for the production of caprolactam. However, today the majority of researchers claim that neutral or weak acid sites affect conversion and selectivity to lactam.

Sato *et al.* (11) studied the Beckmann rearrangement over a highly siliceous ZSM-5 (Si/Al>1000) and tried to determine whether the acidic sites or the more neutral silanols contribute to the reaction. They suggest that both the activity and the selectivity were inversely proportional to the concentration of acid sites of ZSM-5 and even highly siliceous catalysts with almost no strong acidity exhibited high conversion with a high selectivity. The influence of the surface modification by vapor phase treatment with trimethylchlorosilane (TMCS) on the reaction was also studied by Sato *et al.* (11). The researchers tried to block the silanols partly with chlorotrimethylsilane in order to observe the effect of silanols on the surface. Very high selectivity and high conversion with long catalyst life were observed after the

treatment. It is supposed that TMCS causes the reduction of silanols and enhances the hydrophobicity. However, the TMCS treatment has no significant effect for acidic ZSM-5 samples with a Si/Al ratio of 104. It was observed that the catalytic activity and the selectivity for ϵ -caprolactam were directly proportional to the Si/Al ratio of the zeolite and the preferable active sites for this reaction were neutral silanols.

The group of Hölderich (61) carried out studies for the determination of the active sites on the catalysts and the effects of different types of hydroxyl groups on the surface properties of amorphous and crystalline catalysts. Amorphous silica and Silicalite-1 were modified with acidic or basic solutions. Catalysts were characterized by using several techniques such as X-ray diffraction, nitrogen adsorption and FTIR. According to FTIR analysis, rather than terminal silanols, silanol nests and vicinal silanol groups were found to be suitable for the Beckmann rearrangement reaction. The nitrogen adsorption isotherms of treated Silicalite-1 samples showed the change from the monoclinic to the orthorhombic structure, which is detected by the vanishing of the characteristic step. Acid treatment improved the catalytic activity of amorphous silica, where the basic treatment of crystalline Silicalite-1 increased the number of silanol nests. Combining the data with X-ray diffraction results, it is concluded that vicinal silanols and silanol nests are more suitable for the Beckmann rearrangement than terminal silanols and that the presence of the silanol nests on the Silicalite-1 catalyst surface enhances the conversion and selectivity to ϵ -caprolactam. Different types of silanol groups are given in Figure 2.10.

the boron oxide species has a significant effect on the catalytic performance. In case that boron oxide species were extracted by the acid or basic treatment or deactivated by hydration, the conversion decreased to around 70 %. If the boron species are left at the surface or reactivated, then conversion increases up to 98-100 %. This also supported, again, that vicinal silanol groups and silanol nests are important for the Beckmann rearrangement reaction.

O'Sullivan *et al.* (63) examined the relationship between the acidity of a range of zeolites, measured quantitatively by pyridine adsorption via FTIR analysis at different temperatures, and the deposition of coke during the Beckmann rearrangement as well as the effect of this deposition on the catalyst performance.

For this purpose, they used Zeolite β , Mordenite, MCM-41, amorphous silica-alumina, ZSM-5 and zeolite Y that have different acidities and surface areas. The effect of acid strength can be seen clearly from the results that strong acid sites, which are detected by pyridine adsorption, do not exhibit good catalytic performance. The authors concluded that catalysts based on the pore size. The results show that narrow pores in zeolites are affected by coke formation; however there was no strong sensitivity to the pore size.

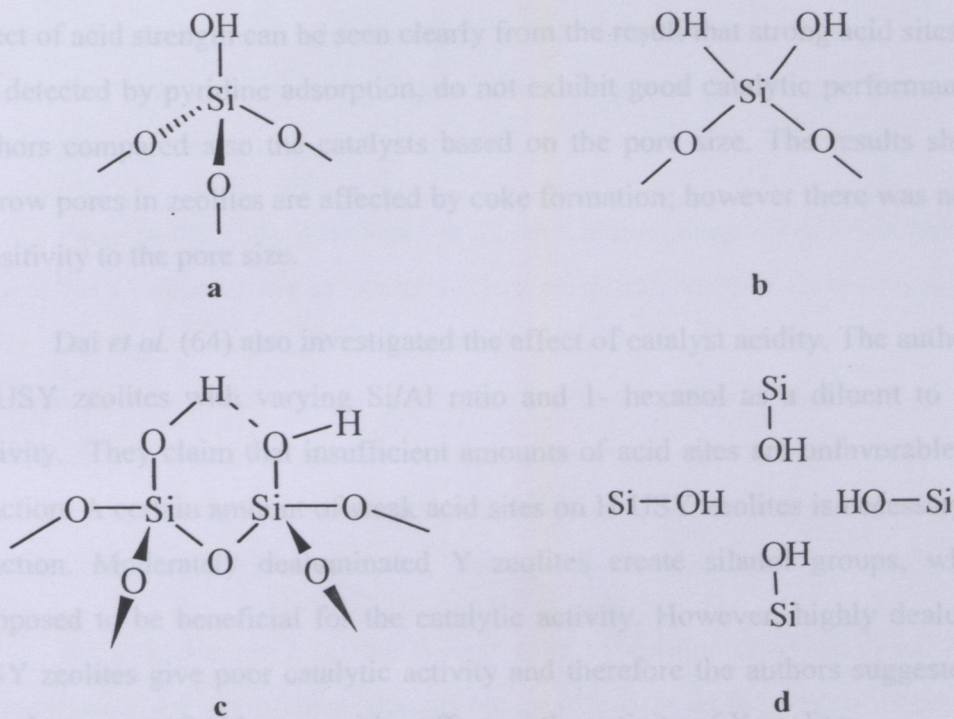


Figure 2.10. Silanol groups a) Isolated silanol, b) Geminal silanol, c) Vicinal silanol, d) Silanol nest.

The Hölderich group (62) investigated the effect of different treatments on the catalytic activities of B-ZSM-5 zeolite in the Beckmann rearrangement. Different calcination procedures, acid treatment with HCl, basic treatment with aqueous ammonia, steaming and water adsorption were applied to the catalysts. They found strong evidence that the boron oxide species has a significant effect on the catalytic performance. In case that boron oxide species were extracted by the acid or basic treatment or deactivated by hydration, the conversion decreased to around 70 %. If the boron species are left at the surface or reactivated, then conversion increases up to 98-100 %. This also supported, again, that vicinal silanol groups and silanol nests are important for the Beckmann rearrangement reaction.

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Dai *et al.* (64) also investigated the effect of catalyst acidity. The authors used H-USY zeolites with varying Si/Al ratio and 1- hexanol as a diluent to enhance activity. They claim that insufficient amounts of acid sites are unfavorable for this reaction. A certain amount of weak acid sites on H-USY zeolites is necessary for the reaction. Moderately dealuminated Y zeolites create silanol groups, which are supposed to be beneficial for the catalytic activity. However, highly dealuminated USY zeolites give poor catalytic activity and therefore the authors suggested that a certain amount of Al has a positive effect on the activity of Y zeolites.

Ouyang *et al.* (65) studied different catalysts in the Beckmann rearrangement reaction such as H- β , H-ZSM-5, and alumina pillared montmorillonite. The acidity was varied by utilizing different Si/Al ratios. The initial catalytic activities increase with increasing the acid amount; on the other hand, catalyst deactivation occurs mainly on the Brönsted acid sites according to the pyridine FTIR analysis. Therefore, the authors concluded that strong acid sites give rise to rapid catalyst deactivation.

2.3.3.2 Deactivation of Catalysts

Deactivation is one of the most severe obstacles for the commercial application of solid acids in the Beckmann rearrangement. The deactivation mechanism and the effect of acid strength on caprolactam selectivity were studied by Takahashi *et al.* (66). For this study, different catalysts with different acidity, such as MFI-type metallosilicates, Mordenite, Zeolite Y, and $\text{SiO}_2\text{-Al}_2\text{O}_3$ were used. The authors concluded that Beckmann rearrangement is initiated on the strong acid sites and cyclohexanone oxime converts to caprolactam immediately. The problem is, that strong adsorption of product results in formation of so called “hard” coke on the active sites. The authors suggest that a proper solvent like methanol or a diluent gas

like CO_2 should be used to remove the product from the active sites. In another study, (67) the same group used different diluents and different gases for the reaction. They concluded again that if CO_2 and methanol are used in the reaction the deactivation rate is depressed. The authors suggested that oxygen atoms in CO_2 could play an important role in deactivation.

Then, in Ref (68), Takahashi *et al.* used altered amounts of O_2 in helium as a diluent gas to observe the effect of oxygen on deactivation of the catalyst. For this study, MFI type catalysts, nickel impregnated $\text{SiO}_2\text{-Al}_2\text{O}_3$, and porous glasses with different surface areas and different acidities were utilized. The group found that catalyst life could be improved by using oxygen. The authors claim that the combination of a certain amount of oxygen as diluent gas and methanol as diluent solvent improves the catalyst life for H-ZSM-5, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and porous glasses.

As a final remark on the deactivation of various solid catalysts, it can be stated that the use of different solvents has an influence on the deactivation behavior.

2.3.3.3 Solvent Effect

The deactivation research results showed that there could be a relation between the solvent used as diluent and the deactivation of catalysts. Therefore, the choice of the solvent became one of the important considerations for the Beckmann rearrangement reaction.

Dai *et al.* (64, 69) also examined the solvent effect in the Beckmann rearrangement reaction by using H-MOR, H-BEA, H-LTL, H-OFF-ERI, and H-USY catalysts. They suggested that if 1-hexanol is used as diluent, catalytic activity, selectivity and catalyst life of zeolites with 12-membered ring structure could be improved.

Komatsu *et al.* (70) studied the effect of the solvent in the vapor phase Beckmann rearrangement of cyclohexanone oxime on a Silicalite-1 catalyst through kinetic measurements. Solvents with various polarities were examined for the reaction. The authors found that ethanol, which has medium polarity, is the most effective solvent in the formation of ϵ -caprolactam.

2.3.3.4 Location of the Reaction

The location of the reaction site in the Beckmann rearrangement reaction is a key subject of many studies. Catalysts having different pore sizes have been tested by several research groups in order to observe the diffusion of the cyclohexanone oxime to the pores and to find out whether the reaction takes place on the external surface of the catalysts or in the pores.

Sato *et al.* (11) concluded that the vapor phase Beckmann rearrangement took place on the outer surfaces of the catalysts, and the external surface area of the zeolite affected the catalytic activity.

Yashima *et al.* (71) examined a range of different catalysts for Beckmann rearrangement. In addition to H-ZSM-5, Silicalite-1, silica gels and H-mordenite, H-Ferrierite, Ca-A, Na-A and different types of clinoptilolite were also tested for this purpose. They concluded that the weaker acidic sites show a higher selectivity to ϵ -caprolactam.

The same authors also investigated separately the influences of the pore size and the solvent on the Beckmann rearrangement. They concluded that, those catalysts such as ferrierite and A type zeolite, which have a smaller pore size than the molecular size of cyclohexanone oxime, show high selectivities for caprolactam formation, while Mordenite and ZSM-5, which have pores larger than the reactant, do not exhibit such high selectivities. They strongly suggested that this reaction proceeds selectively on the active sites on the external surfaces of zeolite crystals.

The effect of surface area on the Beckmann rearrangement was also investigated by Kim *et al.* (72). They used tantalum-pillared Magadiite with different surface areas. They observed that Ta-Magadiite catalysts with relatively large surface areas showed higher catalytic activities.

Hölderich *et al.* (73) reported the effect of crystal size on the Beckmann rearrangement. They obtained the lowest conversion of 43 % (1h TOS; Time on Stream), with intermediate selectivities of about 65 %, when the largest crystals were used. The use of smaller, spherical crystals ($\ll 1 \mu\text{m}$) yielded an improvement in the

conversion of up to 100 % and in the selectivities of up to about 90 %. Their results are given in Table 2.4.

Table 2.4. Influence of the crystal size on the Beckmann rearrangement of cyclohexanone oxime over B-MFI zeolites (73).

Crystal size, μm	Shape	TOS, h	Conversion, %	Selectivity, %
<< 1	Spherical	1	99.8	87.8
		6	99.8	89.3
10-20	Spherical	1	53.9	62.8
		6	23.3	72.2
10x100	Cylindrical	1	43.1	64.7
		6	21.3	64.9

It was observed that when the external surface area was increased by decreasing the crystal size, conversion to ϵ -caprolactam increased significantly as well. The Beckmann rearrangement was concluded to take place on the outer surface of the catalyst rather than within the micropores of the MFI structure although this has been disputed for the liquid phase reaction (74) as well as for the gas phase reaction, where it was shown that both educt and product have access to the pore system of the MFI structure (17).

Weitkamp *et al.* (17) suggested that the Beckmann rearrangement reaction can also take place in the pores. To prove the assumption, sorption experiments with cyclohexanone oxime and caprolactam were carried out at 355 K and 413 K respectively. The authors claim that cyclohexanone oxime as well as caprolactam can diffuse into the pores, even if it is with some difficulties.

Although there are still some discussions about the location of the reaction site, most of the researchers seem to agree that Beckmann rearrangement of cyclohexanone oxime to caprolactam generally takes place on the outer surface, or, because of the mass transfer limitations, at least close to the external surface. In both cases, catalysts which have small particle size and high external surface areas will have big advantages for the Beckmann rearrangement.

Table 3.1. Molar compositions used in the syntheses of colloidal zeolites

	TPAOH	TEOS	Al ₂ O ₃	Ti(Obu) ₄	H ₂ O	EtOH
ZSM-5	12	25	1.67	-	430	100
Silicalite-1	7.8	21.4	-	-	390	85.6
TS-1	7.8	21.4	-	0.33	390	85.6

3. EXPERIMENTAL

3.1. Catalyst Preparation

For the synthesis of colloidal ZSM-5, 13.3 g of TEOS were mixed with 10.2

g of TPAOH. Colloidal ZSM-5, Silicalite-1 and Titanium Silicalite-1 (TS-1) catalysts were synthesized and used in the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam. Chemicals used in the syntheses were tetraethyl orthosilicate (TEOS, Across Organics 98%), Al₂(SO₄)₃ · 18 H₂O (Merck), tetrapropyl ammonium hydroxide (TPAOH, Alfa, 40% aqueous solution), NH₃ (Aldrich, 25% aqueous solution), titanium butoxide (Ti(Obu)₄, Aldrich 98%) and deionized water. 1,7-dichloro-octamethyl-tetrasiloxane (Fluka 95%) was also added in order to crosslink the zeolite particles in the synthesis solution. Two more crosslinkers, 1,3-dichloro-tetramethyl-disiloxane (Fluka 97%) and 1,5-dichloro-hexamethyl-trisiloxane (Fluka 95%), which have different chain lengths were also used for crosslinking reaction in order to observe the influence of the length of the linker. The chain lengths were evaluated by using software Desktop Molecular Modelling (Oxford electronic Publishing). The lengths are 8.18 Å, 10.86 Å and 13.38 Å for 1,3-dichloro-tetramethyl-disiloxane, 1,5-dichloro-hexamethyl-trisiloxane and, 1,7-dichloro-octamethyl-tetrasiloxane, respectively.

A solution containing colloidal zeolite was prepared according to published procedures (1). Silicalite-1 and TS-1 were synthesized using another molar composition, described elsewhere (2). However, the extraction method described in the ref 2 was not applied to the samples. Instead of using the extraction method, samples were dried at 363 K directly after aging. Molar compositions used in the syntheses of ZSM-5, Silicalite-1 and TS-1 are given in Table 3.1.

Table 3.1. Molar compositions used in the syntheses of colloidal zeolites.

	TPAOH	TEOS	Al ₂ O ₃	Ti(OBu) ₄	H ₂ O	EtOH
ZSM-5	12	25	1.67	-	480	100
Silicalite-1	7.8	21.4	-	-	390	85.6
TS-1	7.8	21.4	-	0.33	390	85.6

For the synthesis of colloidal ZSM-5, 13.3 g of TEOS were mixed with 10.2 g of TPAOH solution and the mixture was stirred at RT for 24 hours to allow the hydrolysis of TEOS. To this solution, a freshly prepared 6.45 g of TPA-aluminate solution was added under strong agitation. This TPA-aluminate solution was prepared by adding 5.15 g of a 40% w/w solution of TPAOH to 1.3 g of Al (OH)₃ gel, freshly prepared according to a method described previously (7).

After mixing the silica and alumina sources, the resulting solution was placed in a polypropylene bottle and closed tightly, then aged at RT or at 363 K for the chosen time. Following the aging, 4 mL of synthesis solution was taken by pipette and the required amount of 1,7-dichloro-octamethyl-tetrasiloxane was added into these 4 mL under vigorous stirring at RT. A gel was formed approximately 5 hours after mixing. The gel was aged for 24 hours, dried at 363 K for another 24 hours, and finally calcined at 823 K for 5 hours with a heating rate of 1 K/min.

For the synthesis of colloidal Silicalite-1, 9 g of TEOS were added to a vigorously stirred solution containing 7.9 g of TPAOH. After 30 min, 9 g of distilled water were added and the solution was stirred for another 24 hours at RT. Silicalite-1 samples were also aged at RT or 363 K for various periods. For the preparation of nanosized TS-1, 0.23 g of Ti(OBu)₄ were added to the solution after the hydrolysis of TEOS to provide a molar ratio of Ti/(Ti+Si)= 0. 015. Crosslinking was performed as for ZSM-5.

The effect of the linker amount was investigated for ZSM-5 and Silicalite-1 samples by adding 0.1 mL (0.26 mmol), 0.25 mL (0.65 mmol), 0.5 mL (1.3 mmol) and 1 mL (2.6 mmol) of 1,7-dichloro-octamethyl-tetrasiloxane to 4 mL of the

solution, aged for various periods. After stirring for 5 hours, samples were aged without stirring at RT for 24 hours, dried, and calcined as described above. The synthesis charts of ZSM-5, Silicalite-1, and Ti-Silicalite-1 are given in Figure 3.1.

Samples from syntheses, which should result in the formation of ZSM-5 were mostly X-ray amorphous. In the following, these will be termed as ZSM-5 (prep.), indicating that they were prepared from a solution, which would result in the formation of ZSM-5 under suitable conditions.

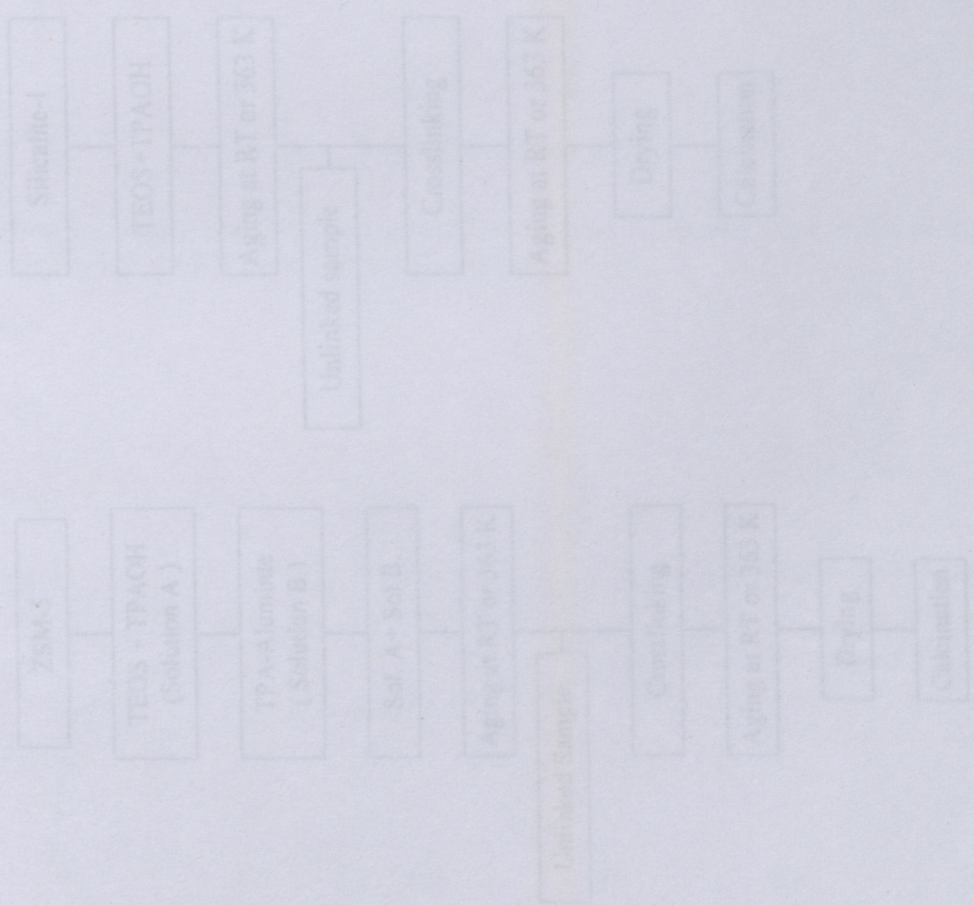


Figure 3.1. Synthesis pathway of ZSM-5, Silicalite-1, and TS-1 catalysts.

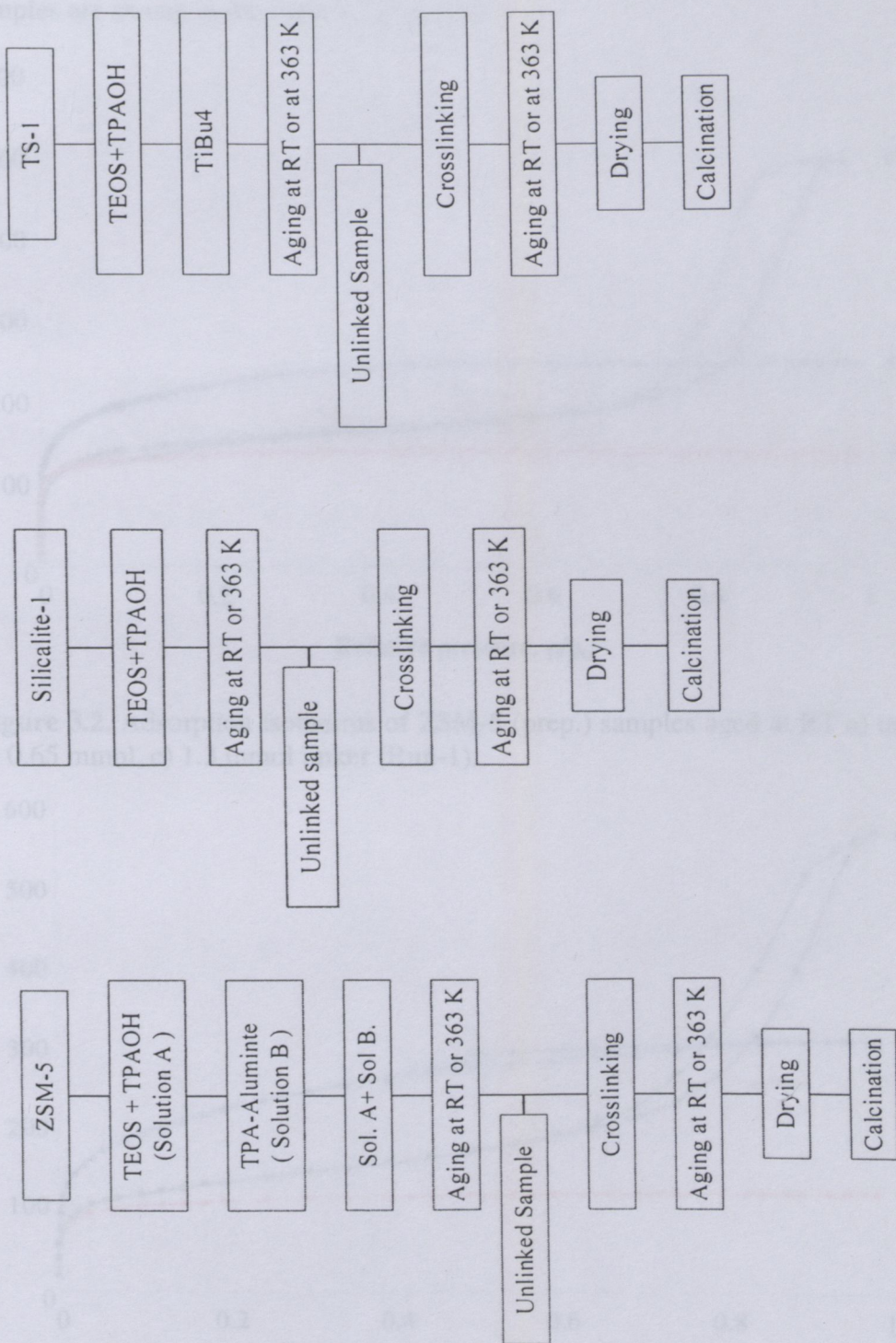


Figure 3.1. Synthesis pathway of ZSM-5, Silicalite-1, and TS-1 catalysts.

Synthesis experiments were repeated 2-3 times for all preparations. Adsorption isotherms obtained for the syntheses were very similar for identically prepared samples. As an example, the adsorption isotherms of ZSM-5 (prep.) samples are shown in the Figure 3.2 and 3.3.

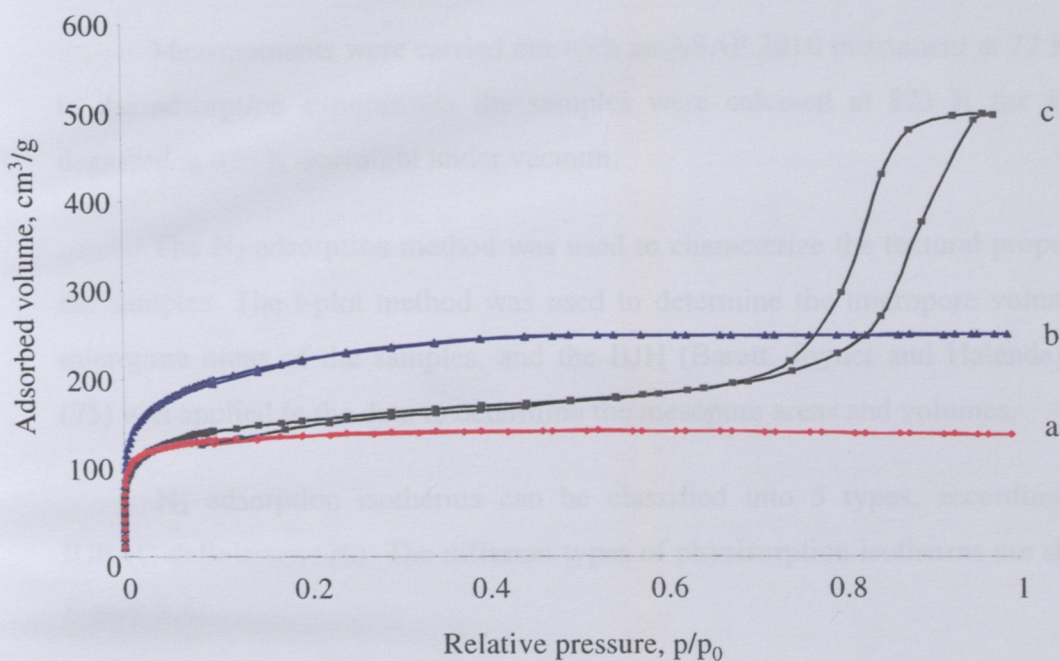


Figure 3.2. Adsorption isotherms of ZSM-5 (prep.) samples aged at RT a) unlinked, b) 0.65 mmol, c) 1.3 mmol linker (Run-1).

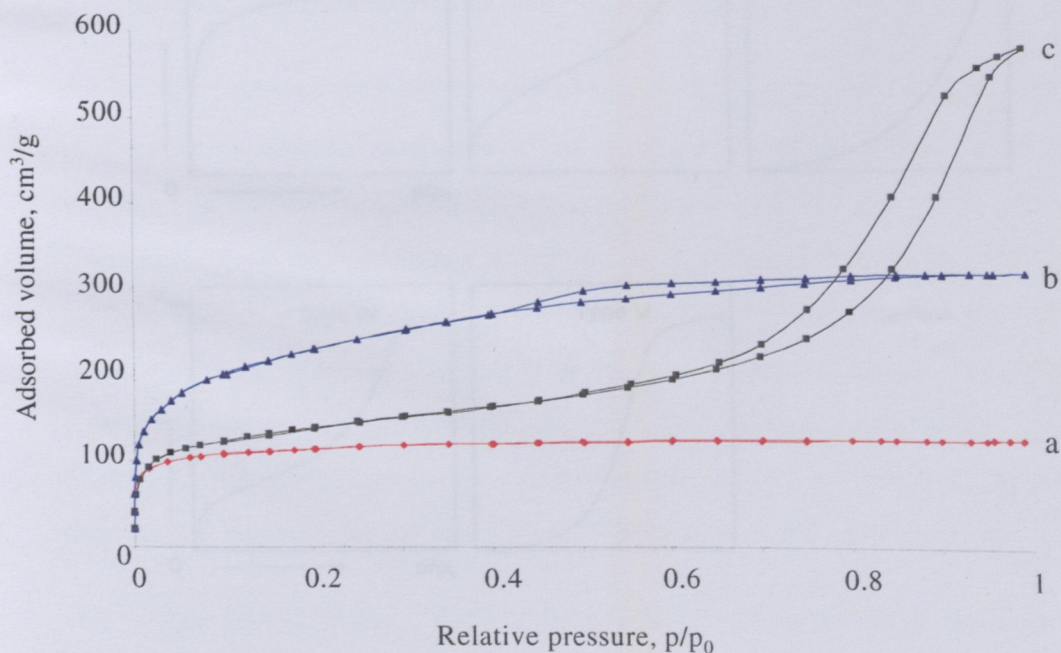


Figure 3.3. Adsorption isotherms of ZSM-5 (prep.) samples aged at 363 K a) unlinked, b) 0.65 mmol, c) 1.3 mmol linker (Run-2).

3.2.Characterization

3.2.1. N₂ Adsorption

Measurements were carried out with an ASAP 2010 instrument at 77 K. Prior to the adsorption experiments the samples were calcined at 823 K for 5 h and degassed at 473 K overnight under vacuum.

The N₂ adsorption method was used to characterize the textural properties of the samples. The t-plot method was used to determine the micropore volumes and micropore areas of the samples, and the BJH (Barett, Joyner and Halenda) model (75) was applied to the data to determine the mesopore areas and volumes.

N₂ adsorption isotherms can be classified into 5 types, according to the IUPAC definitions (76). The different types of physisorption isotherms are shown in Figure 3.4.

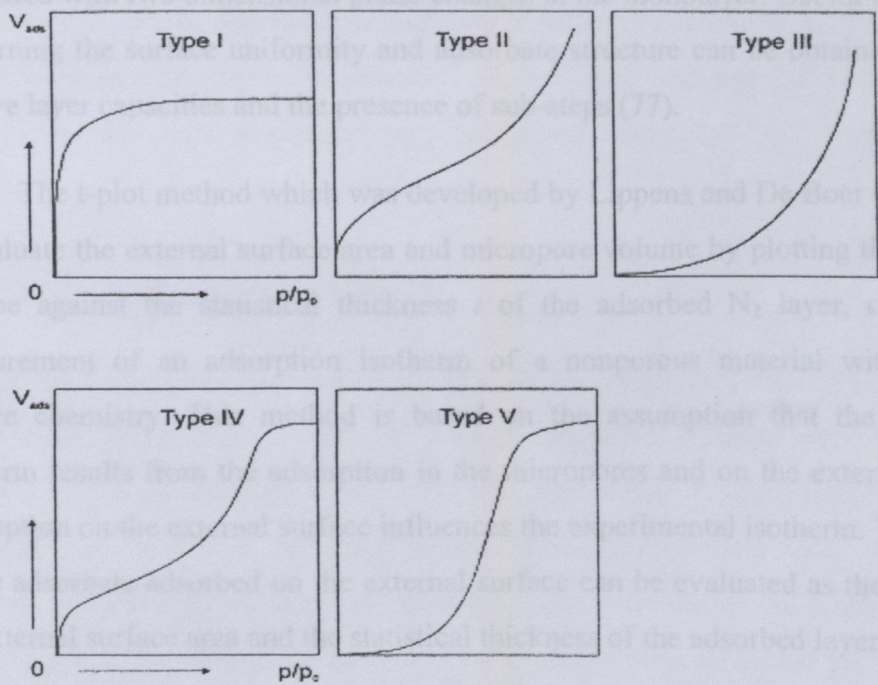


Figure 3.4. Types of adsorption isotherms.

The Type I isotherm referred to as Langmuir isotherm is concave to the p/p_0 axis and approaches a limiting value as $p/p_0 \rightarrow 1$. Type I isotherms are given by microporous solids having relatively small external surface areas. The Type II isotherm is the normal form of an isotherm obtained with nonporous or macroporous adsorbents. It represents monolayer-multilayer adsorption. The reversible Type III isotherm is convex to the p/p_0 axis over its entire range. This type of isotherm is confined to a few systems in which the adsorbate-adsorbent interactions are weak. Characteristics of the Type IV isotherm are its hysteresis loop, which is associated with capillary condensation in mesopores. Type IV isotherms are given by many mesoporous adsorbents.

Type V isotherms are also not common and related to the Type III isotherms. The Type VI isotherm, not shown in the figure, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform nonporous surface. Such isotherms are given by adsorption of simple non-polar molecules (e.g. argon, krypton) on uniform surfaces. The steps become less sharp as temperature is increased. When present, sub-steps are associated with two dimensional phase changes in the monolayer. Useful information concerning the surface uniformity and adsorbate structure can be obtained from the relative layer capacities and the presence of sub-steps (77).

The t-plot method which was developed by Lippens and De Boer (78) is used to evaluate the external surface area and micropore volume by plotting the adsorbed volume against the statistical thickness t of the adsorbed N_2 layer, obtained by measurement of an adsorption isotherm of a nonporous material with identical surface chemistry. This method is based on the assumption that the adsorption isotherm results from the adsorption in the micropores and on the external surface. Adsorption on the external surface influences the experimental isotherm. The volume of the adsorbate adsorbed on the external surface can be evaluated as the product of the external surface area and the statistical thickness of the adsorbed layer.

The Barrett, Joyner, and Halenda (BJH) method, which is based on a model of the adsorbent containing cylindrical pores, is the standard procedure for calculating the pore size distribution in mesoporous materials. The method accounts

for capillary condensation in the pores using the modified Kelvin equation. The pore radius minus the thickness of the adsorbed film replaces the radius of the capillary appearing in the Kelvin equation. The thickness of the adsorbed film is taken from the standard t-curve on a non-porous surface. The pore size distribution was obtained both from the adsorption and desorption branches of the isotherms.

Alternatively, Density Functional Theory (DFT) was applied to the data to obtain the pore size distribution (77). The DFT method has been developed for the pore size analysis of microporous and mesoporous materials. Compared to the classical thermodynamic models, the DFT method describes the behavior of the fluids confined in the pores on a molecular level. This allows relating the molecular properties of gases with their adsorption properties in pores of different sizes.

In order to calculate the pore size distributions, model isotherms are calculated for different pore sizes, pore geometries and surface chemistry. The experimental isotherm is then obtained by superposition of model isotherm for different pore sizes. The extent, to which an isotherm for a given pore size contributes to the experimental isotherm, can then be used to calculate the pore size distribution. Pore size distributions and pore areas were calculated with the NLDFT Kernel implemented in the Autosorb 1.51 software package by Quantachrome Instruments. The data evaluation was performed using the DFT Kernel for N₂ adsorption at 77 K on silica (equilibrium model).

3.2.2. X-Ray Diffraction Analysis

The X-ray diffraction data of the samples were collected on a STOE STADI P transmission diffractometer with a position sensitive detector. The data were recorded over a 2θ range of 5-60° and a step size of 0.01°. The diffractometer was equipped with a CuK α radiation source (8.04 keV or $\lambda=1.5406$ Å). Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder. The X-ray diffraction patterns of the sample were recorded on a computer. Particle size has been analyzed by using Stoe WinXPow software, which is based on the Scherrer equation.

A powder diffraction pattern has several features for zeolite structural analysis: the positions of the peaks, relative intensities of the peaks, the width of the peaks and the background.

The peak positions are determined only by the symmetry and the size of the unit cell. Each peak represents at least one reflection. The 2Θ value is related to the d-spacing of the corresponding reflection by the Bragg equation,

$$n\lambda = 2d_{hkl}\sin\theta \quad 4$$

which describes the diffraction of X-rays from a set of lattice planes, where n is an integer 1,2,3 etc., λ is the wavelength, hkl are the indices of the reflection, d is an interplanar spacing, and Θ is the angle of the incident X-ray beam.

The information on indices and d values of the material can be compared with databases to analyze the sample qualitatively.

The relative intensities of the peaks are determined by the type and positions of the various atoms in the unit cell. The intensity I_{hkl} for each reflection is proportional to the square of the structure factor F_{hkl} and the structure factor can be calculated using the summation

$$F_{hkl} = \sum f_n e^{-B_n} e^{-2\pi i(hx_n + y_n + lz_n)} \quad 5$$

over all n atoms in the unit cell, where f_n is the atomic scattering factor, B_n is the atomic displacement factor, $x_n y_n z_n$ are the coordinates of atom n . It is important to note in equation 4 that the intensity of each reflection is dependent upon the positions of all atoms in the unit cell. Changing just one atom e.g. by ion exchange will have an effect on the intensities of all reflections to different degrees and different directions.

The width of the peaks in the pattern gives an indication of the crystalline quality of the sample. They are dependent on the intrinsic instrumental peak width, the crystallite size and amount of the stress or strain in the material. As the domains of coherent scattering decrease below ca. 1000 Å, the peaks will broaden noticeably. In a first approximation, the Scherrer equation

$$L = \frac{K\lambda}{\beta \cos \theta_{hkl}}$$

6

The ^{29}Si chemical shift (δ) depends sensitively on the type and structural environment of the silicon atom. The ^{29}Si chemical shift can be used to estimate (ca. $\pm 10\%$) the average crystallite size, if measurable broadening of the peaks is observed. The full width at half maximum (FWHM) of a crystallite-size broadened peak is corrected for the instrumental contribution to yield the quantity β . L is the dimension of the crystallite perpendicular to the diffracting net planes; K is a constant, close to unity (often taken as 0.9); and λ is the wavelength of the radiation employed.

The background in a powder pattern indicates whether an amorphous material is present in the sample. A high background relative to the peaks is usually caused either by a large amount of amorphous material or by X-ray fluorescence.

3.2.3. ^{29}Si MAS NMR

^{29}Si MAS NMR measurements were carried out to characterize the Silicalite-1 samples by using a Bruker Avance 500 WB spectrometer with a spinning rate of 10 kHz. The width of the $\tau/4$ pulse was 2.2 μs and the recycle delay was 30 s. The measurements were carried out at RT using a 4 mm Bruker triple resonance probe (DVT 4BL).

^{29}Si MAS NMR has been used to examine the structure of zeolites (79-80). It is possible to obtain detailed information about lattice composition and acidic properties of zeolites.

Framework Si is tetrahedrally coordinated, and thus there are five different structural possibilities. The isolated silicate group, SiO_4 with no connection to other silicon atoms is designated Q^0 ; disilicate groups and chain end groups, Q^1 ; middle groups in rings or chains, Q^2 ; branching groups in layers and double-ring anions, Q^3 ; and finally, three dimensionally crosslinked framework groups, Q^4 . The index n in this Q^n nomenclature is equal to the number of bridging oxygen atoms of the SiO_4 unit under study. Initial studies of the Si chemical shifts of these silicate groups (81) encouraged the conclusion that chemical shifts in the solid state are essentially

similar to those found in solution, with shift ranges from about -65 ppm for the Q^0 unit to -115 ppm for the Q^4 unit.

The ^{29}Si chemical shift (δ) depends sensitively on the type and structural arrangement of the first and second nearest neighbor atoms of the silicon atom. The effect on δ of the type of the atoms directly bound to the Si atom is illustrated in Figure 3.5, which summarizes the δ -ranges observed for different $\text{Si}(\text{O})_{4-n}(\text{OSi})_n$ environments (81).

As in the case of the nearest neighbors, the shift ranges of the different environments overlap, but the assignment of well-separated peaks in the ^{29}Si MAS NMR-Spectrum of a certain silicate or aluminosilicate to the corresponding Si environments is possible. Thus, the quantitative distribution in the structure was determined from the peak intensities using ^{29}Si MAS NMR Spectrum.

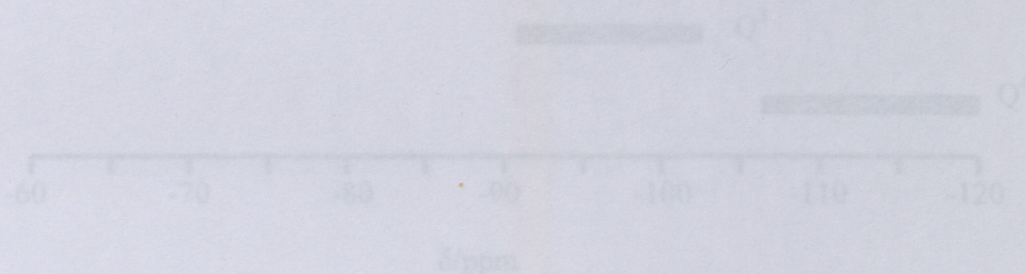


Figure 3.5. Ranges of ^{29}Si chemical shifts of $\text{Si}(\text{O})_{4-n}(\text{OSi})_n$ coordinations (Q^n) in silicates (81).

3.2.4. ^{13}C MAS NMR

^{13}C CP MAS NMR experiments were performed on a Bruker AVANCE DSX spectrometer with a 11.4 T magnet (^1H Larmor frequency of 500 MHz) under Magic Angle Spinning (MAS) using a Bruker 4 mm triple resonance probe. The spinning rate of 2.5 kHz was adjusted to assure an efficient cross polarisation transfer. All samples were measured with a contact time of 1 ms, proton decoupling during acquisition and relaxation delays of 2 s. Typically 1600 – 2600 scans were accumulated. In order to remove the carbon background of the probe, the DEPTM sequence (82) was applied and 2400 scans were accumulated with a recycle delay of 5 s. The spectra were referenced to solid hexamethyl benzene ($\delta(\text{CH}_3) = 17$ ppm).

With the wide chemical shift range, ^{13}C NMR is a sensitive analysis technique, where both physisorbed and chemisorbed species on the materials as well as chemical reactions that take place on the surface can be monitored.

MFI type zeolites consist of parallel, linear channels intersected by sinusoidal channels. Zeolites can be synthesized by using organic templates such as TPAOH, or tetrabutyl ammonium hydroxide (TBAOH). In the resulting material, the TPA^+ cation is located at the channel intersections, with the propyl chains extending into both the linear and sinusoidal channels (Figure 3.6.).

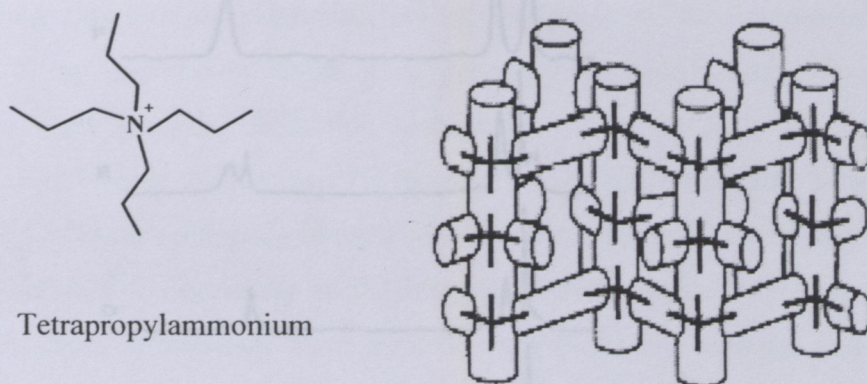


Figure 3.6. Proposed location of TPA occluded in MFI type zeolite (40).

The molecules are held tightly at these sites and can be removed only by calcination. Tight enclathration of the TPA molecules suggests that they must be incorporated into the structure during the process of crystal growth. Based on this information the presence of the zeolite structure can be proven by using the ^{13}C MAS NMR technique.

Burkett and Davis (39) examined the role of TPA ions as a structure-directing agent in the synthesis of Si-ZSM-5. ^{29}Si and ^1H - ^{13}C CP MAS NMR were performed in this study.

The ^{13}C MAS NMR spectrum of TPAOH solution shows resonances at -60 ppm, which are assigned to the methylene carbon bonded to the nitrogen, at -12.6

and -16 ppm, which are assigned to the methylene and methyl carbons in the chain of TPAOH. When TPA^+ is occluded in the zeolite channels, the resonance of the methylene carbon at -60 ppm is shifted to -62.6 ppm and the signal at -12.6 ppm splits into two peaks, typically at -10.1 ppm and -11.3 ppm.

3.2.5. The high resolution of the ^{13}C MAS NMR spectra of organic templates in zeolites is demonstrated in Figure 3.7 by the ^{13}C MAS NMR spectrum of the TPA^+ enclathrated in the zeolite ZSM-5 structure in the course of synthesis.

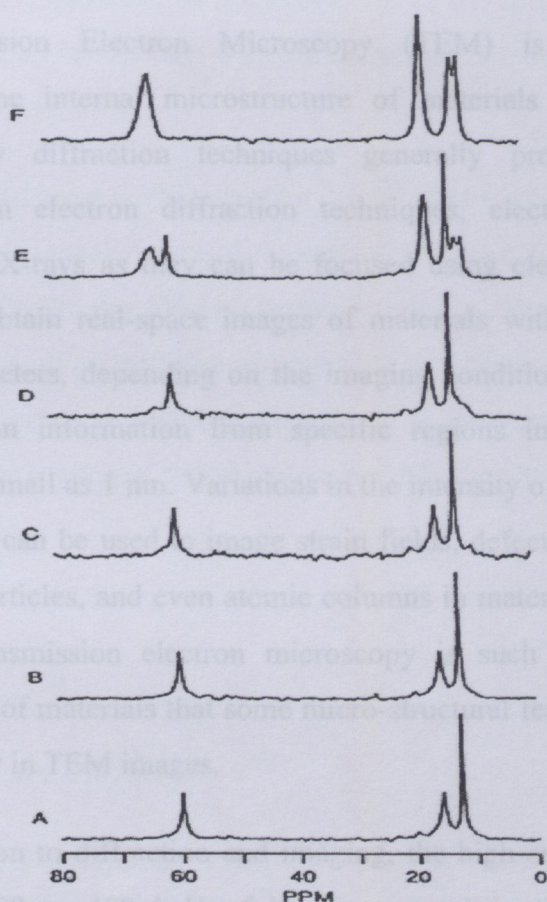


Figure 3.7. ^{13}C MAS NMR spectra of freeze dried samples collected during the TPA^+ mediated synthesis of Si-ZSM-5 a) unheated gel, b) heated at 383 K for 1 day, c) heated at 383 K 2 days, d) heated at 383 K for 3 days, e) heated at 383 K for 10 days, f) heated at 383 K for 10 days (D_2O washed). Taken from ref (39).

As seen from Figure 3.7, the unheated gel gives essentially the spectrum of free TPA^+ , which suggests that a zeolitic structure has not yet formed. On the other

hand, prolonging the aging time up to 10 days gives rise to a shift of the chemical shift from -60 ppm to -62 ppm, and a splitting of the signal at -12.6 ppm to -10 and -11 ppm, which is interpreted as evidence of TPA^+ cations occluded in the zeolite structure.

3.2.5. Transmission Electron Microscopy

Images of the nanosized zeolites were recorded using a Transmission Electron Microscope (TEM). TEM images were obtained with a Hitachi H-7500 Microscope operated at 100 kV.

Transmission Electron Microscopy (TEM) is the premier tool for understanding the internal microstructure of materials at the nanometer level. Although X-ray diffraction techniques generally provide better quantitative information than electron diffraction techniques, electrons have an important advantage over X-rays as they can be focused using electromagnetic lenses. This allows one to obtain real-space images of materials with resolutions approaching tenths of nanometers, depending on the imaging conditions, and to simultaneously obtain diffraction information from specific regions in the images (e.g., small precipitates) as small as 1 nm. Variations in the intensity of electron scattering across a thin specimen can be used to image strain fields, defects such as dislocations and second-phase particles, and even atomic columns in materials under certain imaging conditions. Transmission electron microscopy is such a powerful tool for the characterization of materials that some micro-structural features are defined in terms of their visibility in TEM images.

In addition to diffraction and imaging, the high-energy electrons (usually in the range of 100 to 400 keV of kinetic energy) in the TEM cause electronic excitations of the atoms in the specimen. Two important spectroscopic techniques make use of these excitations by incorporating suitable detectors into the transmission electron microscope, Energy-Dispersive X-Ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS).

3.2.6. Diffuse Reflectance Ultraviolet Analysis (DRUV)

DRUV-Vis spectra of the calcined TS-1 samples were recorded on a VARIAN Cary 5G spectrometer interfaced with a computer. BaSO_4 was used as a reference and the Kubelka-Munk function $F(R_\infty)$ was applied to analyze the data.

Ultraviolet Diffuse Reflectance Spectroscopy (DRUV) is one of the most important spectral techniques used for the determination of the valence and coordination state of titanium and titanium silicalites (82).

The DRUV spectrum with a maximum at about 200-212 nm and absorption onset at about 260-280 nm (82) is due to a charge-transfer (CT) process in isolated (TiO_4) or (HOTiO_3) units.

The second band is characteristic for Ti (IV) species in large titania particles (as in the case of anatase) with a maximum at about 312-328 nm and absorption onset at about 370-380 nm. DRUV spectroscopy is generally used to characterize all types of titanium silicalites; the presence of the former band in the spectrum is accepted as evidence of isolated Ti (IV) in a framework position, whereas the appearance of the band above 330 nm is an indication of extra framework titanium containing species.

3.3. Modification

3.3.1. Acid Treatment

Catalysts were modified before the catalytic test reaction. One group of samples was acid treated without calcination; they will be called UAT, (Uncalcined and Acid Treated). For these samples, TPA^+ cations were kept in the structure partly in order to use mostly the external surface area of the catalysts. Another group of samples was calcined at 823 K, acid treated and calcined again. For the acid treatment, 0.2 M HNO_3 was utilized. 100 mL of acid was used for 1 g of catalyst. The solution was stirred at RT for 3 h, filtered and washed with 500 mL of water and 50 mL of acetone. The filtrate was dried at RT overnight, and calcined again at 823.

K with a heating rate of 1K/min. These samples will be called CAT (calcined, acid treated and calcined again).

Table 3.2. Catalysts used in the reaction.

It is known that the acid treatment can also partially destroy the zeolite framework. Consequently, this generates the secondary pores in the micropore region (83). The treatment might cause lattice defects such as silanol nests. The possible effect of acid treatment is given in Figure 3.8.

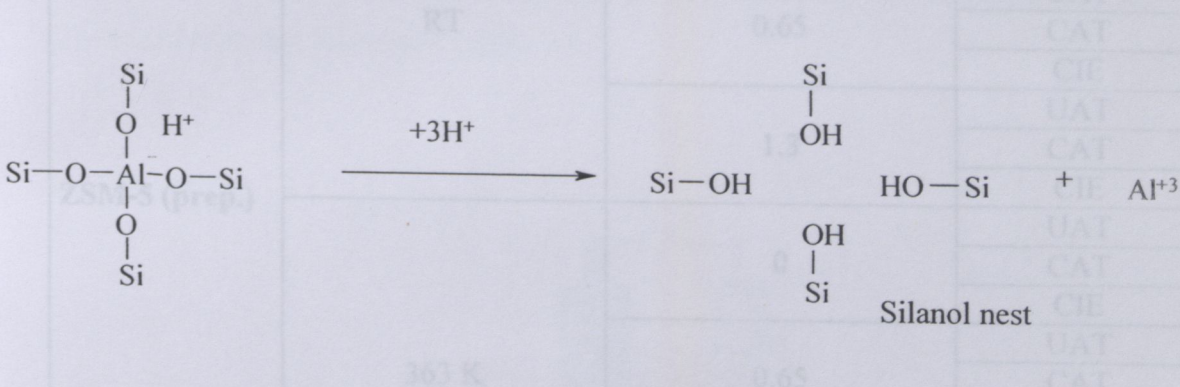


Figure 3.8. Proposed effect of acid treatment.

Regarding the concentration and characteristics of silanol groups on the silicate surface a number of studies was carried out (83-84). Silanol nests are supposed to be effective for the Beckmann rearrangement (60). Acid treatment was used to enhance the catalytic activity of the zeolites.

3.3.2. Ion exchange

Ion exchanged samples were also used in the reaction. For these treatments, 0.2 M NH₄NO₃ solution was used and 1 g of catalyst was added to 100 mL of salt solution and stirred for 3 h at RT. After the treatment, the solution was filtered and washed with 500 mL of distilled water and dried overnight at RT. Ion exchanged samples will be termed CIE (Calcined Ion Exchanged).

Although no sodium is used to synthesize zeolites and thus calcination should directly result in the formation of the proton form of the zeolites, an additional ion exchange treatment was applied to the samples to improve the activity without destroying the structure.

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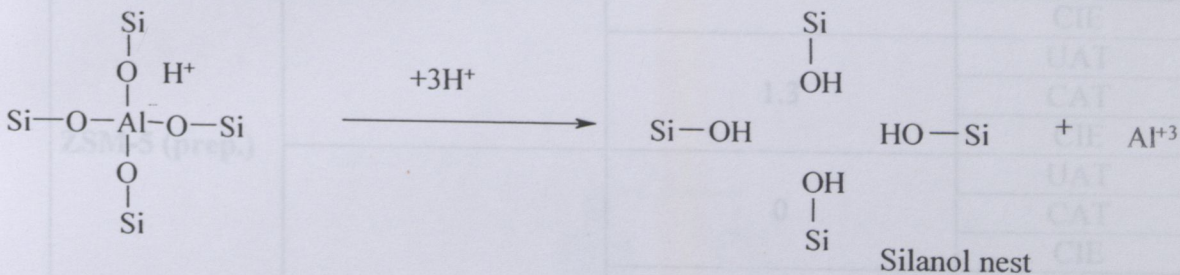


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Ion exchanged samples were also used in the reaction. For these treatments, 0.2 M NH_4NO_3 solution was used and 1 g of catalyst was added to 100 mL of salt solution and stirred for 3 h at RT. After the treatment, the solution was filtered and washed with 500 mL of distilled water and dried overnight at RT. Ion exchanged samples will be termed CIE (Calcined Ion Exchanged).

Although no sodium is used to synthesize zeolites and thus calcination should directly result in the formation of the proton form of the zeolites, an additional ion exchange treatment was applied to the samples to improve the activity without destroying the structure.

The synthesized samples and their synthesis parameters are listed in Table 3.2.

Table 3.2. Catalysts used in the reaction.

Catalyst	Aging Temperature	Linker amount, mmol	Modification
ZSM-5 (prep.)	RT	0	UAT
			CAT
			CIE
		0.65	UAT
			CAT
			CIE
		1.3	UAT
			CAT
			CIE
	363 K	0	UAT
			CAT
			CIE
		0.65	UAT
			CAT
			CIE
		1.3	UAT
			CAT
			CIE
Silicalite-1	RT	0	UAT
			CAT
			CIE
		0.65	UAT
			CAT
			CIE
		1.3	UAT
			CAT
			CIE
	363 K	0	UAT
			CAT
			CIE
		0.65	UAT
			CAT
			CIE
		1.3	UAT
			CAT
			CIE
TS-1	363 K	0	CAT
		1.3	CAT

3.4. Test Reaction

3.4.1. Beckmann Rearrangement of Cyclohexanone Oxime to ϵ -Caprolactam

The vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam was carried out at atmospheric pressure in a plug flow reactor at 553 K. The reactor scheme is given in Figure 3.9.

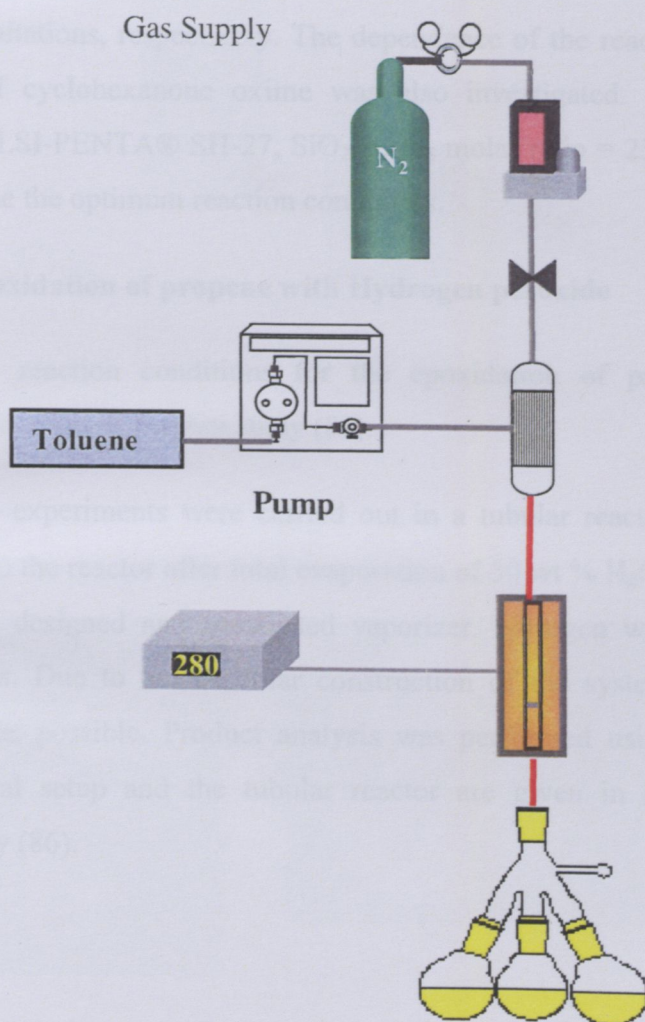


Figure 3.9. Experimental setup.

After the powdered catalysts were compressed into small pellets, they were crushed and sieved to 250-500 μm . 2 g of quartz was added to the 0.2 g of catalyst

and activated overnight under air at 623 K before being used in the reaction. A mixture of cyclohexanone oxime and toluene was supplied from a syringe pump at a constant rate to an evaporator. N₂ was used as the carrier gas. For the system, a stainless steel plug-flow reactor is used with a diameter of 10 mm, catalyst bed height is around 3.5 cm. Products were collected by condensation for 2 min after 1 hour and 4 hours and analyzed in an off-line gas chromatograph (HP 68H; 528) equipped with a capillary column (30 Cpsil-8; G/355) and an FID (Flame ionization detector).

Reactions were carried out with different catalyst particle sizes and flow rates to determine the conditions, which will eliminate the internal and external mass transfer limitations, respectively. The dependence of the reaction rate on the partial pressure of cyclohexanone oxime was also investigated. A commercial ZSM-5 catalyst (ALSI-PENTA® SH-27, SiO₂/Al₂O₃ molar ratio = 23-27) was used in order to determine the optimum reaction conditions.

3.4.2. Epoxidation of propene with Hydrogen peroxide

The reaction conditions for the epoxidation of propene with hydrogen peroxide are given in another study (85).

The experiments were carried out in a tubular reactor. Hydrogen peroxide was fed into the reactor after total evaporation of 50 wt % H₂O₂ solutions at 373 K in a specially designed and passivated vaporizer. Nitrogen was used as carrier and balance gas. Due to the modular construction of the system, a fast exchange of reactors was possible. Product analysis was performed using an online GC. The experimental setup and the tubular reactor are given in Figures 3.10 and 3.11 respectively (86).

Figure 3.11. Tubular reactor with inlet and outlet top cover.

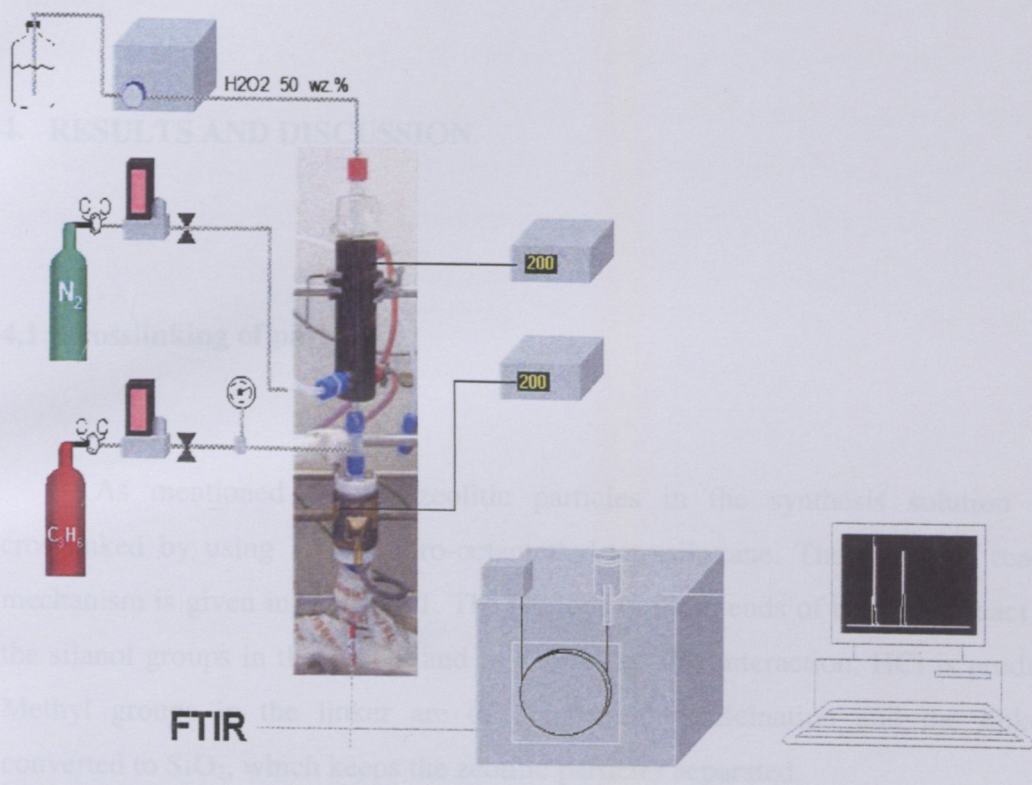


Figure 3.10. Schematic experimental setup.

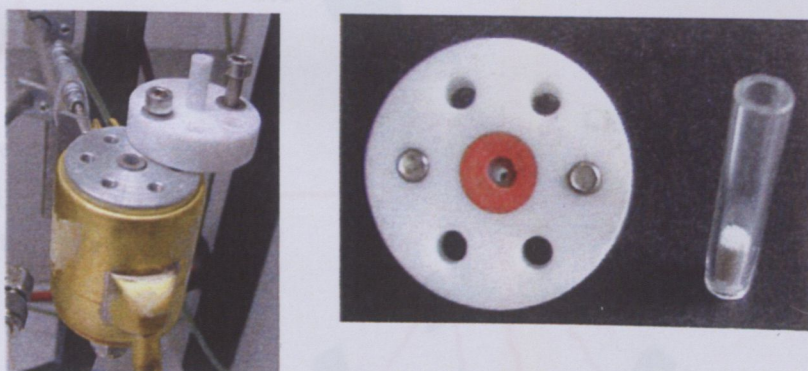


Figure 3.11. Tubular reactor with inlet and teflon top cover.

4. RESULTS AND DISCUSSION

4.1. Crosslinking of particles

As mentioned before, zeolitic particles in the synthesis solution were crosslinked by using 1,7-dichloro-octamethyl-tetrasiloxane. The proposed reaction mechanism is given in Figure 4.1. The Cl^- ions on both ends of the linker react with the silanol groups in the zeolite and as a result of this interaction, HCl is produced. Methyl groups in the linker are decomposed by calcination and the linker is converted to SiO_2 , which keeps the zeolitic particles separated.

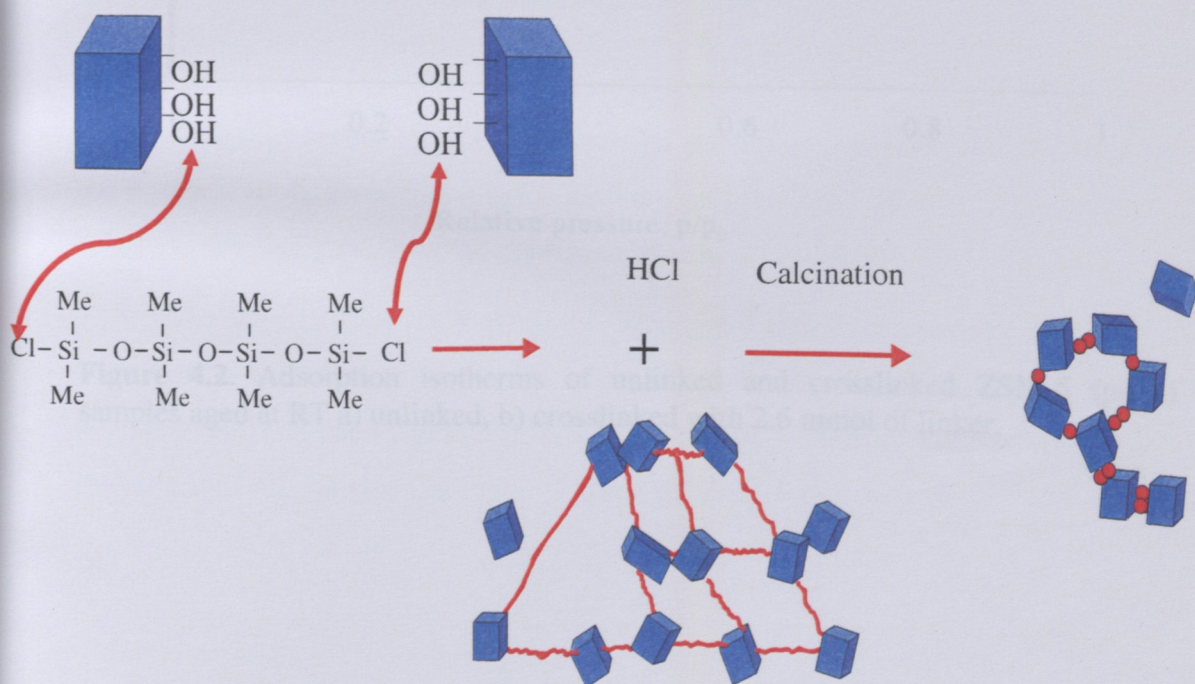


Figure 4.1. The proposed crosslinking reaction.

The crosslinking effect and the mesopores created by crosslinking of the particles were analyzed by N_2 adsorption. The isotherms of unlinked samples resemble the Type I isotherm. The isotherms obtained in this study for crosslinked samples also exhibit a sharp increase at low pressures, which is characteristic for microporous solids. However, in addition, they show appreciable N_2 uptake at higher pressures, which is indicative of mesoporosity. The adsorption isotherms of unlinked and crosslinked ZSM-5 and Silicalite-1 samples are given in Figures 4.2 and 4.3 respectively.

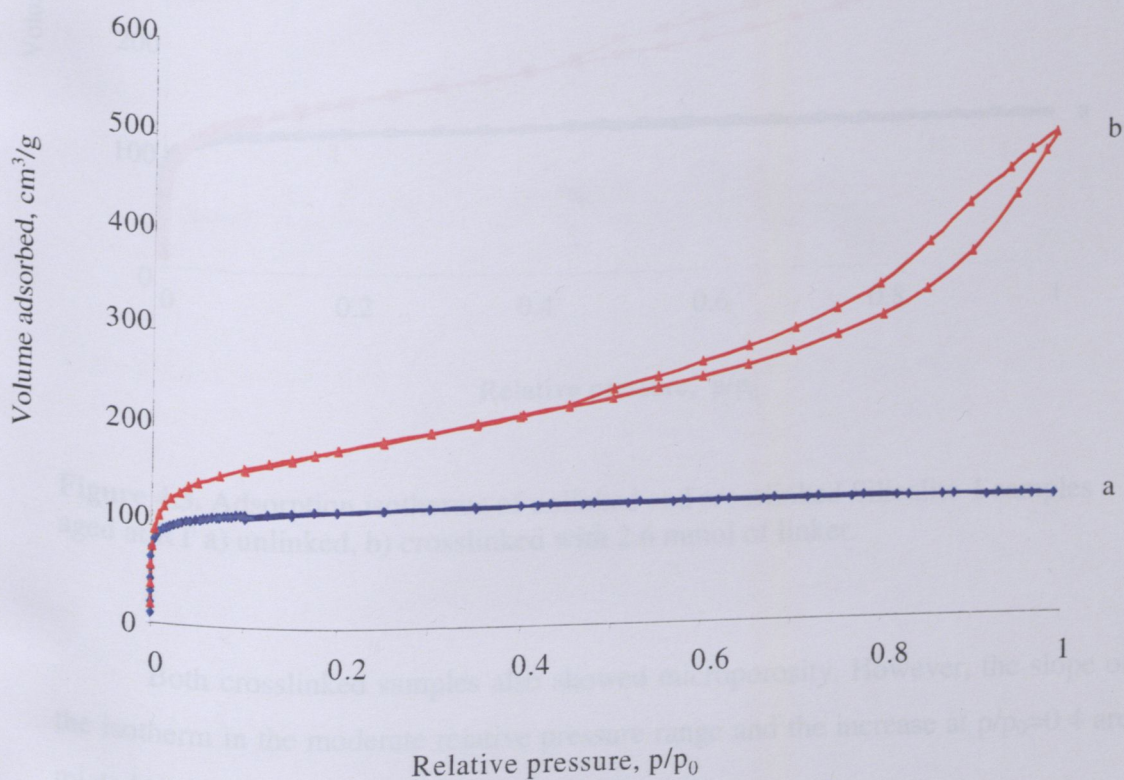


Figure 4.2. Adsorption isotherms of unlinked and crosslinked ZSM-5 (prep.) samples aged at RT a) unlinked, b) crosslinked with 2.6 mmol of linker.

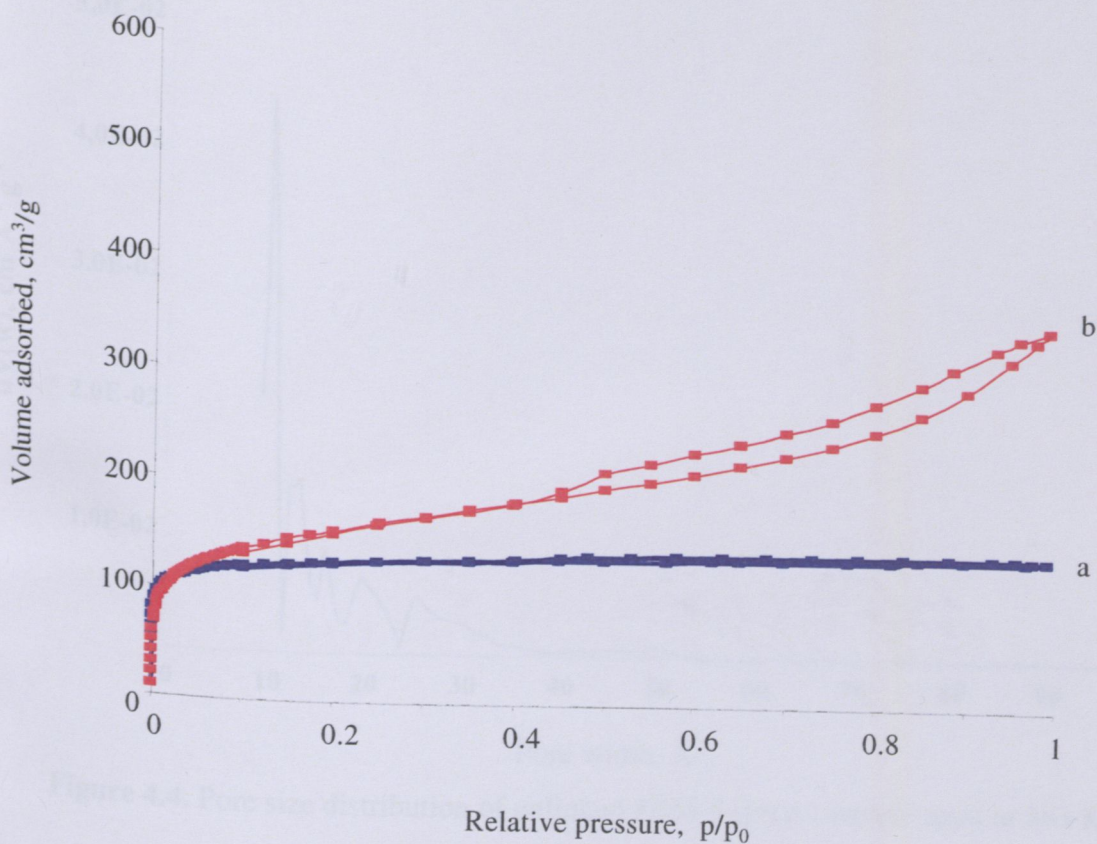


Figure 4.3. Adsorption isotherms of unlinked and crosslinked Silicalite-1 samples aged at RT a) unlinked, b) crosslinked with 2.6 mmol of linker.

Both crosslinked samples also showed microporosity. However, the slope of the isotherm in the moderate relative pressure range and the increase at $p/p_0=0.4$ are related to the contribution of the mesopore structure.

The quantitative analysis of the adsorption measurements also proves the formation of the mesoporous structure after crosslinking of the particles. Pore size distribution of unlinked and crosslinked ZSM-5 (prep.) samples are determined with the DFT method and given in Figure 4.4 and Figure 4.5, respectively.

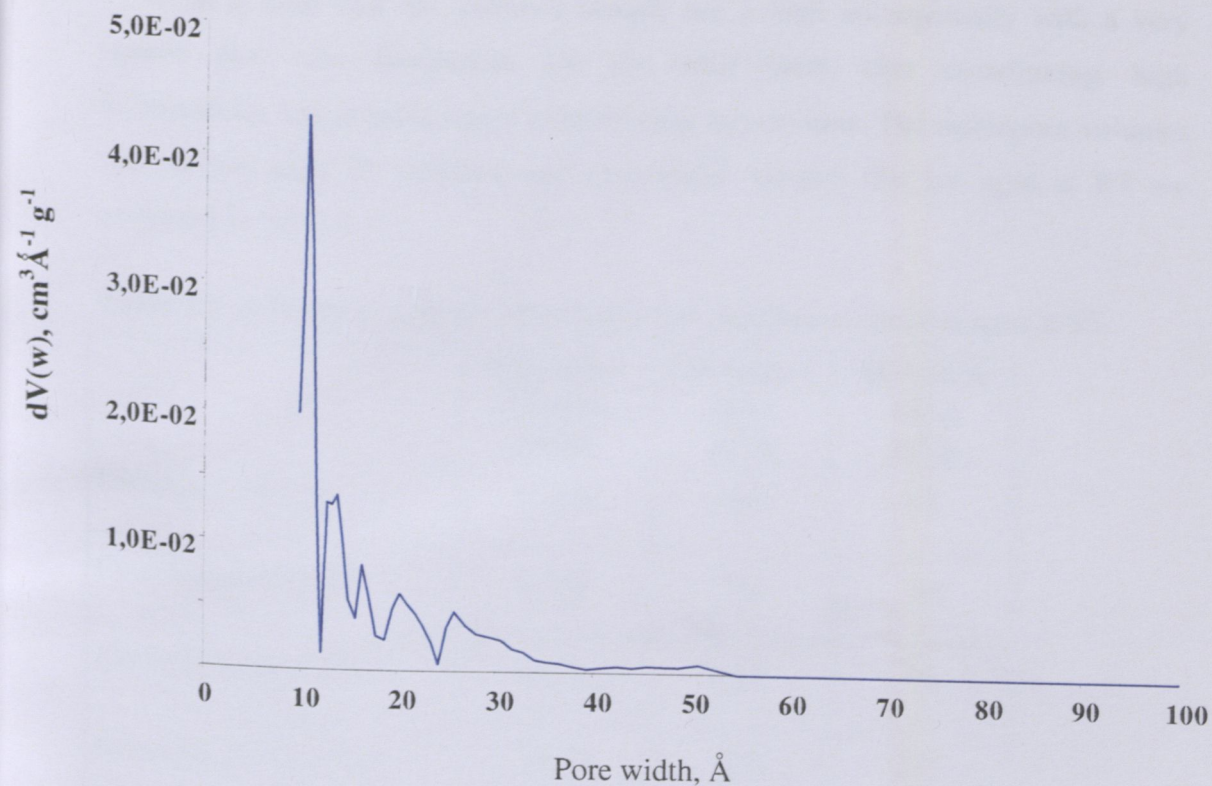


Figure 4.4. Pore size distribution of unlinked ZSM-5 (prep.) sample aged at 363 K.

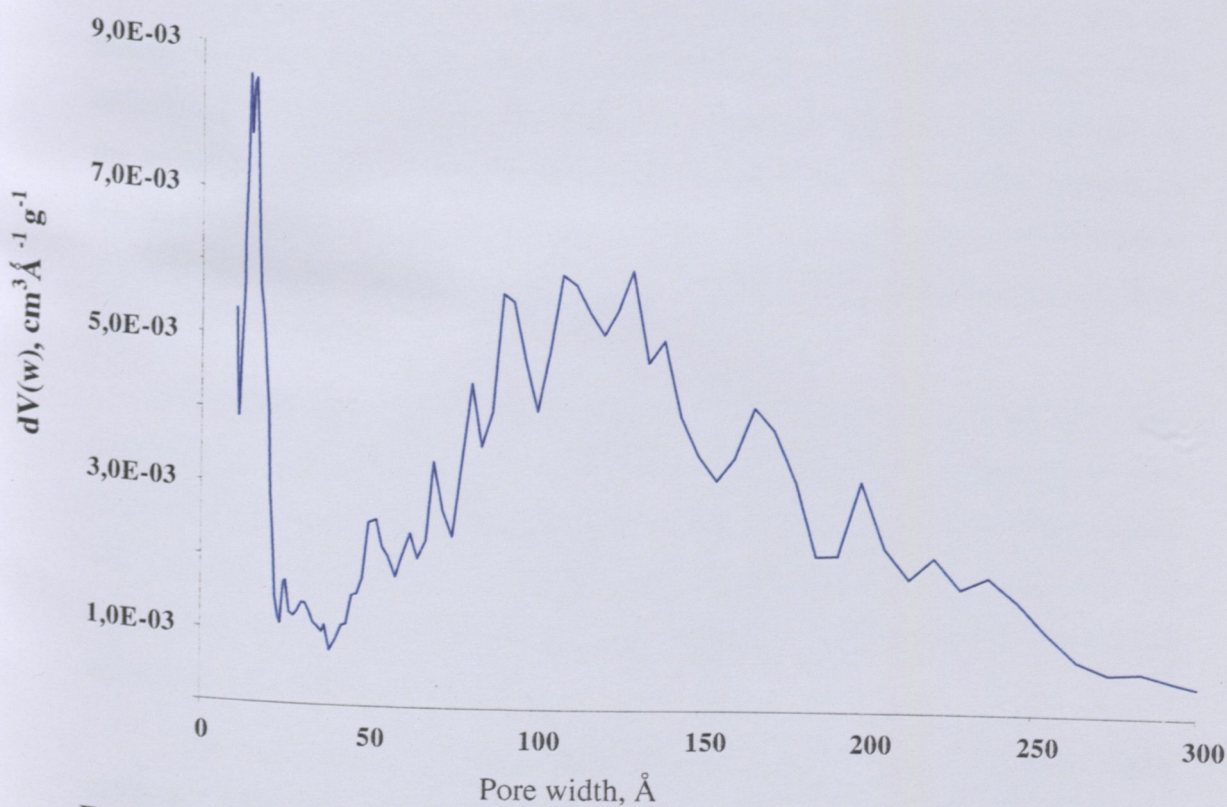


Figure 4.5. Pore size distribution of ZSM-5 (prep.) sample crosslinked with 2.6 mmol of linker and aged at 363 K.

It is clear that the unlinked sample has a high microporosity with a very narrow pore size distribution. On the other hand, after crosslinking, high mesoporosity and a broad range of pore sizes are obvious. The micropore volumes and surface areas for unlinked and crosslinked samples that are aged at RT are presented in Table 4.1.

Table 4.1. Adsorption analysis of unlinked and crosslinked samples aged at RT.

	Micropore Volume, cm³/g	Micropore Area, m²/g	Mesopore Area, m²/g
Unlinked ZSM-5	0.156	562	67
Crosslinked ZSM-5	0.094	334	356
Unlinked Silicalite-1	0.149	525	70
Crosslinked Silicalite-1	0.069	228	282

As shown in Table 4.1, the micropore volumes and areas decrease, while the mesopore surface areas increase for crosslinked samples. The zeolite fractions of the crosslinked samples decrease when they are crosslinked. Therefore, the decrease in the micropore volumes and areas after crosslinking can be related to the decrease in the zeolite fraction for the crosslinked sample. The high increase in the mesopore volumes and areas can be regarded as an evidence of the mesoporous structure formed by crosslinking.

Crosslinking of small zeolitic particles in the synthesis solution has been examined by Agren *et al.* (1). They synthesized colloidal ZSM-5 samples and then crosslinked nanoparticles in the solution with 1,7-dichloro-octamethyl-tetrasiloxane. The nitrogen adsorption isotherms of the samples provided evidence for the formation of an additional mesopore system. The results obtained in this study are in agreement with Agren's results (1).

The crosslinking procedure was also monitored by using ²⁹Si MAS NMR analysis. Unlinked and crosslinked Silicalite-1 samples for both aging temperatures were analyzed. The NMR spectra are shown in Figure 4.6.

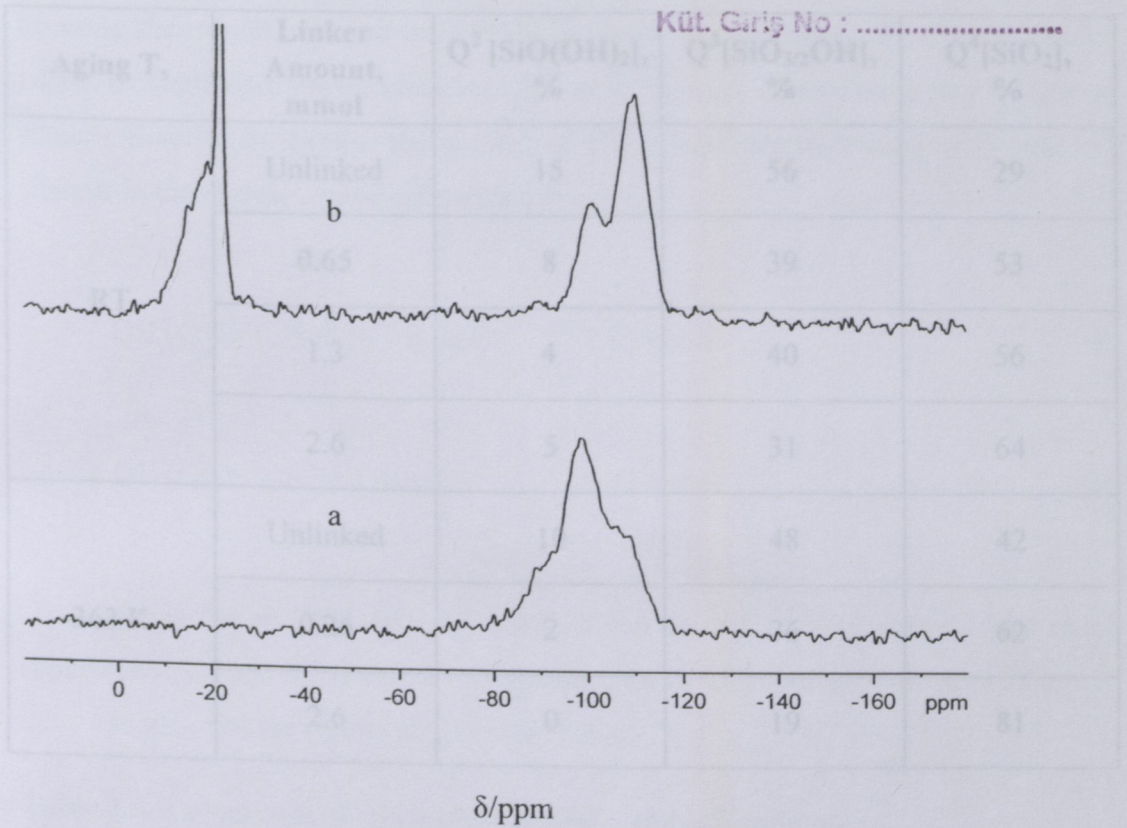


Figure 4.6. ^{29}Si MAS NMR spectra for Silicalite-1 samples aged at RT a) unlinked, b) crosslinked with 2.6 mmol of linker.

In the unlinked samples, three broad resonances are observed with chemical shifts of -88 ppm, -98 ppm and -109 ppm, which can be assigned to Q^2 , Q^3 , and Q^4 silicon atoms.

After crosslinking, two new lines are observed at -18 ppm and -22 ppm, which are attributed to the T-groups in the silicon linker. The concentration of Q^2 and Q^3 groups decreases, while the intensity of the Q^4 group increases. This can be ascribed to the reaction between silanol groups and silicone crosslinker.

The analysis results showed that the silicone crosslinker reacts with the hydroxyl groups and creates a micro-mesoporous structure. It can be concluded that crosslinking of particles is possible for both ZSM-5 and Silicalite-1 samples. Relative concentrations of the different silicon species in the Silicalite-1 samples are listed in Table 4.2.

Table 4.2. Amounts in percentage of the silanol groups in the Silicalite-1 samples.

Aging T,	Linker Amount, mmol	Q ² [SiO(OH) ₂], %	Q ³ [SiO _{3/2} OH], %	Q ⁴ [SiO ₂], %
RT	Unlinked	15	56	29
	0.65	8	39	53
	1.3	4	40	56
	2.6	5	31	64
363 K	Unlinked	10	48	42
	0.26	2	36	62
	2.6	0	19	81

Table 4.3. The amount of OH groups in 4 mL synthesis solution

From the ²⁹Si NMR data, one can calculate the fraction of silanol groups, which are consumed in the crosslinking. As an example, after drying a 4 mL Silicalite-1 synthesis solution, which was aged at RT, 0.61 g of solid sample was obtained. When this sample was heated up to 1473 K, the weight loss is around 39.6%, which means 60.4% of the sample is SiO₂. The amount of the SiO₂ can be calculated as follows;

$$m_{SiO_2} = 0.61g * \frac{60.4}{100} = 0.37g$$

7

Then, the number of moles of silica is;

$$n_{Si} = \frac{0.37\text{ g}}{60\text{ g/mol}} = 6.1\text{ mmol}$$

8

The number of Q^2 , Q^3 and Q^4 groups in this 4 mL solution can be calculated by using the results obtained from NMR analysis. The unlinked Silicalite-1 sample, which is mentioned above, includes 15% of Q^2 groups. Considering that Q^2 group silanols have 2 OH groups, the number of OH groups corresponding to Q^2 and Q^3 silanols in the sample can be estimated as;

$$OH(Q^2) = 0.15 \times 2 \times 6.1 \text{ mmol} = 1.84 \text{ mmol} \quad 9$$

$$OH(Q^3) = 0.56 \times 6.1 \text{ mmol} = 3.43 \text{ mmol} \quad 10$$

When the above values are added, it can be said that 6.1 mmol of unlinked sample have around 5.3 mmol of OH groups. Similar calculations were applied to the other samples and the results are listed in Table 4.3.

Table 4.3. The amount of OH groups in 4 mL synthesis solution.

Aging T,	Linker used, mmol	OH (Q^2), mmol	OH (Q^3), mmol	OH (Q^2+Q^3), mmol	OH reacted, mmol	Linker reacted, mmol	Unreacted linker, mmol
RT	unlinked	1.84	3.43	5.27	-	-	-
	0.65	0.98	2.39	3.37	1.90	0.65	-
	1.3	0.49	2.45	2.94	2.3	1.15	0.15
	2.6	0.61	1.9	2.51	2.8	1.4	1.2
363 K	unlinked	1.32	3.16	4.48	-	-	-
	0.26	0.26	2.37	2.63	1.85	0.26	-
	2.6	0	1.25	1.25	3.23	1.62	0.98

According to the NMR analysis, when 2.6 mmol linker is used, for example, for the RT aged sample, the decrease in the silanol groups is 2.8 mmol. Keeping in mind that 2 mmol of OH groups can react with 1 mmol of linker, it can be said that 1.4 mmol of linker should have been used in the reaction and 1.2 mmol of linker should be remaining in the solution assuming that each linker reacts with both ends with the colloidal particles.

On the other hand, when lower amounts of linker were used, the decrease in the total concentration of silanol groups was higher than the linker amount used. This means that all the linker was used in the reaction, and, in addition, condensation process for the rest of the silanols proceeded further since samples were aged for another 24 h after linking as well.

In order to investigate what the effect of the linker chain length on the textural properties of the materials is, different linkers, which are shorter than 1,7-dichloro-octamethyl-tetrasiloxane, namely 1,3-dichloro-tetramethyl-disiloxane and 1,5-dichloro-hexamethyl-trisiloxane were used to crosslink the particles in the Silicalite-1 synthesis solutions. The effect of the length of the linker was investigated for Silicalite-1 samples aged at RT and at 363 K. The adsorption isotherms of such samples are given in Figure 4.7 and 4.8 respectively.

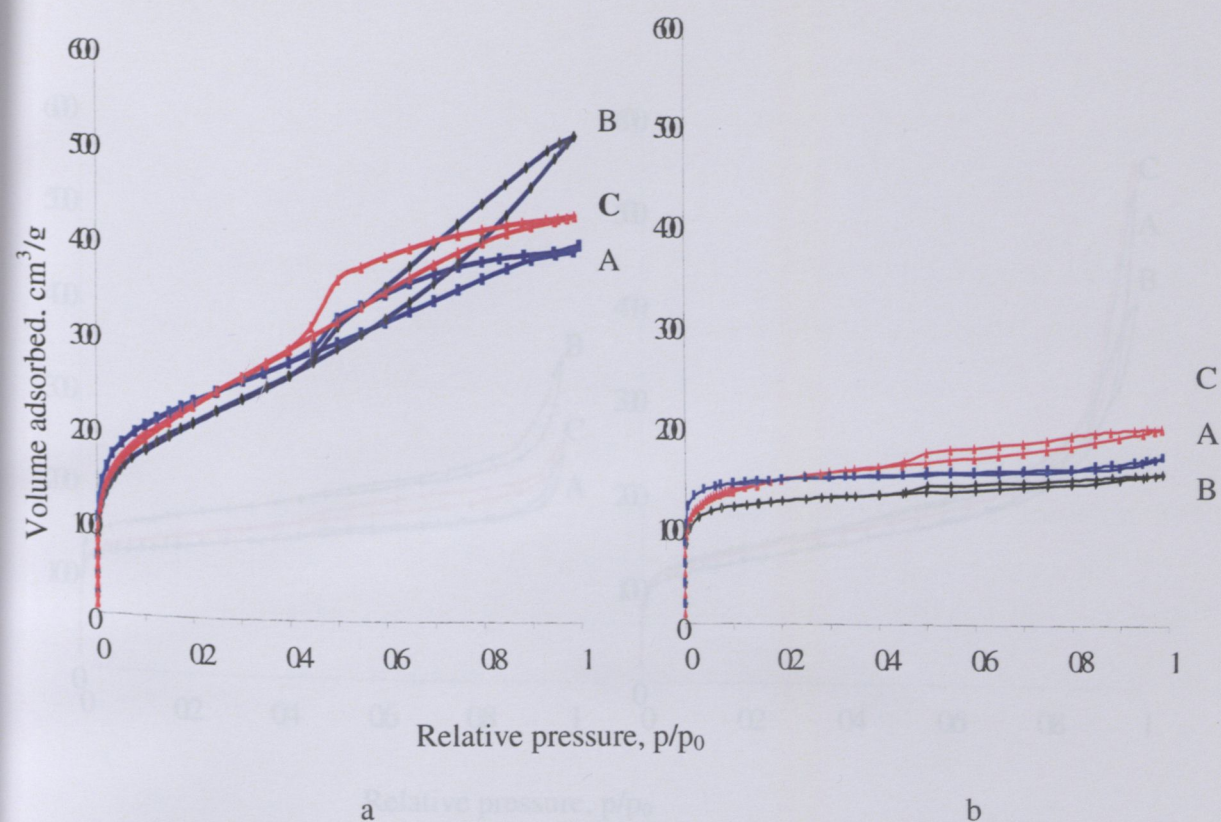


Figure 4.7. Adsorption isotherms of Silicalite-1 aged at RT and crosslinked with a) 0.65 mmol, b) 1.3 mmol of linker

A: 1.3-dichloro-tetramethyl-disiloxane
 B: 1.5-dichloro-hexamethyl-trisiloxane
 C: 1.7-dichloro-octamethyl-tetrasiloxane

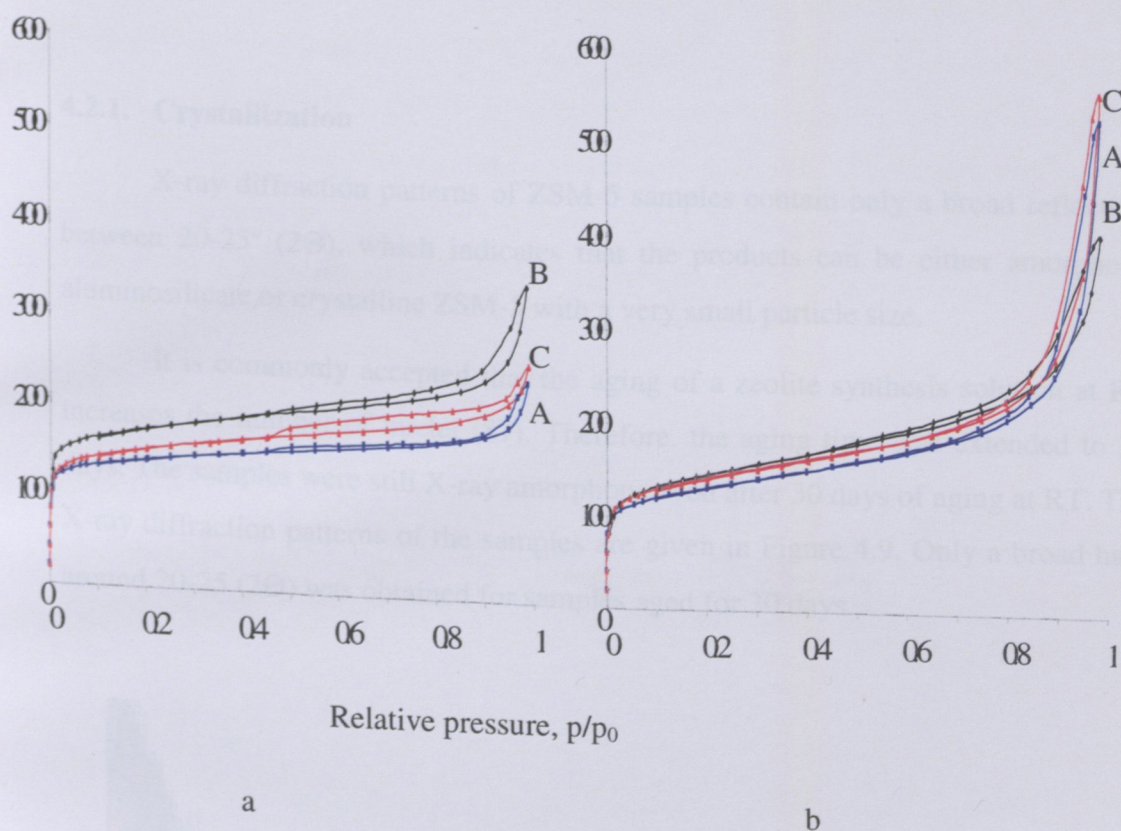


Figure 4.8. Adsorption isotherms of Silicalite-1 aged at 363 K and crosslinked with a) 0.65 mmol, b) 1.3 mmol of

- A: 1.3-dichloro-tetramethyl-disiloxane
- B: 1.5-dichloro-hexamethyl-trisiloxane
- C: 1.7-dichloro-octamethyl-tetrasiloxane

As seen from Figure 4.7 and Figure 4.8, the adsorption behavior of the samples is relatively similar. The chain length of the crosslinker has no significant effect on the textural properties. This suggests that linker primarily prevents neat packing of the colloidal particles and thus helps to create the mesopore system.

4.2. ZSM-5

4.2.1. Crystallization

X-ray diffraction patterns of ZSM-5 samples contain only a broad reflection between $20\text{--}25^\circ$ (2Θ), which indicates that the products can be either amorphous aluminosilicate or crystalline ZSM-5 with a very small particle size.

It is commonly accepted that the aging of a zeolite synthesis solution at RT increases the number of nuclei (87). Therefore, the aging time was extended to 30 days. The samples were still X-ray amorphous even after 30 days of aging at RT. The X-ray diffraction patterns of the samples are given in Figure 4.9. Only a broad halo around $20\text{--}25$ (2Θ) was obtained for samples aged for 30 days.

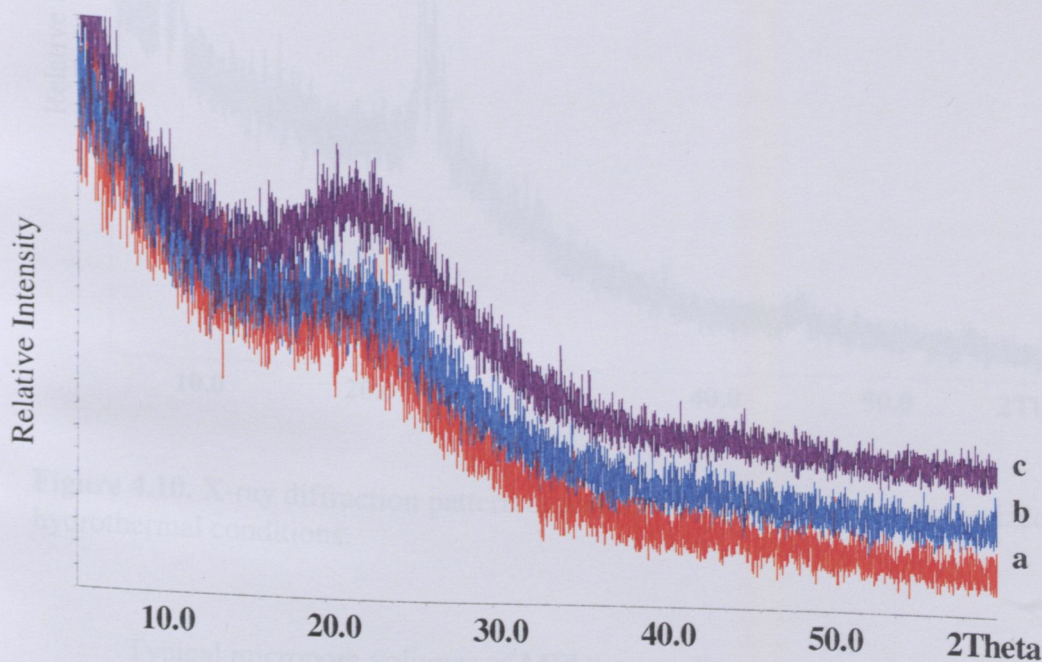


Figure 4.9. X-ray diffraction patterns of calcined ZSM-5 samples aged at RT for a) 1 day, b) 7 days, c) 30 days.

However, it should be considered that with X-ray diffraction analysis, small particles of approximately less than 10 nm might not be detected. Further investigations using other characterization methods are thus needed in order to

determine the degree of crystallinity of the sample. Although the ZSM-5 samples used in the catalytic tests were amorphous, they became crystalline after hydrothermal treatment at 453 K. As stated before such samples are termed as ZSM-5 (prep.), indicating that they were prepared from a solution, which would result in the formation of ZSM-5 under suitable conditions. One should keep in mind, though, that such samples do not contain crystalline ZSM-5. The X-ray diffraction pattern of ZSM-5 (prep.) samples after hydrothermal treatment at 453 K for 5 days is given in Figure 4.10.

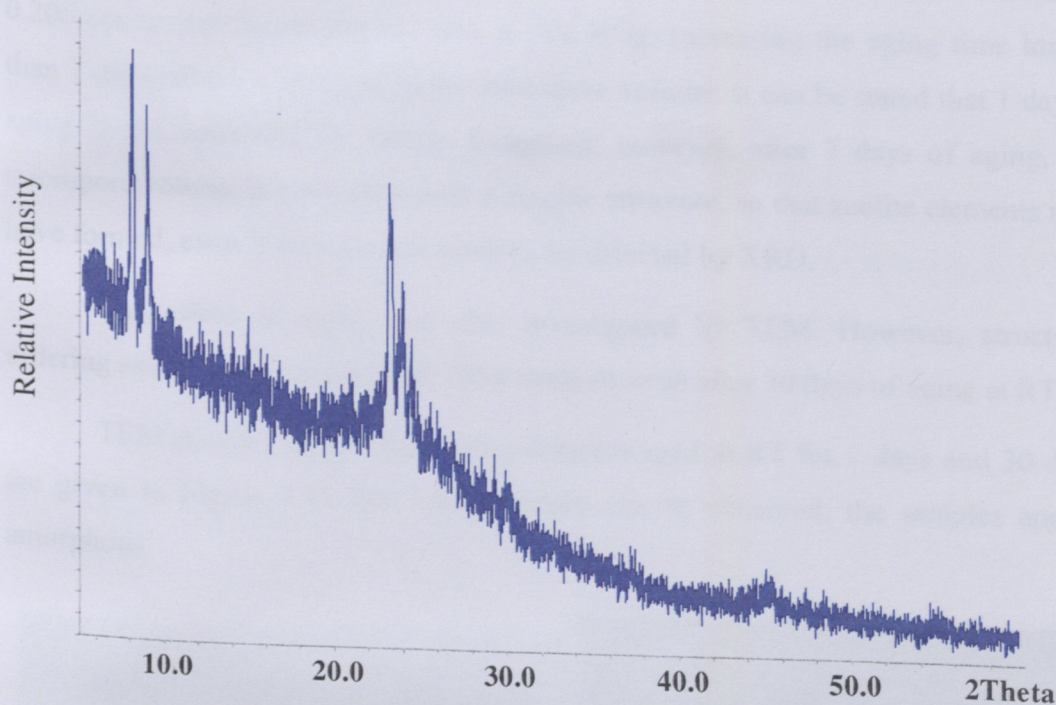


Figure 4.10. X-ray diffraction pattern of a calcined ZSM-5 sample synthesized under hydrothermal conditions.

Typical micropore volumes of MFI type zeolites are reported to be $0.19 \text{ cm}^3/\text{g}$ for N_2 as sorptive (76). The micropore volumes and areas of the prepared samples are given in Table 4.4.

Table 4.4. Adsorption analysis of calcined ZSM-5 (prep.) samples aged at RT.

Aging time, days	Micropore Volume, cm ³ /g	Micropore Area, m ² /g
1	0.156	562
7	0.206	726
30	0.168	544

As shown in Table 4.4, after 7 days of aging at RT, the micropore volume is 0.206 cm³/g and the micropore area is 726 m²/g. Increasing the aging time longer than 7 days causes a decrease in the micropore volume. It can be stated that 1 day of aging is not sufficient for zeolite formation; however, after 7 days of aging, the micropore volume is consistent with a zeolitic structure, so that zeolite elements may have formed, even if they are too small to be detected by XRD.

The effect of aging was also investigated by TEM. However, structural ordering could not be detected by TEM analysis even after 30 days of aging at RT.

TEM pictures of ZSM-5 (prep.) samples aged at RT for 7 days and 30 days are given in Figure 4.11. No lattice fringes can be observed, the samples appear amorphous.

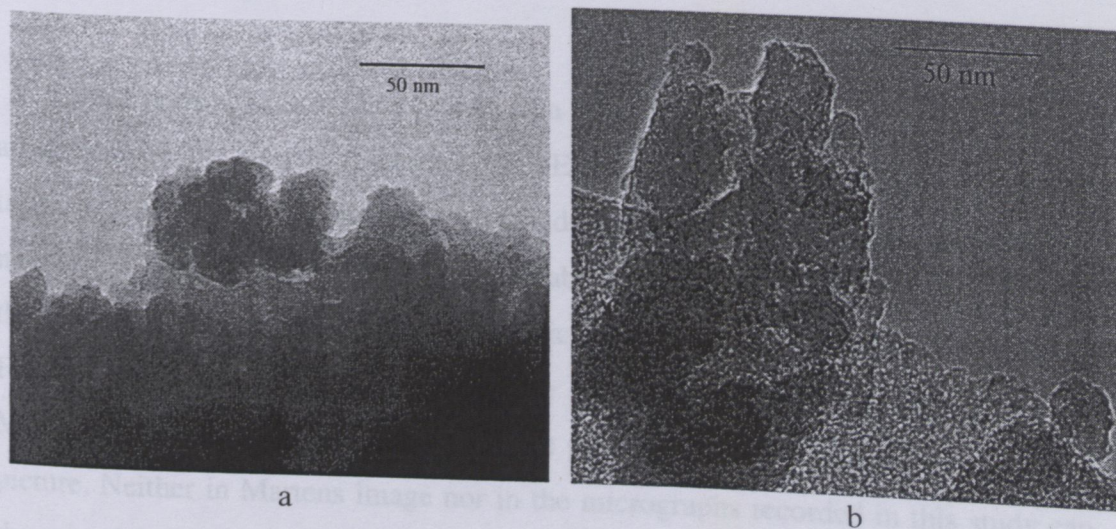


Figure 4.11. TEM pictures of ZSM-5 (prep.) samples aged for a) 7 days (recorded on the Hitachi 7500), b) 30 days.

The aging time effect was also studied for ZSM-5 (prep.) samples at 363 K for 7, 10 and 16 days, to enhance the crystallization. X-ray diffraction data of ZSM-5 (prep.) samples, which were aged at 363 K, are given in Figure 4.12. According to X-ray diffraction, ZSM-5 (prep.) samples are amorphous even after 16 days of aging at 363 K. Only a broad reflection was detected between 20-25° (2 Θ).

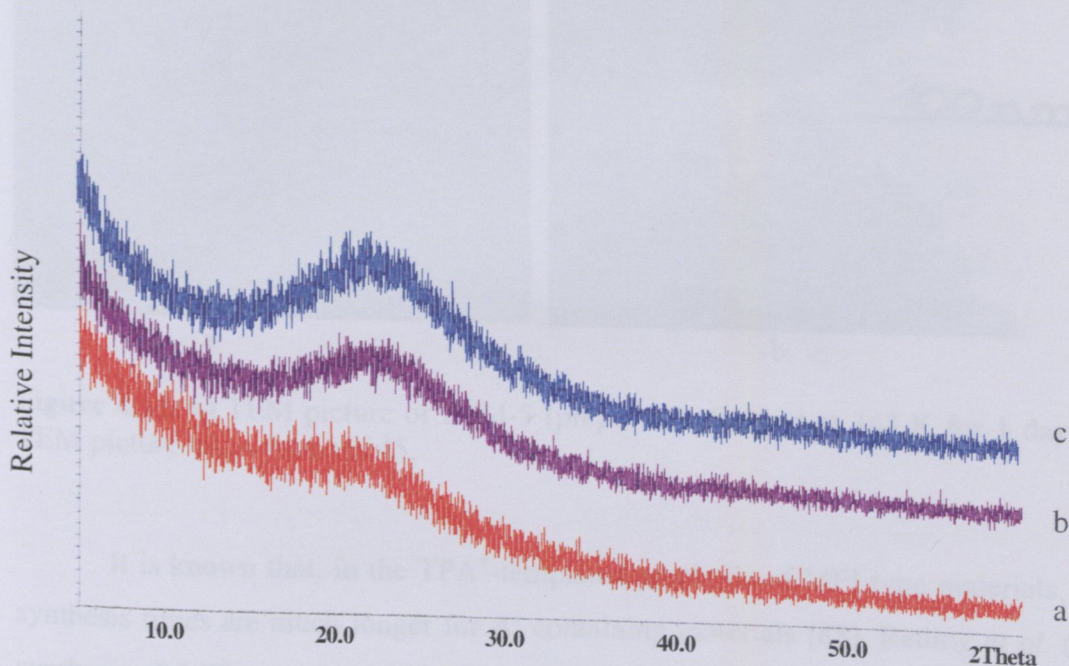


Figure 4.12. X-ray diffraction pattern of calcined ZSM-5 (prep.) samples aged at 363 K for a) 1 day, b) 7 days, c) 16 days.

In Figure 4.13 a, a TEM picture of a ZSM-5 (prep.) sample is presented. The appearance of the sample resembles the TEM picture in Figure 4.13 b, which was taken from Marten's study (45) as evidence of the rectangular geometry of nanoslabs. In this study, the sizes of nanoslabs are claimed to be $4 \times 4 \text{ nm}^2$, assuming that they have a rectangular shape, and a thickness of 1.3 nm as derived from Atomic Force Microscopy (AFM). Although the picture resembles those presented in Martens study, it is difficult to interpret the geometry of the particles from the TEM picture. Neither in Martens image nor in the micrographs recorded in this study can the nanoslabs be identified.

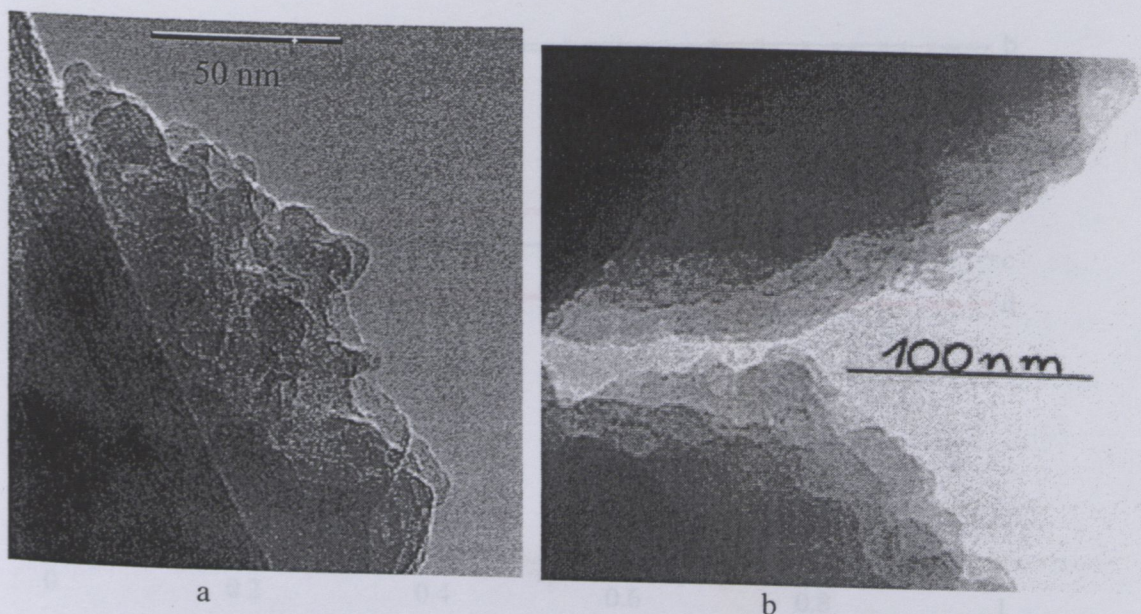


Figure 4.13. a) TEM picture of ZSM-5 (prep.) sample aged at 363 K for 1 day, b) TEM picture taken from ref 45.

Figure 4.14. Aging time effect for calcined ZSM-5 (prep.) samples aged at 363 K for 1 day.

It is known that, in the TPA^+ -templated synthesis of MFI type materials, the synthesis times are much longer for Al containing materials (88). Reding *et al.* (89) synthesized MFI type nano-crystals and investigated the possibility of producing acidic materials by incorporating aluminum. The authors presented evidence that 12 days of hydrothermal treatment is necessary to obtain a crystalline product when aluminum is present in the synthesis mixture. Synthesis conditions for nanosized zeolites might thus not be appropriate to obtain crystalline ZSM-5.

Adsorption isotherms of calcined ZSM-5 (prep.) samples, which had been aged at 363 K for various times, are given in Figure 4.14.

Aging Time, days	Micro pore Volume, cm^3/g	Micro pore Area, m^2/g
1	0.124	430
7	0.131	600
10	0.128	458
16	0.104	196

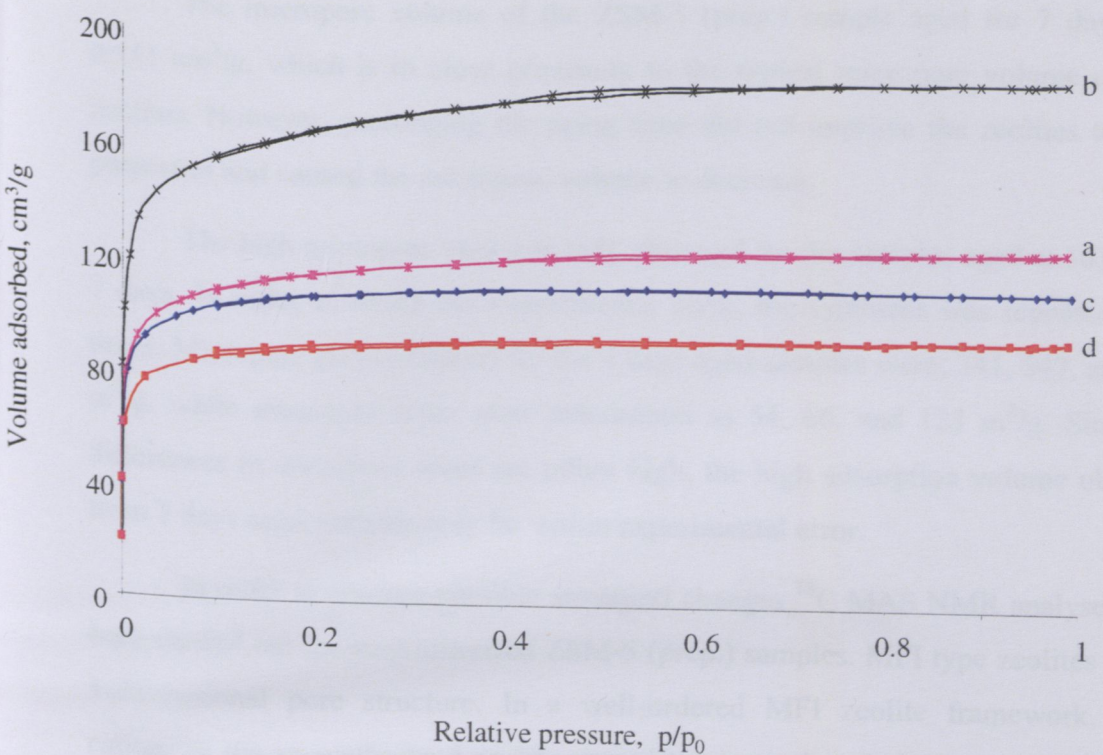


Figure 4.14. Aging time effect for calcined ZSM-5 (prep.) samples aged at 363 K for a) 1 day, b) 7 days, c) 10 days, d) 16 days.

As shown in Figure 4.14, microporosity can be observed even after 1 day of aging. All isotherms resemble Type I, which is expected for microporous samples (76). Microporosity decreases with increasing the aging time except for the sample that is aged for 7 days at 363 K. In this case, very high microporosity was observed. Micropore volumes and areas of samples are given in Table 4.5.

Table 4.5. DFT analyses of calcined ZSM-5 (prep.) samples aged at 363 K.

Aging Time, days	Micropore Volume, cm ³ /g	Micropore Area, m ² /g
1	0.124	430
7	0.151	600
10	0.128	459
16	0.104	380

The micropore volume of the ZSM-5 (prep.) sample aged for 7 days was $0.151 \text{ cm}^3/\text{g}$, which is in close proximity to the typical micropore volume of MFI zeolites. However, prolonging the aging time did not improve the zeolites textural properties and caused the micropore volume to decrease.

The high micropore area was only observed for the samples aged at 363 K for 7 days. In order to check the experimental error, the synthesis was repeated three times. Micropore areas obtained for the 7 days aged samples were; 341, 547, and $600 \text{ m}^2/\text{g}$. while mesopore areas were determined as 54, 66, and $123 \text{ m}^2/\text{g}$. Since the differences in micropore areas are rather high, the high adsorption volume obtained from 7 days aged samples may be within experimental error.

In order to observe possible structural changes ^{13}C MAS NMR analyses have been carried out for as-synthesized ZSM-5 (prep.) samples. MFI type zeolites have a 3-dimensional pore structure. In a well-ordered MFI zeolite framework, TPA^+ cations in the as-synthesized zeolite extend two propyl moieties into the sinusoidal channels, the other two into the straight channels. In this case, a resonance at -12.6 ppm splits into two peaks, typically at -10.1 ppm and -11.3 ppm, and the resonance at -60 ppm shifts to -62.6 ppm, which indicates that TPA^+ ions are occluded in the pore structure.

The ^{13}C MAS NMR-Spectra of the as-synthesized ZSM-5 (prep.) samples aged at RT and at 363 K are given in Figures 4.15 and 4.16, respectively.

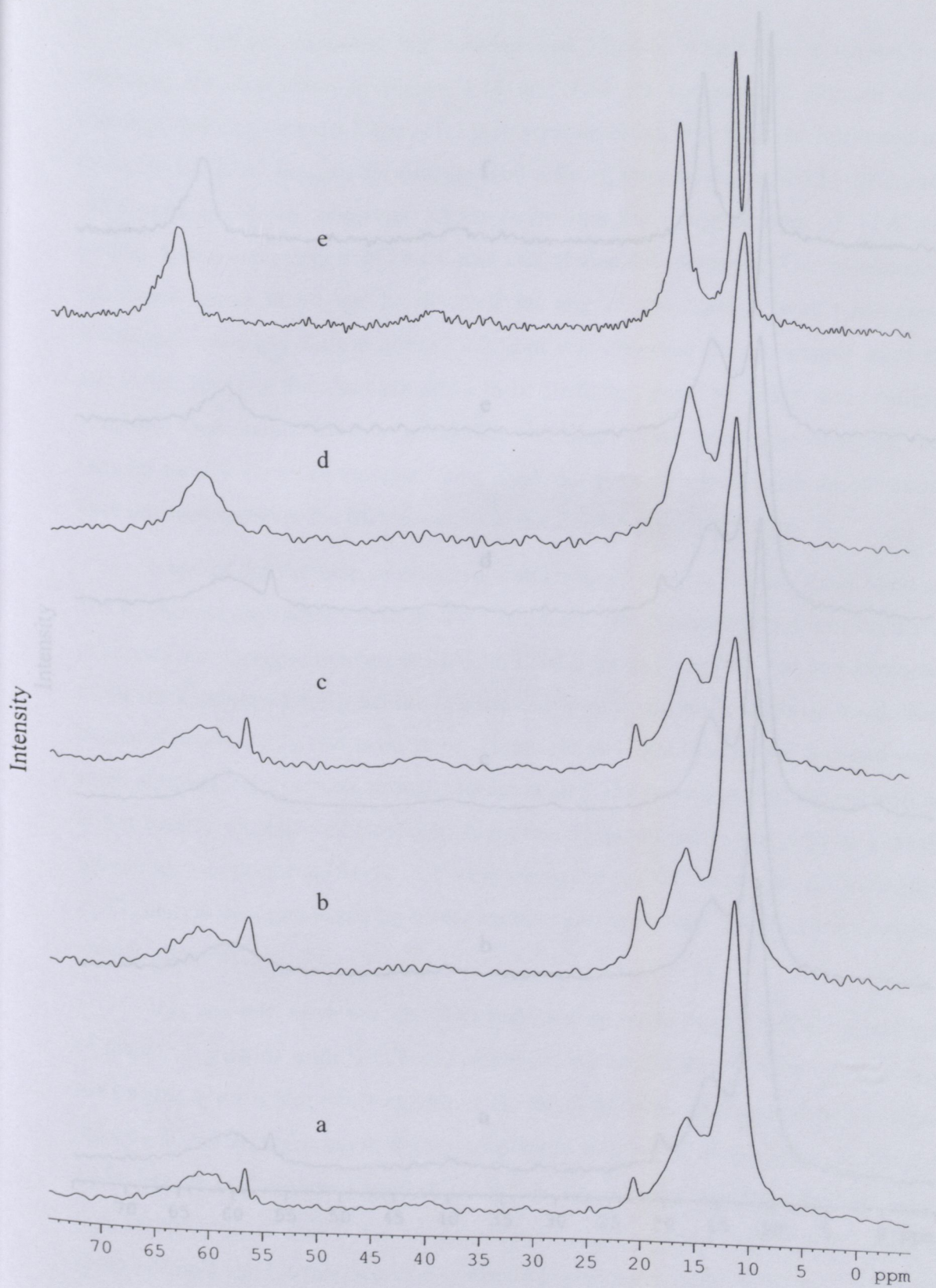


Figure 4.15. ^{13}C MAS NMR spectra of as-synthesized ZSM-5 (prep.) samples aged at RT for a) 1 day, b) 7 days, c) 30 days, d) 30 days (washed), e) conventional ZSM-5.

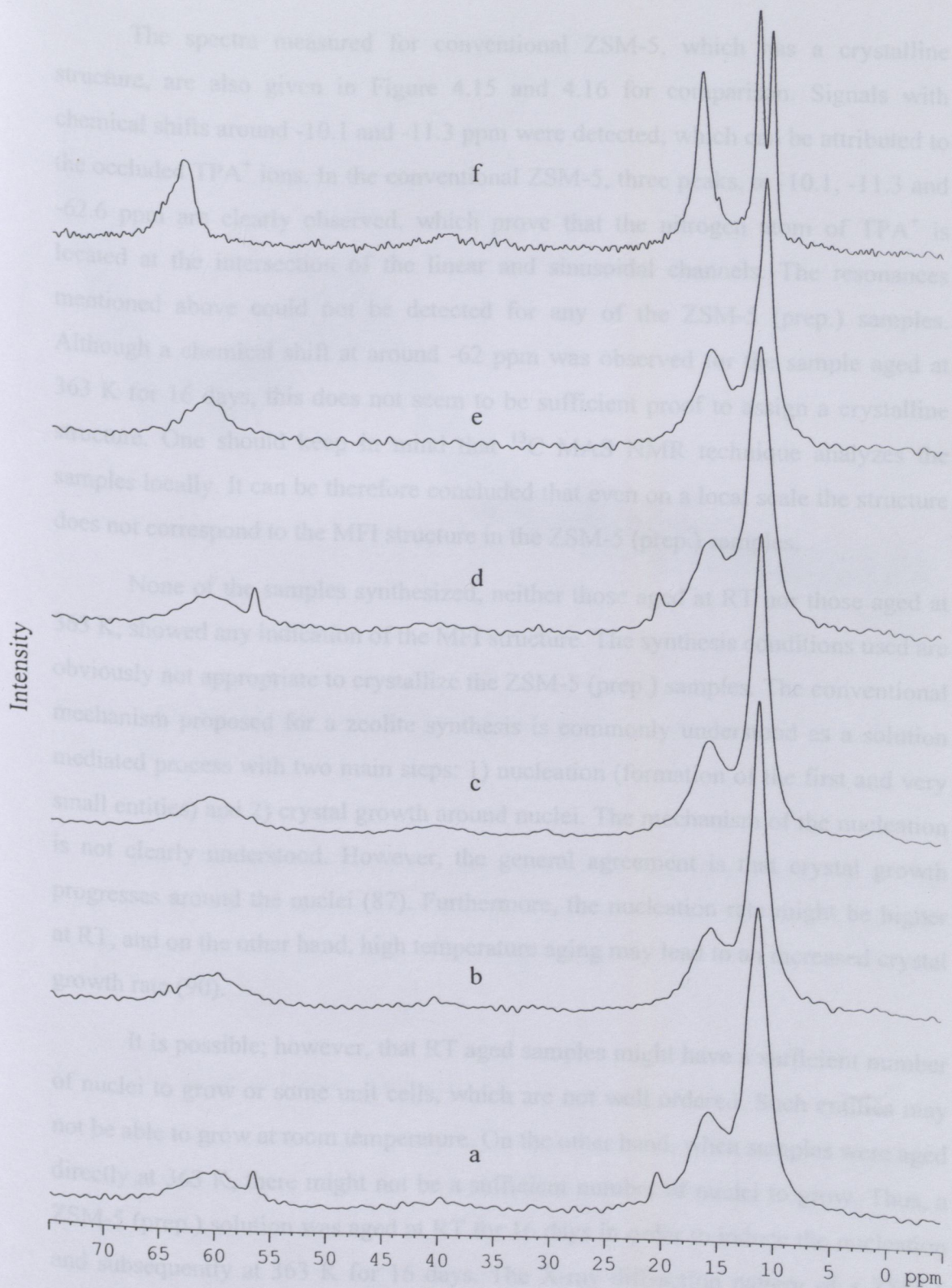


Figure 4.16. ^{13}C MAS NMR spectra of as-synthesized ZSM-5 (prep.) samples aged at 363 K for a) 1 day, b) 7 days, c) 10 days, d) 16 days, e) 16 days (washed), f) conventional ZSM-5.

The spectra measured for conventional ZSM-5, which has a crystalline structure, are also given in Figure 4.15 and 4.16 for comparison. Signals with chemical shifts around -10.1 and -11.3 ppm were detected, which can be attributed to the occluded TPA^+ ions. In the conventional ZSM-5, three peaks, at -10.1, -11.3 and -62.6 ppm are clearly observed, which prove that the nitrogen atom of TPA^+ is located at the intersection of the linear and sinusoidal channels. The resonances mentioned above could not be detected for any of the ZSM-5 (prep.) samples. Although a chemical shift at around -62 ppm was observed for the sample aged at 363 K for 16 days, this does not seem to be sufficient proof to assign a crystalline structure. One should keep in mind that ^{13}C MAS NMR technique analyzes the samples locally. It can be therefore concluded that even on a local scale the structure does not correspond to the MFI structure in the ZSM-5 (prep.) samples.

None of the samples synthesized, neither those aged at RT nor those aged at 363 K, showed any indication of the MFI structure. The synthesis conditions used are obviously not appropriate to crystallize the ZSM-5 (prep.) samples. The conventional mechanism proposed for a zeolite synthesis is commonly understood as a solution mediated process with two main steps: 1) nucleation (formation of the first and very small entities) and 2) crystal growth around nuclei. The mechanism of the nucleation is not clearly understood. However, the general agreement is that crystal growth progresses around the nuclei (87). Furthermore, the nucleation rate might be higher at RT, and on the other hand, high temperature aging may lead to an increased crystal growth rate (90).

It is possible; however, that RT aged samples might have a sufficient number of nuclei to grow or some unit cells, which are not well ordered. Such entities may not be able to grow at room temperature. On the other hand, when samples were aged directly at 363 K, there might not be a sufficient number of nuclei to grow. Thus, a ZSM-5 (prep.) solution was aged at RT for 16 days in order to induce the nucleation and subsequently at 363 K for 16 days. The X-ray diffraction pattern of a ZSM-5 (prep.) sample aged in this two-step synthesis is presented in Figure 4.17.

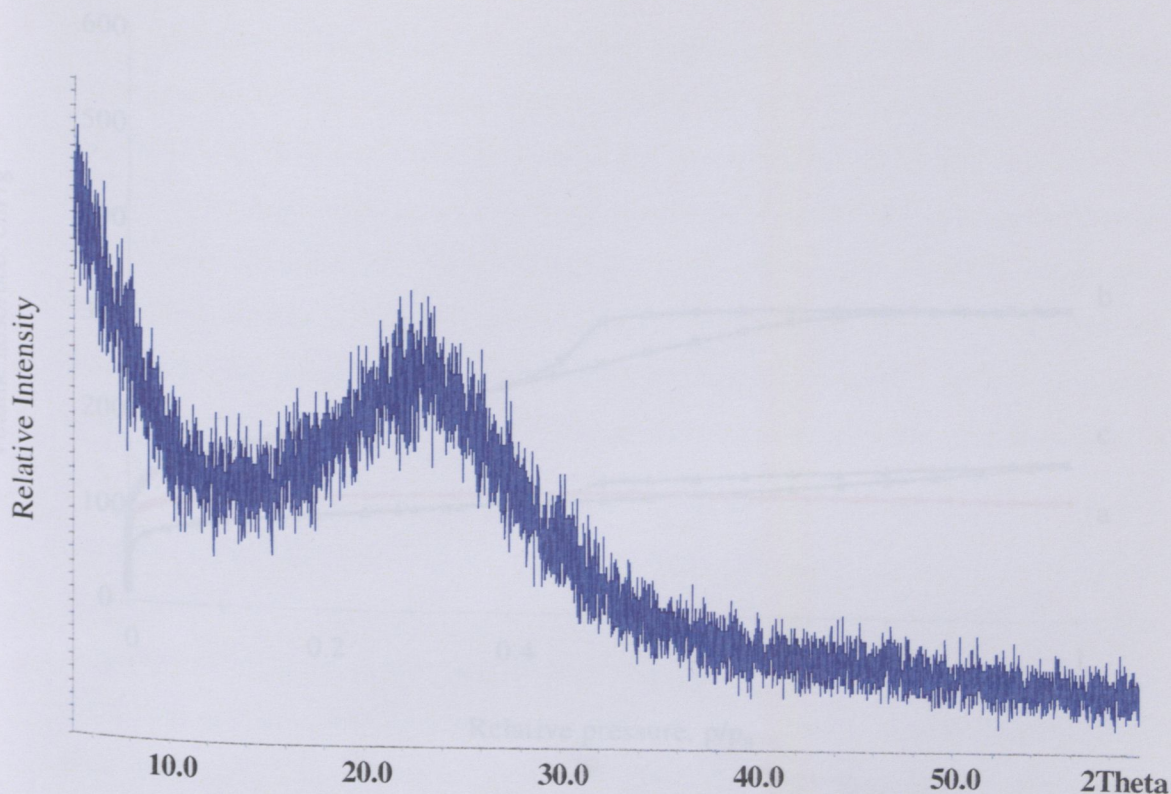


Figure 4.17. XRD pattern of calcined ZSM-5 (prep.) sample synthesized with two-step aging.

The XRD pattern obviously does not show any Bragg reflections. The samples were still amorphous after 32 days of aging (16 days at RT and 16 days at 363 K). Only a broad signal could be detected around 25°.

4.2.2. The Effect of Linker Amount

The effect of the linker amount was examined for the samples aged at RT and at 363 K. Adsorption isotherms of these ZSM-5 (prep.) samples are shown in Figure 4.18 and 4.19, respectively.

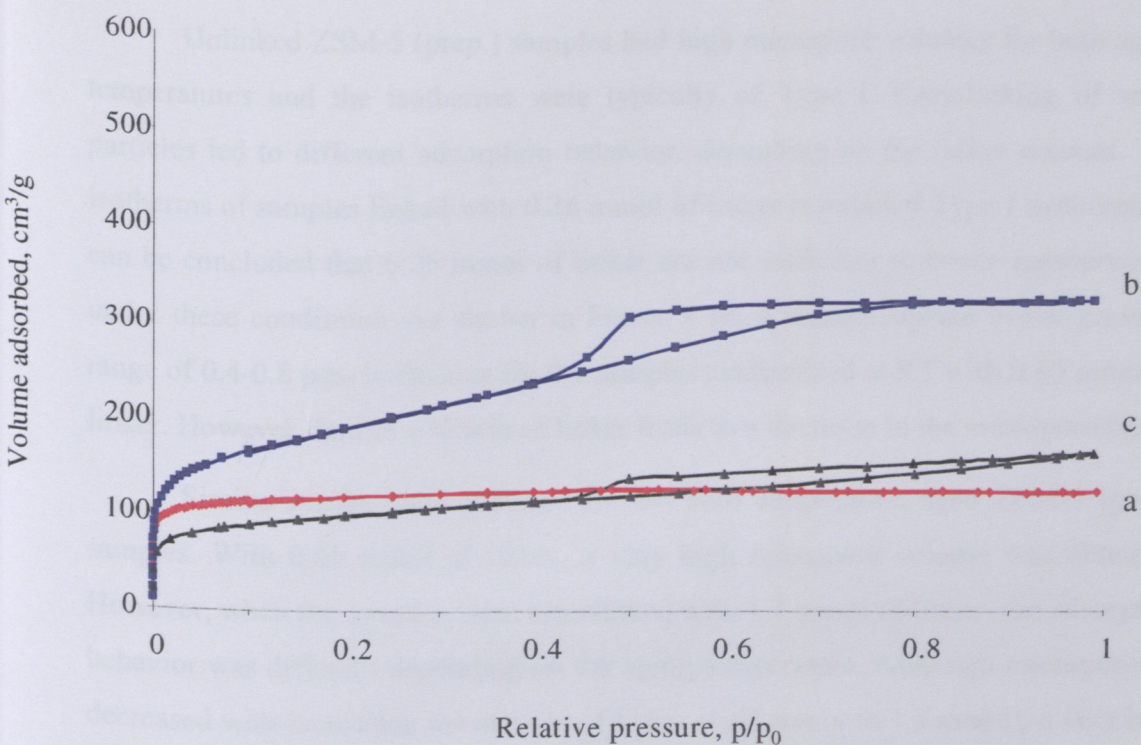


Figure 4.18. Adsorption isotherms of calcined ZSM-5 (prep.) samples aged at RT a) unlinked, b) 0.65 mmol, c) 1.3 mmol of linker.

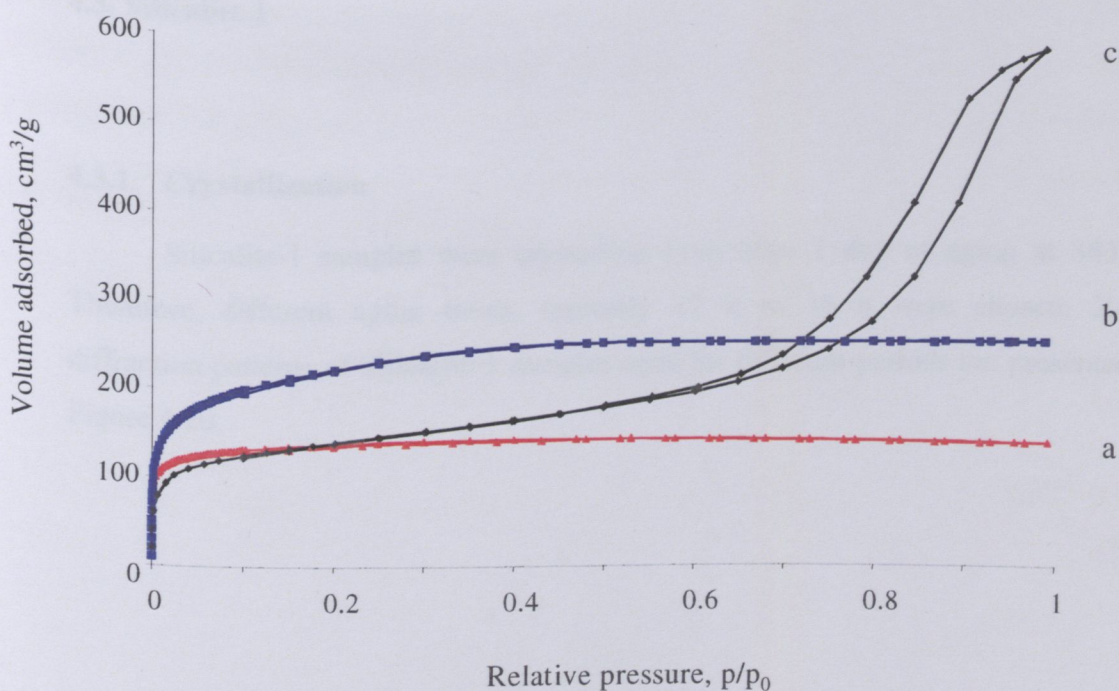


Figure 4.19. Adsorption isotherms of calcined ZSM-5 (prep.) samples aged at 363 K a) unlinked, b) 0.65 mmol, c) 1.3 mmol of linker.

Unlinked ZSM-5 (prep.) samples had high micropore volumes for both aging temperatures and the isotherms were typically of Type I. Crosslinking of small particles led to different adsorption behavior, depending on the linker amount. The isotherms of samples linked with 0.26 mmol of linker resembled Type I isotherms. It can be concluded that 0.26 mmol of linker are not sufficient to create mesoporosity under these conditions. As shown in Figure 4.18, a sharper uptake in the pressure range of 0.4-0.8 p/p_0 is obvious for the samples synthesized at RT with 0.65 mmol of linker. However, further addition of linker leads to a decrease in the microporosity.

Similar results were obtained for the high temperature aged ZSM-5 (prep.) samples. With 0.65 mmol of linker, a very high micropore volume was obtained. However, when the samples were crosslinked with 1.3 mmol of linker, the adsorption behavior was different depending on the aging temperature. Although microporosity decreased with increasing the amount of linker (0.65 mmol to 1.3 mmol), a very high total adsorbed volume was detected. The syntheses were repeated for both aging temperatures and the same adsorption isotherms were observed.

4.3. Silicalite-1

4.3.1. Crystallization

Silicalite-1 samples were crystalline even after 1 day of aging at 363 K. Therefore, different aging times, typically 12 h to 36 h were chosen. X-ray diffraction patterns of Silicalite-1 samples aged for different periods are presented in Figure 4.20.

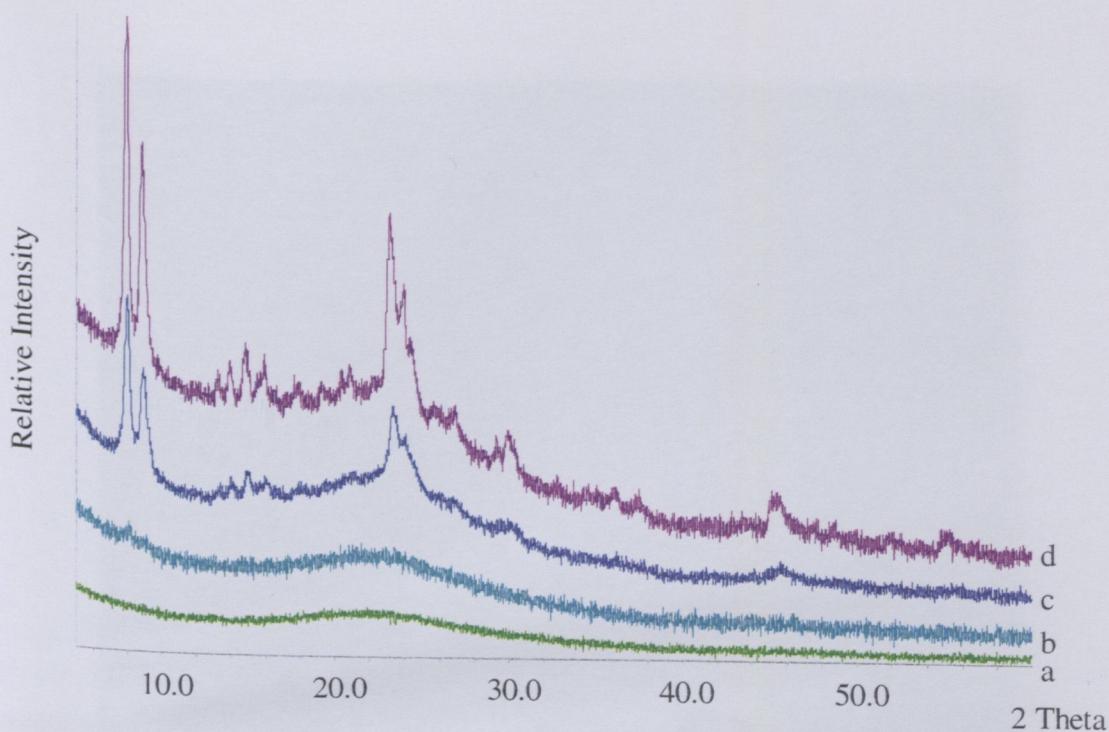


Figure 4.20. X-ray diffraction patterns of Silicalite-1 samples aged for a) 12 h, b) 18 h, c) 24 h, d) 36 h.

Silicalite-1 samples aged at 363 K have sharp reflections at 3-9° and 20-25° (2 θ), characteristic for MFI type zeolites. When Silicalite-1 samples are aged for 24 hours, it is possible to obtain crystalline materials. First indications of crystallinity can even be seen after 18 h around 8-9°, where reflections are beginning to appear.

TEM pictures of Silicalite-1 samples aged for 1 day and 2 days at 363 K are presented in Figure 4.21 and Figure 4.22, respectively. As can be seen from the figures, Silicalite-1 samples have a well-ordered structure in contrast to the ZSM-5 (prep.) samples.

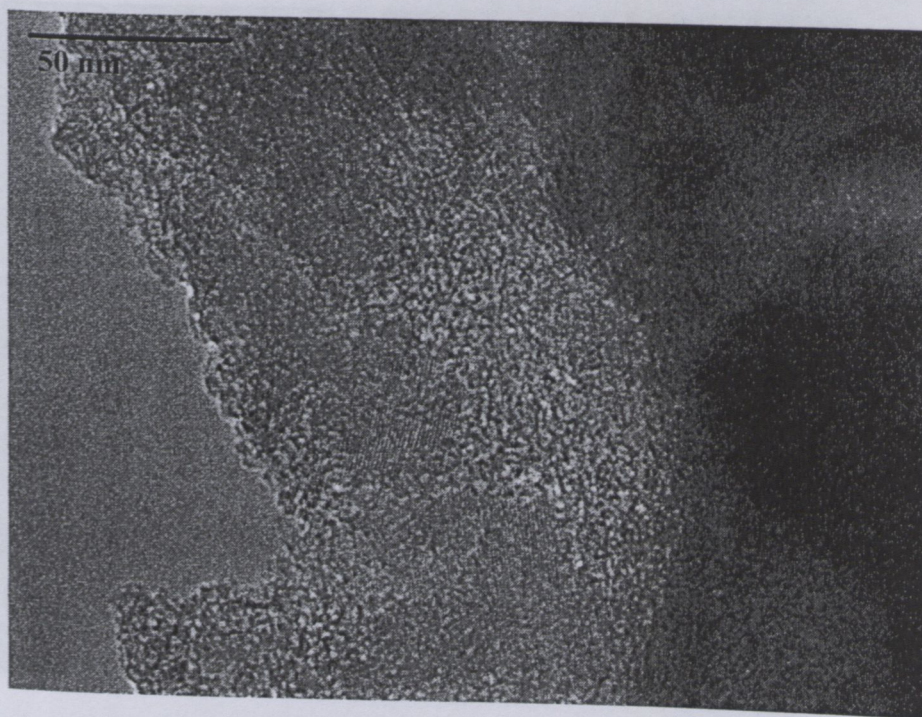
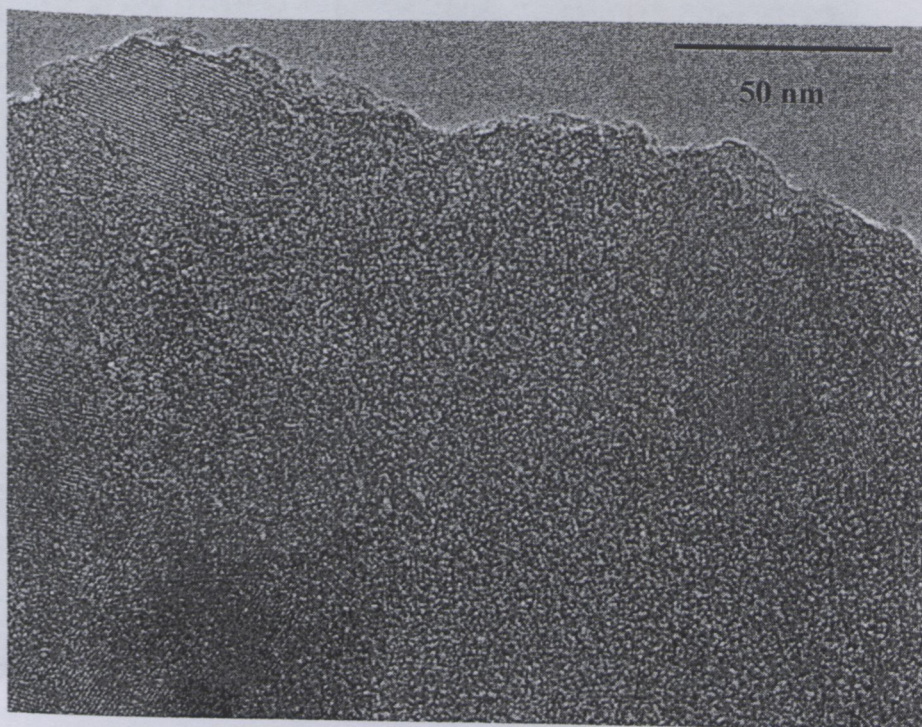
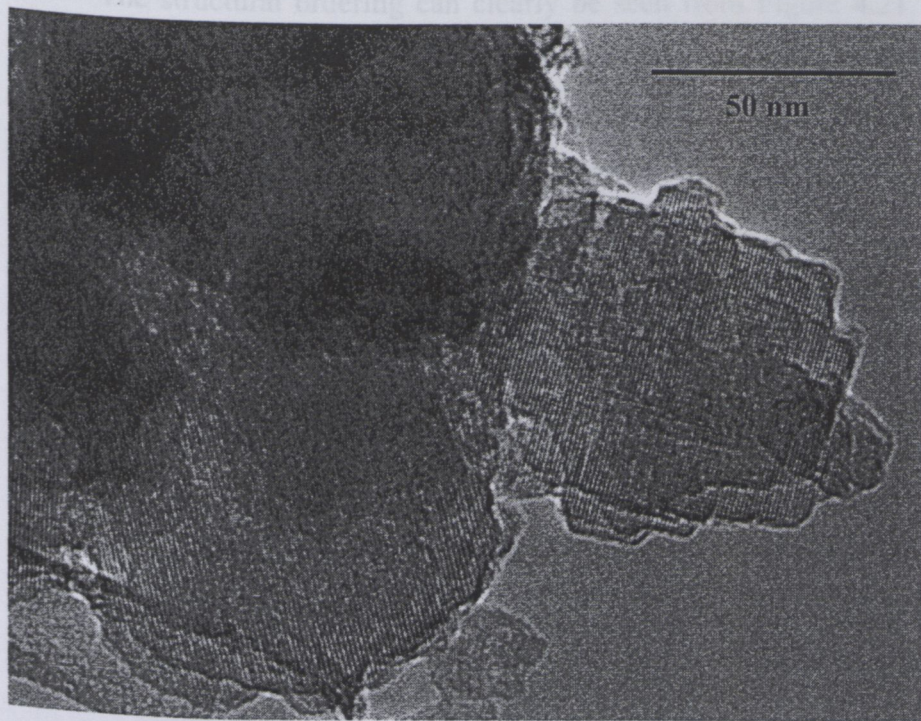


Figure 4.21. TEM pictures of Silicalite-1 sample aged at 363 K for 24 h.

Figure 4.22. TEM pictures of Silicalite-1 sample aged at 363 K for 48 h.



where p is the particle density. The particle diameters are listed in Table 4.6.

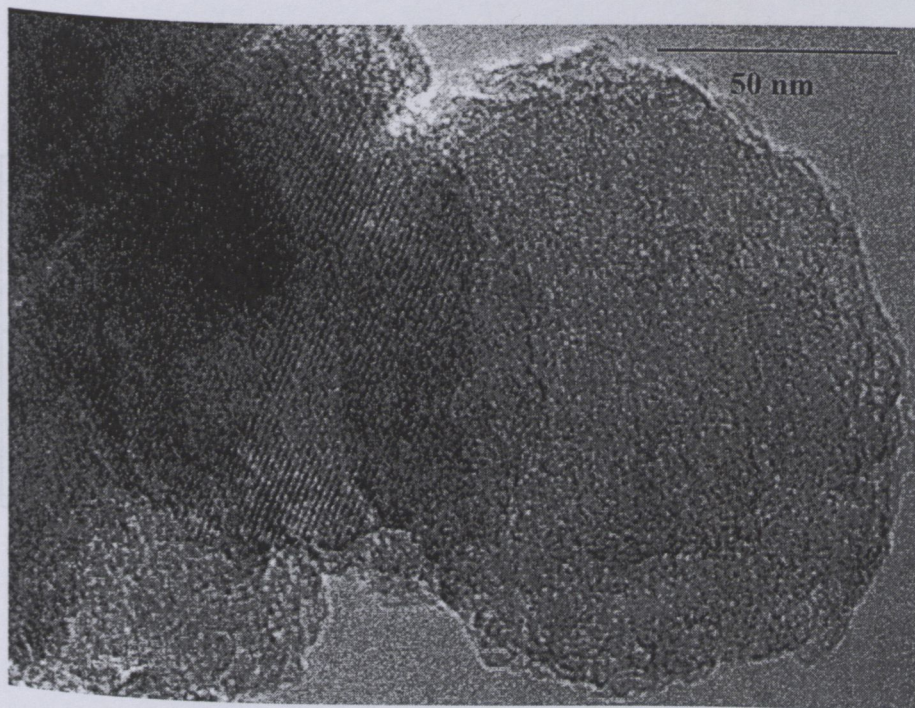


Figure 4.22. TEM pictures of Silicalite-1 sample aged at 363 K for 48 h.

The structural ordering can clearly be seen from Figure 4.21. The extended aging time at 363 K, leads to particle growth. The particle size analysis has been carried out for the Silicalite-1 samples aged at 363 K for 24 h and 48 h using X-ray line broadening. For this purpose, the measurements were repeated over a 2θ range of $6-11^\circ$ and a step size of 0.5.

Particle sizes of the Silicalite-1 samples were also obtained from adsorption analysis assuming that particles have spherical shape. The relation between particle diameter and the specific surface area are given by the equation

$$a = \frac{6}{\rho d}$$

11

where ρ is the particle density. The particle diameters are listed in Table 4.6.

Table 4.6. Particle size analyses of Silicalite-1 samples aged at 363 K.

Aging Time, h	Particle size, nm	
	From surface area	XRD analysis
24	23	22±2
48	24	36±5

As seen from Table 4.6, particle sizes obtained from adsorption measurement and XRD analysis are in good agreement for the sample aged for 24 h. However, the particle size for 48 h aged sample is lower if calculated from the surface area. One should keep in mind though that, the particle size calculated from the surface area could also be the size of agglomerates, not necessarily that of primary particles. In addition, particle size analysis using X-ray line broadening, considers only crystalline domains. Combining the XRD analysis with the TEM pictures, which

show an increase in the particle size depending on the aging time, it can be concluded that, samples have crystalline particles around 22 ± 2 nm after 24 h and 36 ± 5 nm after 48 h of aging. However, smaller sized amorphous material must also be present.

^{13}C MAS NMR measurements were performed on Silicalite-1 samples aged at 363 K. The spectra are given in Figure 4.23. After 24 h of aging at 363 K, a decrease of the chemical shift from -60 ppm to -62 ppm can clearly be seen in the spectra; on the other hand, splitting at -10 ppm and -11 ppm could not be observed. For the Silicalite-1, which is aged for 48 h, there is a clear splitting of the resonances at around -10 ppm and -11 ppm, which arises from the different surroundings of the propyl chains extending in the two different channels of the ZSM-5 structure. This can be concluded as evidence that the TPA^+ cation is occluded in the MFI structure. The Silicalite-1 samples aged at 363 K for 24 h or more have local formations of the MFI type structure according to the ^{13}C MAS NMR analysis. These samples also showed crystalline patterns in the XRD analysis. Thus, the ^{13}C MAS NMR analyses are in agreement with the XRD analyses.

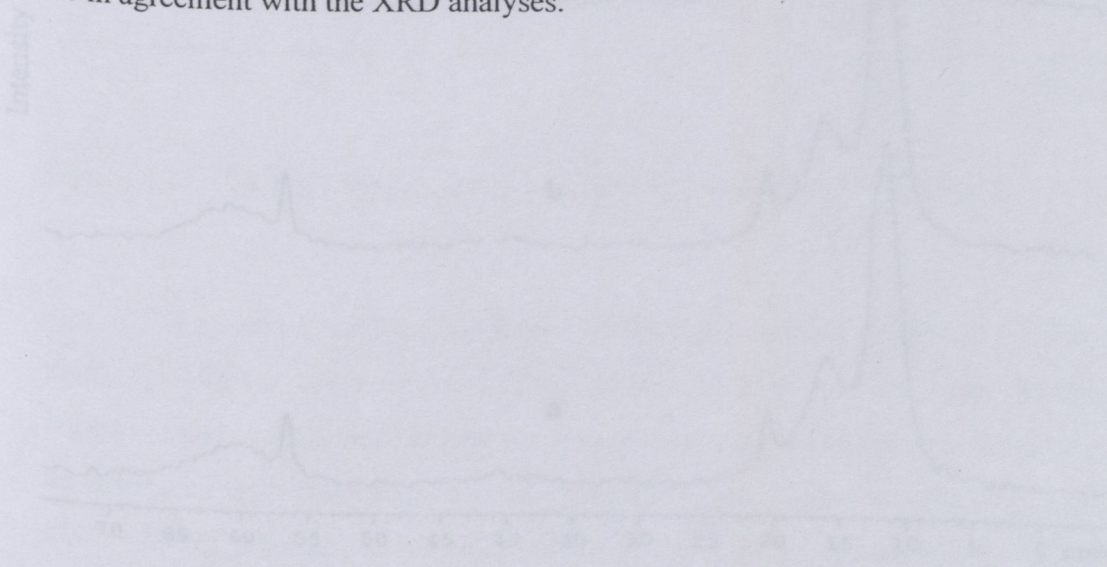


Figure 4.23. ^{13}C MAS NMR spectra of as synthesized Silicalite-1 samples aged at 363 K for (a) 12 h, (b) 18 h, (c) 24 h, (d) 48 h (without), (e) without ZSM-5.

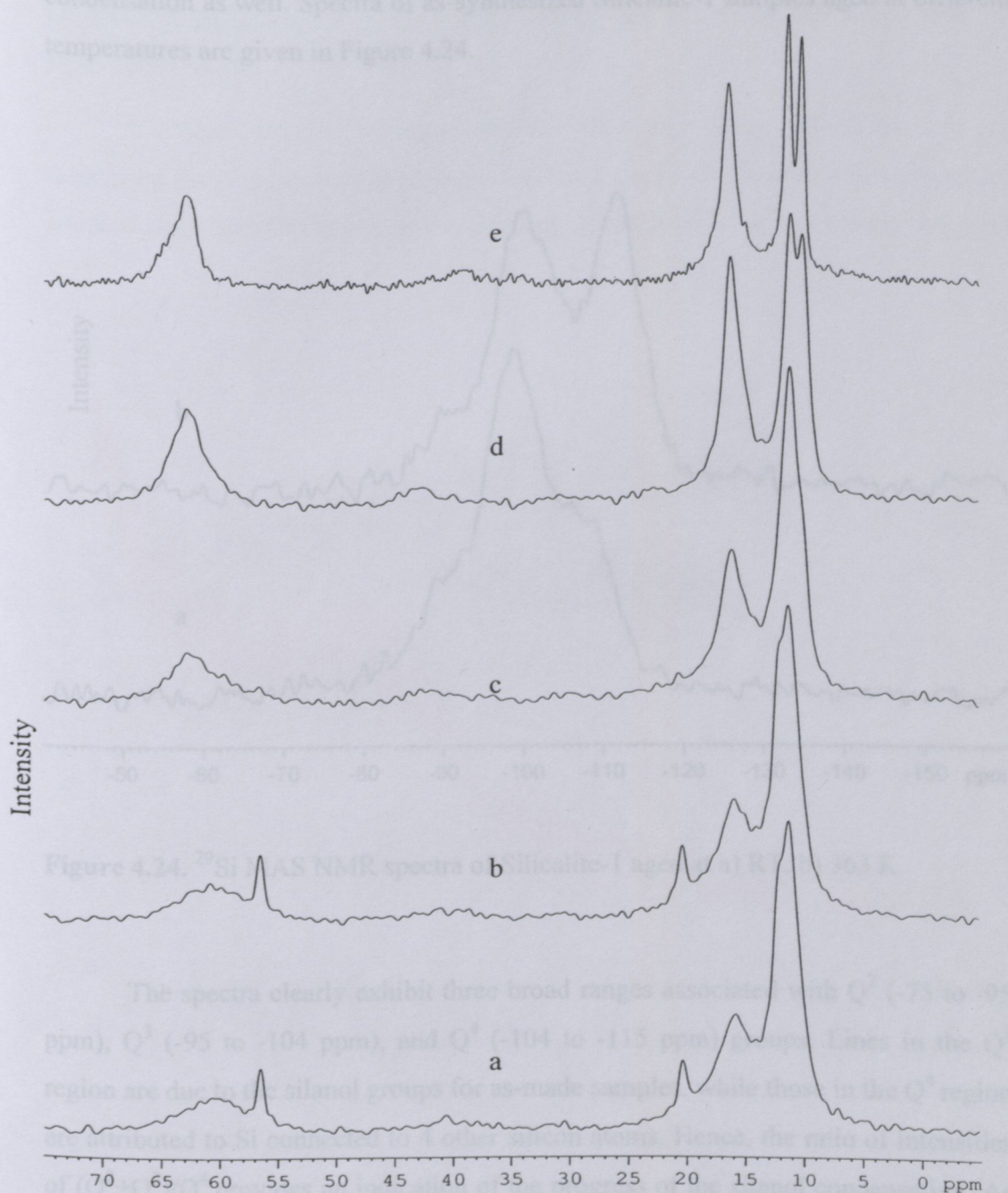


Figure 4.23. ^{13}C MAS NMR spectra of as-synthesized Silicalite-1 samples aged at 363 K for a) 12 h, b) 18 h, c) 24 h, d) 48 h (washed), e) conventional ZSM-5.

^{29}Si MAS NMR identifies silicon species and gives information about silanol condensation as well. Spectra of as-synthesized Silicalite-1 samples aged at different temperatures are given in Figure 4.24.

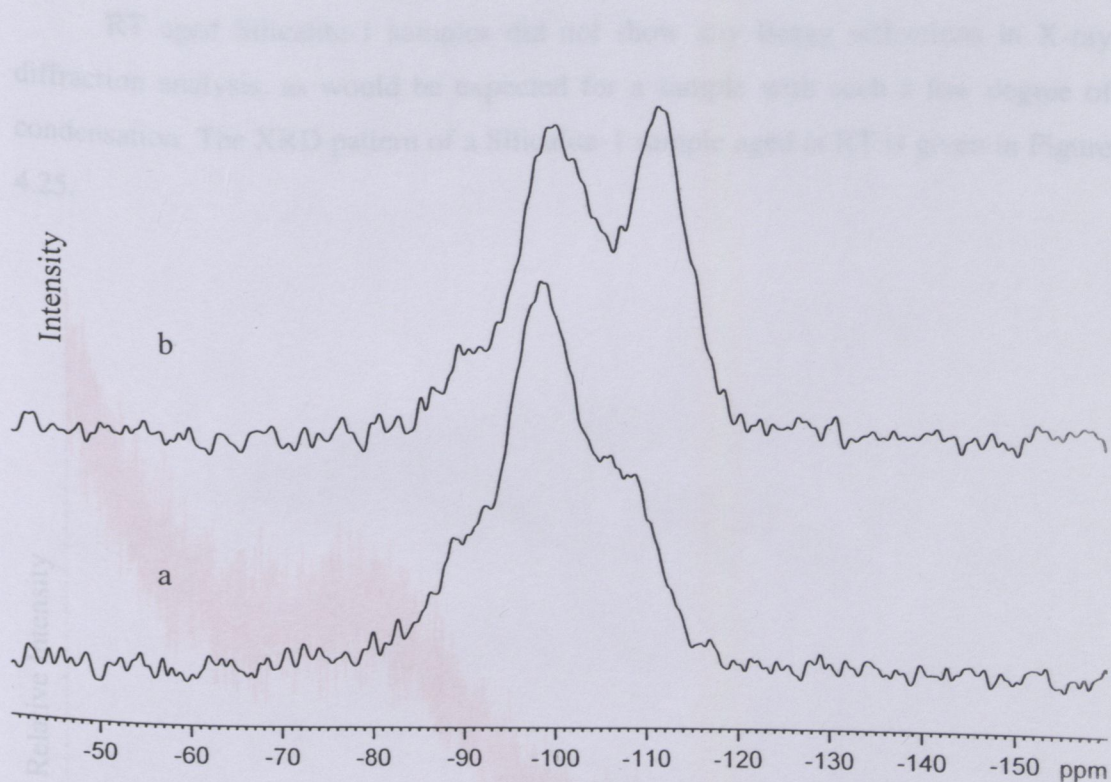


Figure 4.24. ^{29}Si MAS NMR spectra of Silicalite-1 aged at a) RT, b) 363 K.

The spectra clearly exhibit three broad ranges associated with Q^2 (-75 to -95 ppm), Q^3 (-95 to -104 ppm), and Q^4 (-104 to -115 ppm) groups. Lines in the Q^3 region are due to the silanol groups for as-made samples, while those in the Q^4 region are attributed to Si connected to 4 other silicon atoms. Hence, the ratio of intensities of $(\text{Q}^2 + \text{Q}^3)/\text{Q}^4$ provides an indication of the progress of the silanol condensation. As can be seen in Figure 4.24, Q^2 and Q^3 signal intensities decrease and Q^4 signal intensities increase with increasing aging temperature. $(\text{Q}^2 + \text{Q}^3)/\text{Q}^4$ and Q^3/Q^4 ratios are 2.44 and 1.9 for samples aged at RT and 1.4 and 1.1 for the crystalline Silicalite-1 sample. In case that the Silicalite-1 sample is aged at 363 K for 48 hours, the latter ratio decreases to 0.75. The Q^3/Q^4 ratio is reported to be between 0.6 and 0.8 in ref (91), 0.84 in ref (10), and 0.79 in ref (43). It is also suggested that upon completion of crystallization the final value for Q^3/Q^4 is about 0.08 (91). Keeping in mind that

the Silicalite-1 samples aged at 363 K are crystalline, the increase in the intensity of Q^4 bands is expected and gives further support for the X-ray diffraction and ^{13}C MAS NMR results.

RT aged Silicalite-1 samples did not show any Bragg reflections in X-ray diffraction analysis, as would be expected for a sample with such a low degree of condensation. The XRD pattern of a Silicalite-1 sample aged at RT is given in Figure 4.25.

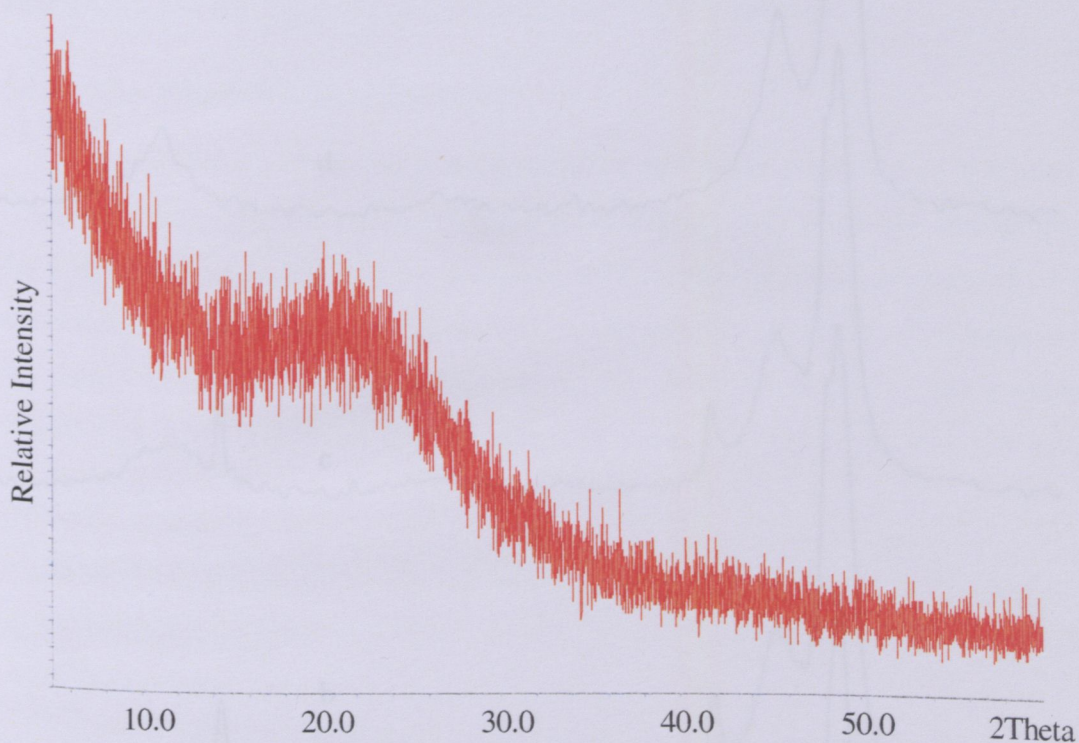


Figure 4.25. XRD pattern of a calcined Silicalite-1 sample aged at RT for 1 day.

^{13}C MAS NMR measurements were performed on Silicalite-1 samples in order to obtain indications for crystallinity in RT aged samples. The spectra of the silicalite samples are given in Figure 4.26.

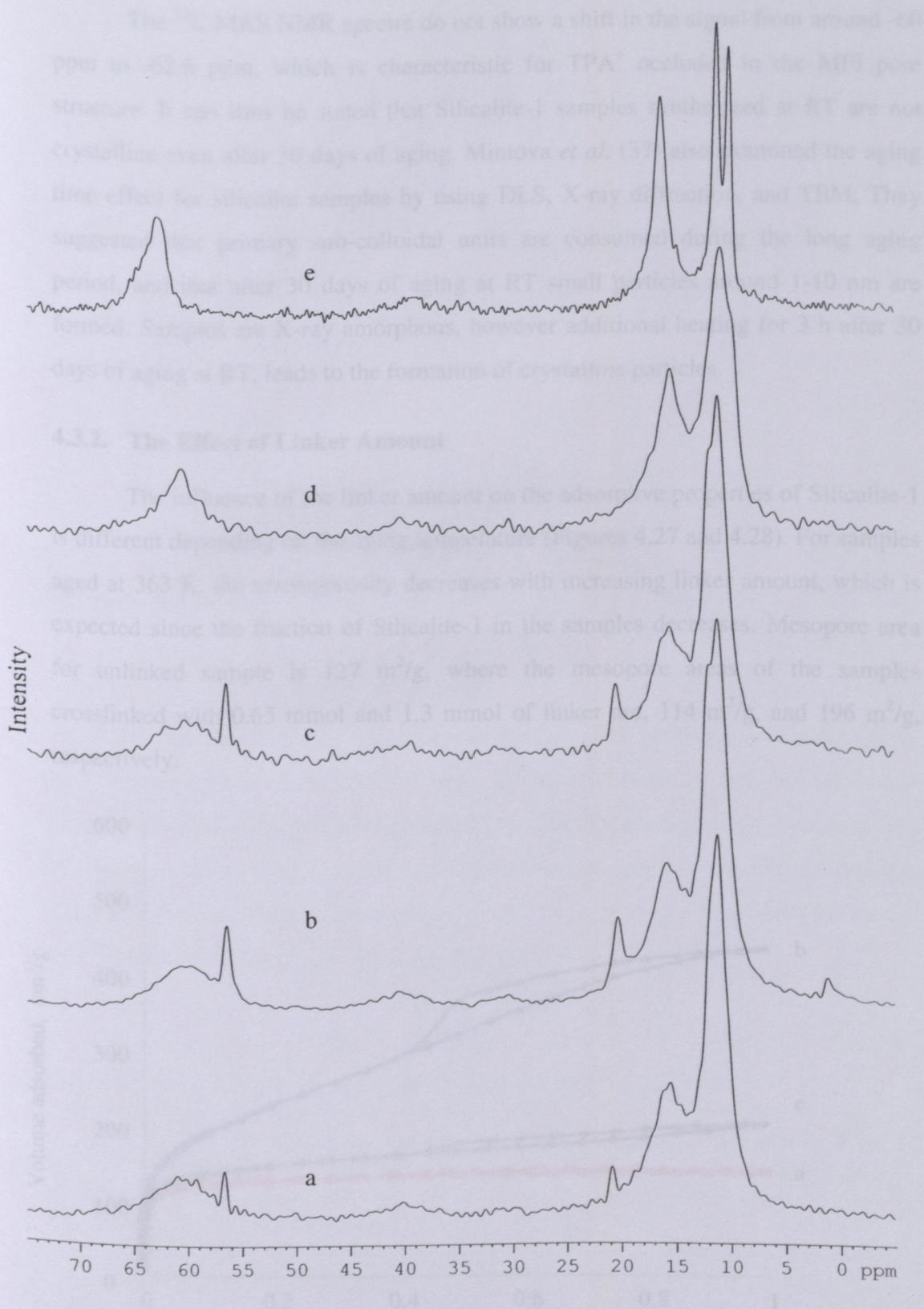


Figure 4.26. ^{13}C MAS NMR spectra of as-synthesized Silicalite-1 samples aged at RT for a) 1 day, b) 7 days, c) 30 days, d) 30 days (washed), e) conventional ZSM-5.

The ^{13}C MAS NMR spectra do not show a shift in the signal from around -60 ppm to -62.6 ppm, which is characteristic for TPA^+ occluded in the MFI pore structure. It can thus be stated that Silicalite-1 samples synthesized at RT are not crystalline even after 30 days of aging. Mintova *et al.* (37) also examined the aging time effect for silicalite samples by using DLS, X-ray diffraction, and TEM. They suggested that primary sub-colloidal units are consumed during the long aging period, and that after 30 days of aging at RT small particles around 1-10 nm are formed. Samples are X-ray amorphous, however additional heating for 3 h after 30 days of aging at RT, leads to the formation of crystalline particles.

4.3.2. The Effect of Linker Amount

The influence of the linker amount on the adsorptive properties of Silicalite-1 is different depending on the aging temperature (Figures 4.27 and 4.28). For samples aged at 363 K, the microporosity decreases with increasing linker amount, which is expected since the fraction of Silicalite-1 in the samples decreases. Mesopore area for unlinked sample is $127\text{ m}^2/\text{g}$, where the mesopore areas of the samples crosslinked with 0.65 mmol and 1.3 mmol of linker are, $114\text{ m}^2/\text{g}$, and $196\text{ m}^2/\text{g}$, respectively.

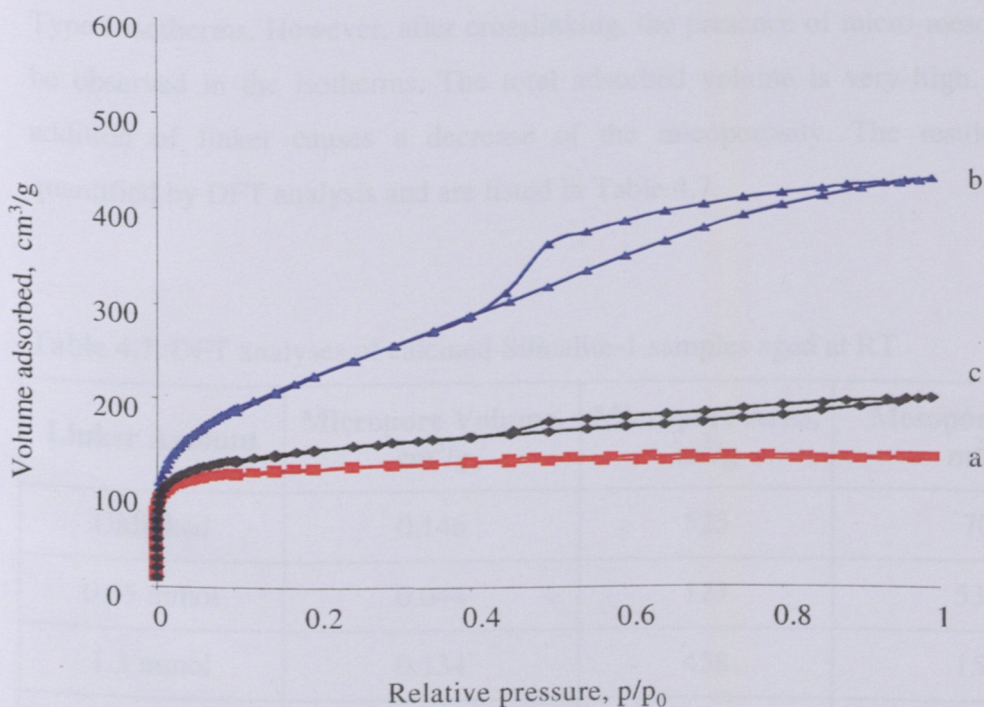


Figure 4.27. Adsorption isotherms of Silicalite-1 samples aged at RT a) unlinked, b) 0.65 mmol, c) 1.3 mmol of linker.

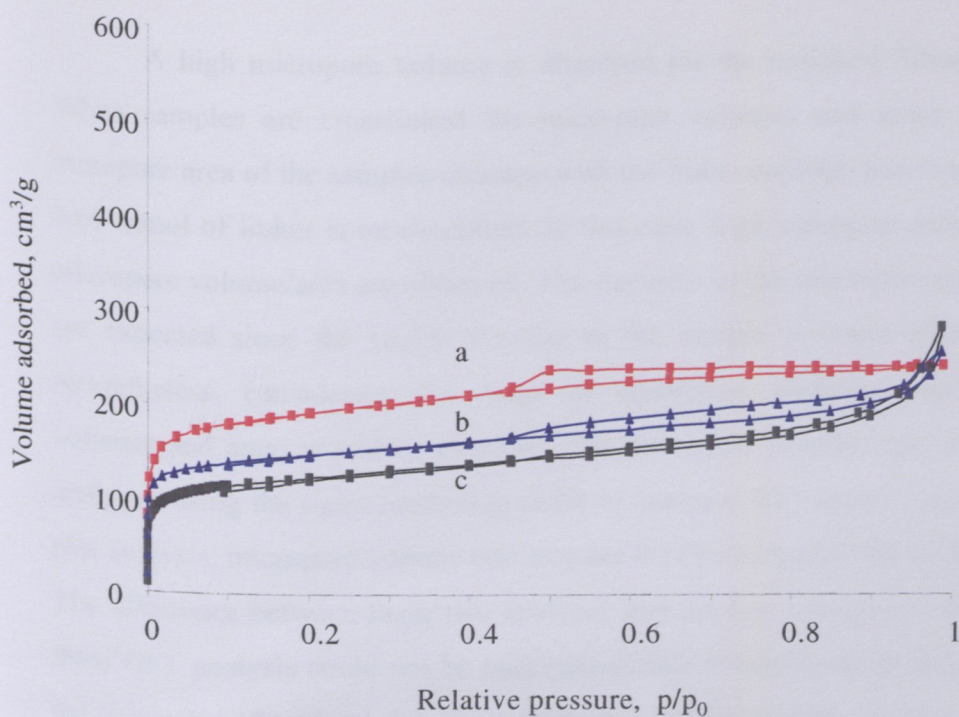


Figure 4.28. Adsorption isotherms of Silicalite-1 samples aged at 363 K a) unlinked, b) 0.65 mmol, c) 1.3 mmol of linker.

On the other hand, the adsorption isotherms of RT aged samples are similar to the isotherms measured for ZSM-5 (prep.). Unlinked Silicalite-1 samples also show Type I isotherms. However, after crosslinking, the presence of micro-mesopores can be observed in the isotherms. The total adsorbed volume is very high. Increased addition of linker causes a decrease of the microporosity. The results can be quantified by DFT analysis and are listed in Table 4.7.

Table 4.7. DFT analyses of calcined Silicalite-1 samples aged at RT.

Linker Amount	Micropore Volume, cm^3/g	Micropore Area, m^2/g	Mesopore Area, m^2/g
Unlinked	0.146	525	70
0.65 mmol	0.044	123	531
1.3 mmol	0.134	458	152
2.6 mmol	0.070	228	282

A high micropore volume is observed for the unlinked Silicalite-1 sample. When samples are crosslinked the micropore volumes and areas decrease. The mesopore area of the samples increase with the linker amount, however, sample with 0.65 mmol of linker is an exception. In this case, high mesopore area but very low micropore volume/area are observed. The decrease in the micropore volume and area are expected since the zeolite fraction in the sample is lower after crosslinking. Nevertheless, considering the shape of adsorption isotherm, higher micropore volumes and areas would be expected. The micropore volumes and areas were also analyzed using the t-plot method in order to compare the values. According to the t-plot analysis, micropore volume and area are $0.119 \text{ cm}^3/\text{g}$ and $248 \text{ m}^2/\text{g}$, respectively. The difference between these two analyses and the low micropore volume obtained from DFT analysis could not be understood. One should keep in mind, though, that the extraction of textural data from isotherms for the micropore range is still a very difficult task.

On the other hand, the decrease in the mesopore areas observed for the samples that have more than 0.65 mmol of linker may be because of the pore blocking. When the linker concentration increases, linker molecules can react with each other and might cover the particles or block the pores.

^{29}Si MAS NMR analysis was also applied in order to examine the linker effect. The spectra measured for Silicalite-1 samples aged at RT are given in Figure 4.29.

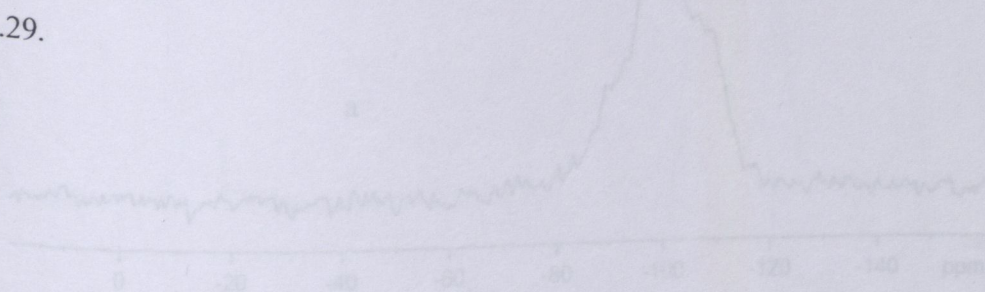


Figure 4.29. ^{29}Si MAS NMR spectra of Silicalite-1 samples aged at RT a) unlinked, b) 0.26 mmol, c) 0.65 mmol, d) 1.3 mmol, e) 2.6 mmol of linker.

Three broad resonances are detected with chemical shifts of -80 ppm , -98 ppm and -108 ppm , which can be assigned to Q^2 , Q^3 , and Q^4 silicon atoms. In the crosslinked samples, the relative intensity of the Q^2 and Q^3 lines are strongly

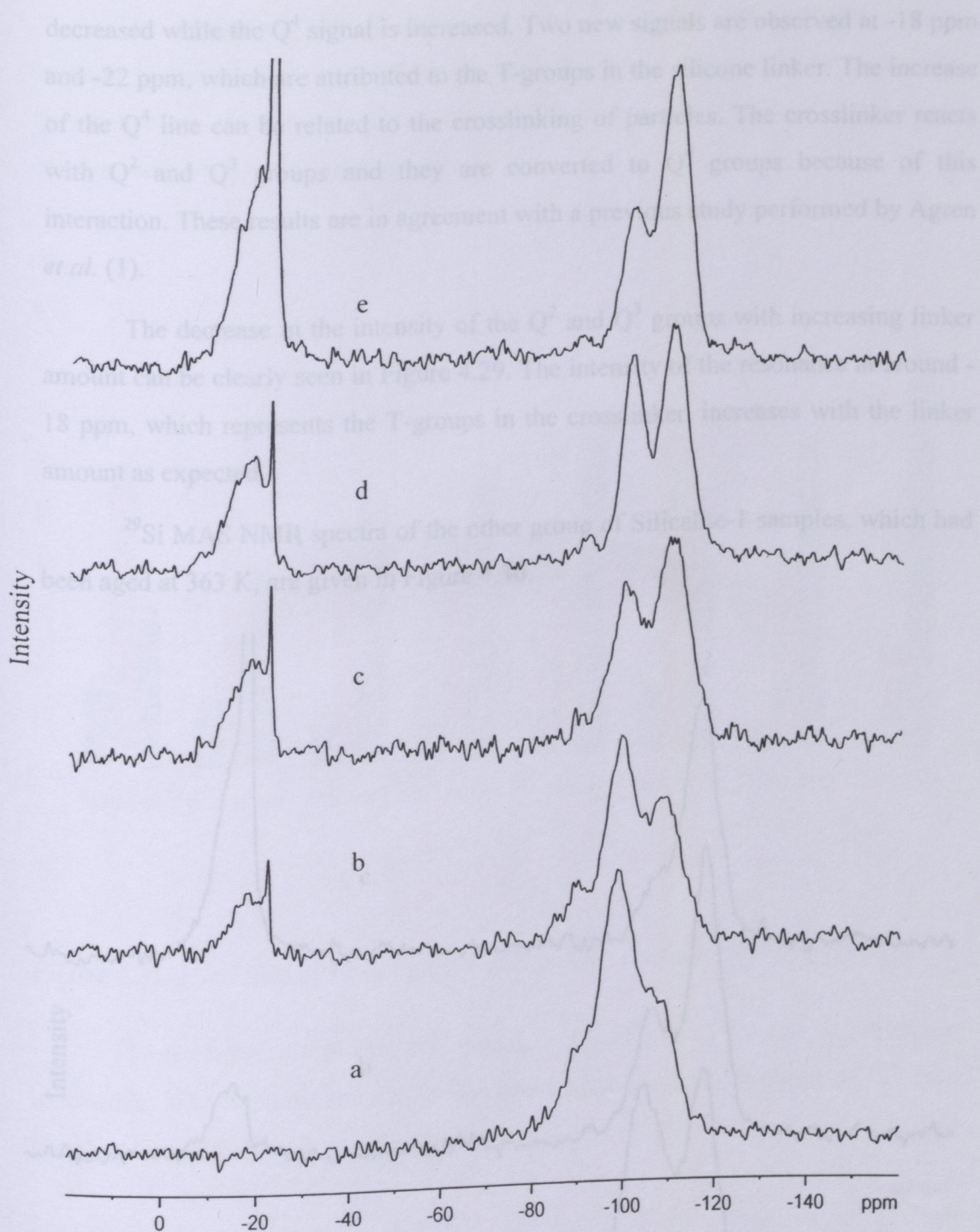


Figure 4.29. ^{29}Si MAS NMR spectra of Silicalite-1 samples aged at RT a) unlinked, b) 0.26 mmol, c) 0.65 mmol, d) 1.3 mmol, e) 2.6 mmol of linker.

Three broad resonances are detected with chemical shifts of -89 ppm, -98 ppm and -108 ppm, which can be assigned to Q^2 , Q^3 , and Q^4 silicon atoms. In the crosslinked samples, the relative intensity of the Q^2 and Q^3 lines are strongly

decreased while the Q^4 signal is increased. Two new signals are observed at -18 ppm and -22 ppm, which are attributed to the T-groups in the silicone linker. The increase of the Q^4 line can be related to the crosslinking of particles. The crosslinker reacts with Q^2 and Q^3 groups and they are converted to Q^4 groups because of this interaction. These results are in agreement with a previous study performed by Agren *et al.* (1).

The decrease in the intensity of the Q^2 and Q^3 groups with increasing linker amount can be clearly seen in Figure 4.29. The intensity of the resonance at around -18 ppm, which represents the T-groups in the crosslinker, increases with the linker amount as expected.

^{29}Si MAS NMR spectra of the other group of Silicalite-1 samples, which had been aged at 363 K, are given in Figure 4.30.

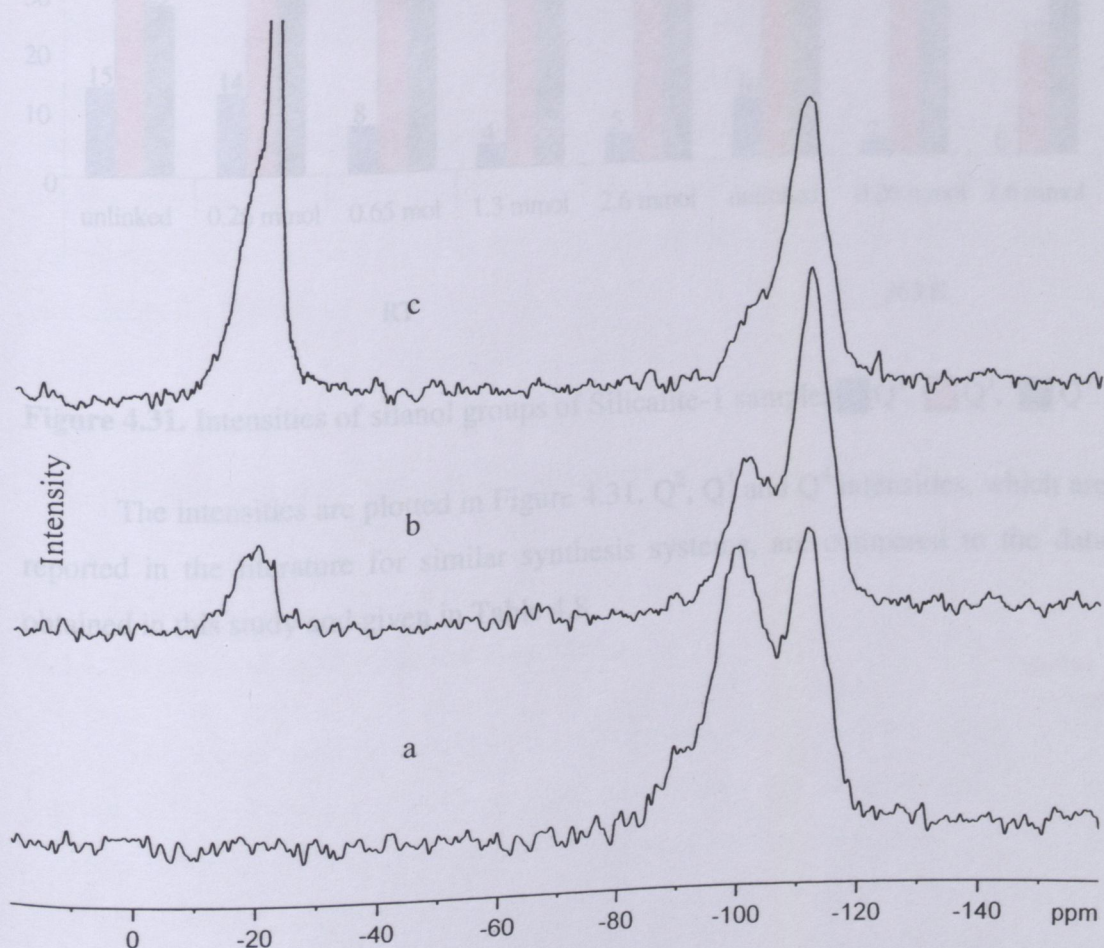


Figure 4.30. ^{29}Si MAS NMR spectra of Silicalite-1 samples, aged at 363 K a) unlinked, b) 0.26 mmol, c) 2.6 mmol of linker.

The decrease in the intensities of the Q^2 and Q^3 bands and the parallel increase in the intensities of Q^4 groups can be clearly seen in Figure 4.31. The crosslinker has reacted with silanol groups. Therefore, the intensities of Q^4 bands increase with increasing linker amount.

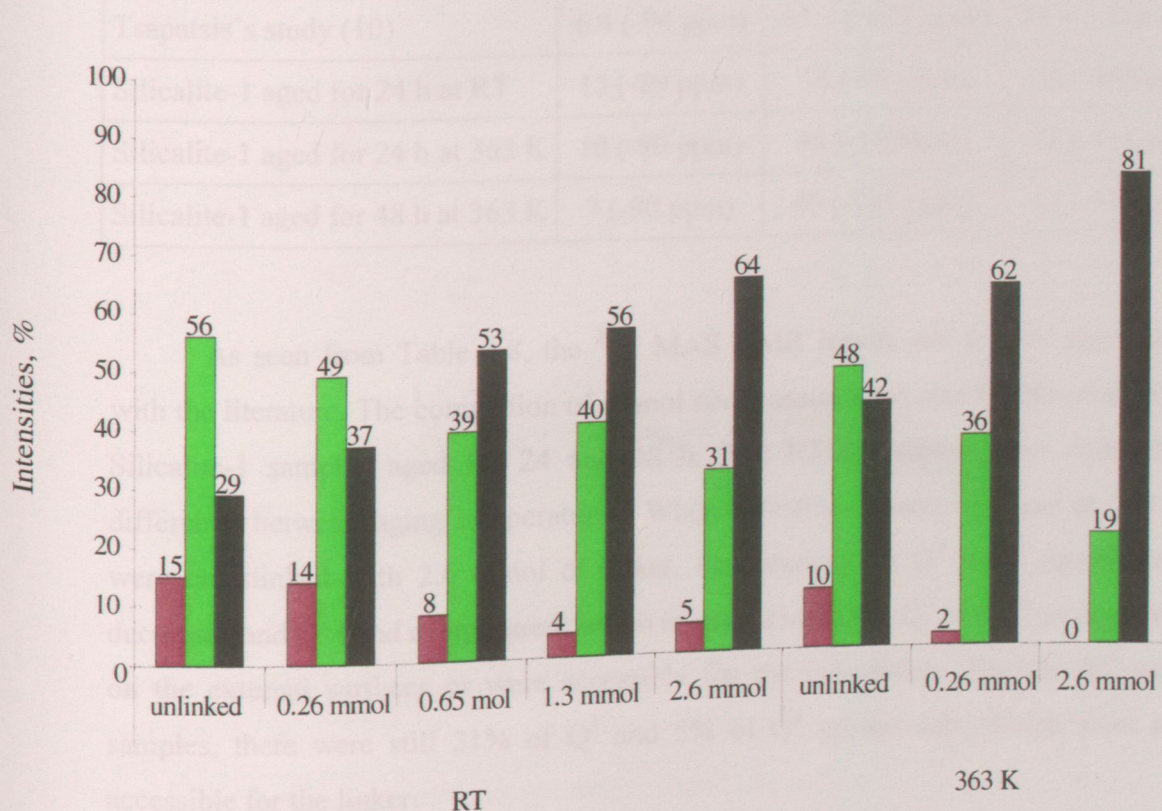


Figure 4.31. Intensities of silanol groups of Silicalite-1 samples Q^2 , Q^3 , Q^4 .

The intensities are plotted in Figure 4.31. Q^2 , Q^3 and Q^4 intensities, which are reported in the literature for similar synthesis systems, are compared to the data obtained in this study and given in Table 4.8.

Table 4.8. Relative intensities and the peak positions of the ^{29}Si MAS NMR signals of TPA-Silicalite-1.

	Q^2	Q^3	Q^4
Marten's study (43)	8.3	40.6	51.1
Tsapatsis's study (10)	6.4 (-94 ppm)	43.5 (-103 ppm)	50.1 (-112 ppm)
Silicalite-1 aged for 24 h at RT	15 (-89 ppm)	56 (-98 ppm)	29 (-108 ppm)
Silicalite-1 aged for 24 h at 363 K	10 (-90 ppm)	48 (-100ppm)	42 (-111 ppm)
Silicalite-1 aged for 48 h at 363 K	7 (-90 ppm)	40 (-101 ppm)	53 (-111 ppm)

As seen from Table 4.8, the ^{29}Si MAS NMR results are in nice agreement with the literature. The completion of silanol condensation can also be observed with Silicalite-1 samples aged for 24 and 48 h. The NMR analyses also showed a difference between aging temperatures. When Silicalite-1 samples aged at 363 K were crosslinked with 2.6 mmol of linker, the intensity of Q^3 band significantly decreased and Q^2 band disappeared, which means most of the Q^2 and Q^3 groups were on the external surfaces or were accessible for the crosslinker. For the RT aged samples, there were still 31% of Q^3 and 5% of Q^2 groups left, which were not accessible for the linker.

4.4. Test Reaction-Beckmann Rearrangement

4.4.1. Optimization of Reaction Conditions

The initial experiments for the Beckmann rearrangement reaction were carried out to determine suitable reaction conditions, i.e. to make sure that the reaction proceeds without mass transfer limitations on the grain level. It is known that when internal diffusion limits the reaction, the rate of reaction decreases with increasing particle diameter. Commercial MFI type zeolite was used for the Beckmann rearrangement in these experiments. Catalysts of different particle sizes were examined in the reaction for this purpose.

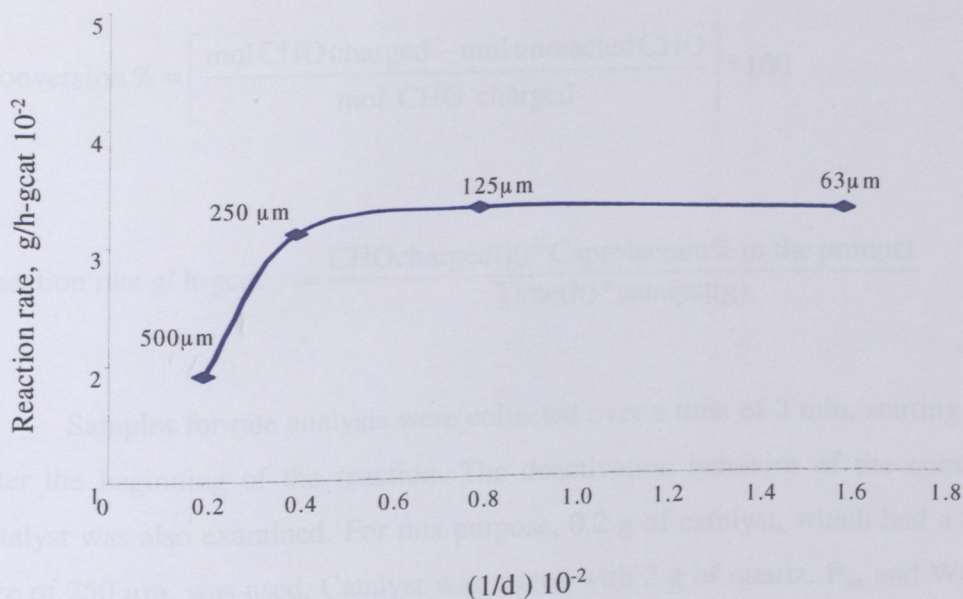


Figure 4.32. Reaction rate as a function of particle size for commercial ZSM-5 sample.

The results of these experiments are shown in Figure 4.32. It can be seen that, catalyst samples having particle sizes larger than 250 μm exhibit significant internal diffusion limitations. Diffusion limitations disappear totally for particle sizes of 125 μm. Since it was very difficult to obtain sufficient amounts of catalyst samples of 125 μm, the catalytic tests, which will be presented in the next chapter, were carried out with samples having particle sizes of 250 μm.

The error introduced by using 250 μm instead of 125 μm particles will be most pronounced for the samples with the highest catalytic activity. In order to estimate the maximum amount of error that may originate from the use of 250 μm particles, one of the Silicalite-1 samples of 250 μm (aged at 363 K and linked with 0.65 mmol of linker), which exhibited a high reaction rate, was ground to 125 μm and tested in the Beckmann rearrangement reaction. The reaction rates of the samples with 250 μm and 125 μm of particle sizes were determined to be $27.3 \cdot 10^{-2} \text{ gh}^{-1} \text{ gcat}^{-1}$ and $33.7 \cdot 10^{-2} \text{ gh}^{-1} \text{ gcat}^{-1}$, respectively. The effect of the particle size on the rate will be lower for most of the other samples, which are not as active.

The conversion of cyclohexanone oxime and the reaction rate were calculated from the following relationships:

$$\text{Conversion \%} = \left[\frac{\text{mol CHO charged} - \text{mol unreacted CHO}}{\text{mol CHO charged}} \right] * 100 \quad 12$$

$$\text{Reaction rate g/ h-gcat} = \frac{\text{CHOcharged(g)} * \text{Caprolactam\% in the product}}{\text{Time(h)} * \text{catalyst(g)}} \quad 13$$

Samples for rate analysis were collected over a time of 2 min, starting 55 min after the beginning of the reaction. The deactivation behavior of the commercial catalyst was also examined. For this purpose, 0.2 g of catalyst, which had a particle size of 250 μm , was used. Catalyst was mixed with 2 g of quartz. P_{ox} and W/F were chosen as 2.18 kPa, and 1.25 gh/mol, respectively. Time on stream was extended until 6 hours and the decrease of the reaction rate over time was observed. The results are presented in Figure 4.33.

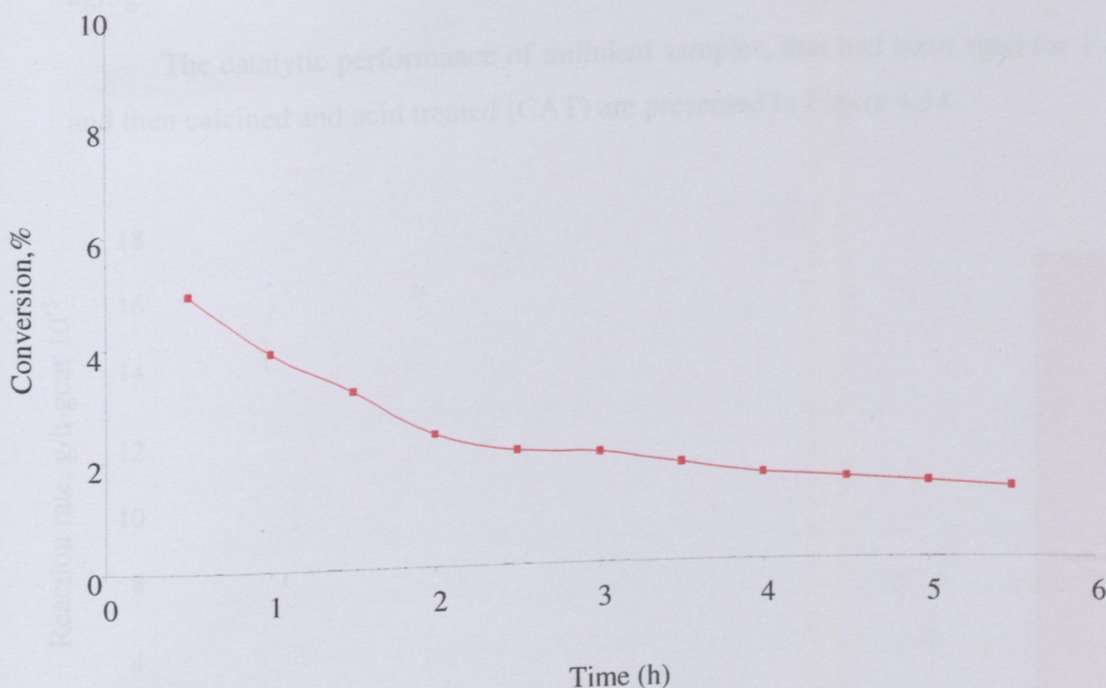


Figure 4.33. Deactivation of commercial ZSM-5.

The experiments with the commercial catalyst allowed to adjust the reaction conditions so that further experiments were carried out under kinetic control. The reaction conditions used for unlinked and crosslinked samples are given in Table 4.9.

Table 4.9. Reaction conditions

Catalyst weight, g	P _{oxime.} , kPa	Total flow, mol/h	W/F, gh/mol	Particle size, μm
0.2	2.18	0.16	1.25	250

4.4.2. The Effect of Temperature

As mentioned before, ZSM-5 (prep.) samples, which had been aged for 1 day, were X-ray amorphous, while Silicalite-1 samples were crystalline after 1 day of aging.

The catalytic performance of unlinked samples, that had been aged for 1 day and then calcined and acid treated (CAT) are presented in Figure 4.34.

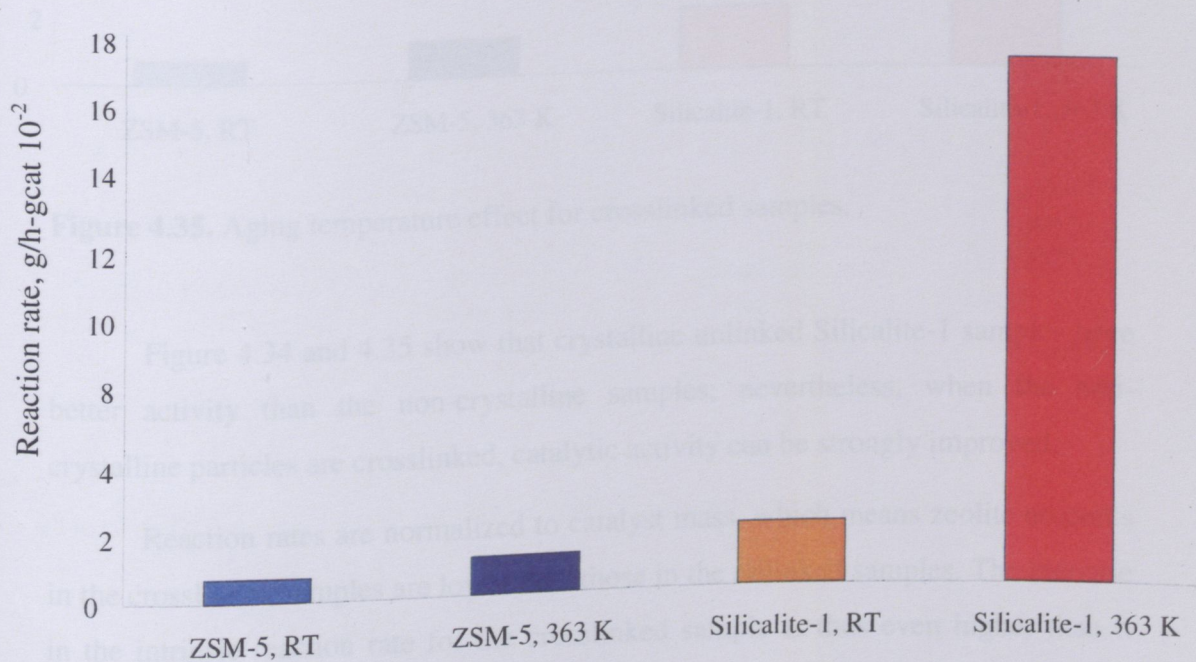


Figure 4.34. Reaction rates of unlinked ZSM-5 (prep.) and unlinked Silicalite-1 samples aged at different temperatures.

As shown in the figure, unlinked ZSM-5 (prep.) samples do not have significant catalytic activity. Aging temperature affects only slightly the catalytic performance of ZSM-5 (prep.) samples if they are not crosslinked. On the other hand, aging temperature has a strong effect for Silicalite-1. The Silicalite-1 samples, aged at 363 K and which are crystalline, have a high catalytic activity. This pronounced effect could be due to the positive influence of crystallinity. The catalytic activities of crosslinked samples are consistently higher. Catalytic activity increases regardless of crystallinity. The results are shown in Figure 4.35.

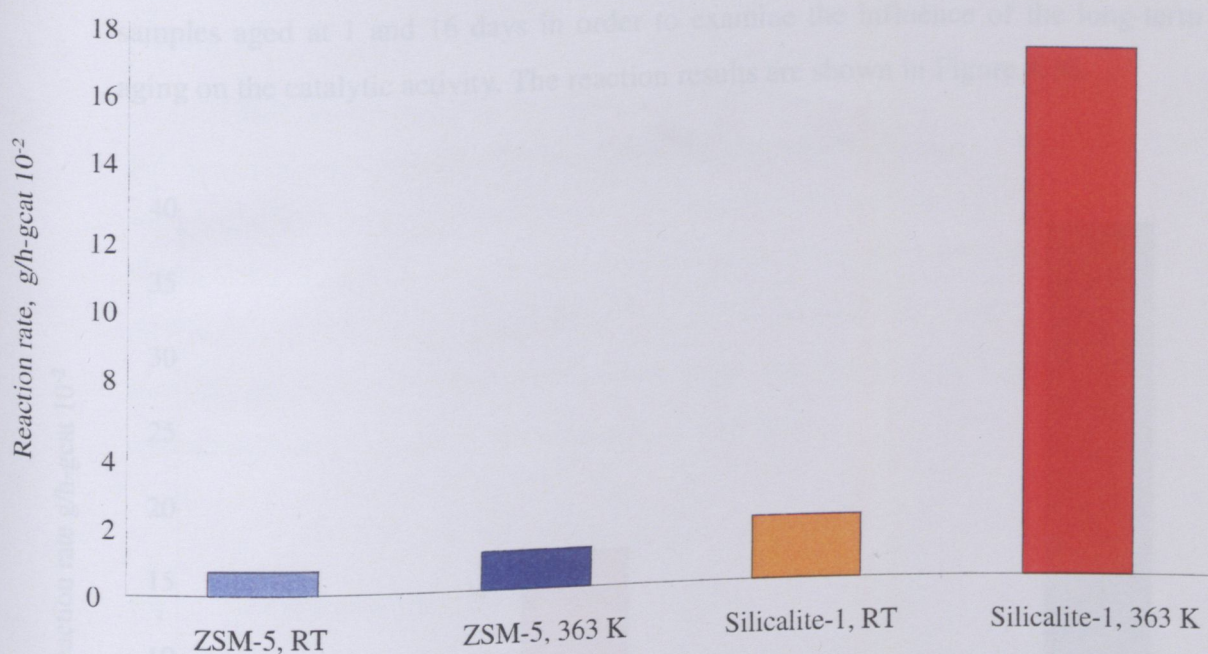


Figure 4.35. Aging temperature effect for crosslinked samples.

Figure 4.34 and 4.35 show that crystalline unlinked Silicalite-1 samples have better activity than the non-crystalline samples; nevertheless, when the non-crystalline particles are crosslinked, catalytic activity can be strongly improved.

Reaction rates are normalized to catalyst mass, which means zeolite amounts in the crosslinked samples are lower than those in the unlinked samples. The increase in the intrinsic reaction rate for the crosslinked sample is thus even higher than it appears from the figure.

In the unlinked samples, small zeolitic entities can agglomerate and acidic centers might be blocked. On the other hand, with crosslinking the particles, a mesopore structure is formed and acid centers are expected to be more accessible. This is probably the reason for the improved catalytic activity of the crosslinked samples.

ZSM-5 (prep.) samples are not crystalline even after aging at 363 K for 16 days. X-ray diffraction and ^{13}C -NMR results are in agreement with each other that there is no ordered structure under these conditions. The effect of aging time on catalytic activity was investigated using unlinked and crosslinked ZSM-5 (prep.) samples aged at 1 and 16 days in order to examine the influence of the long-term aging on the catalytic activity. The reaction results are shown in Figure 4.36.

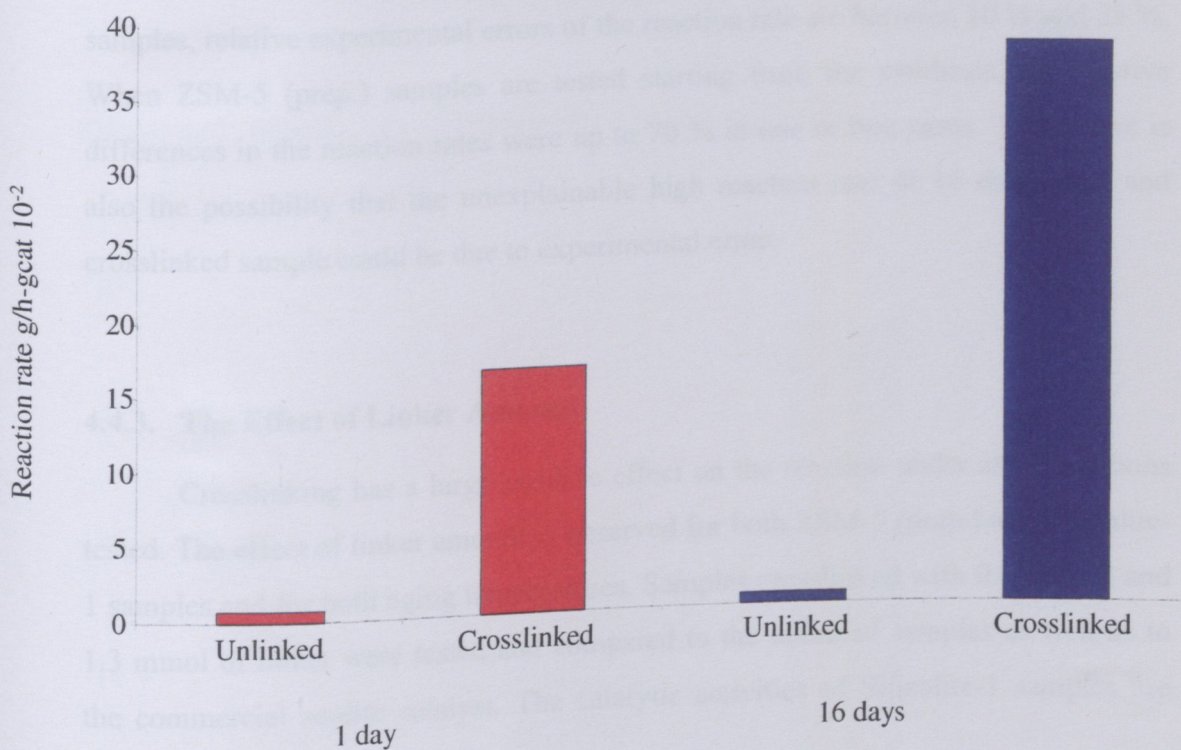


Figure 4.36. Reaction results of ZSM-5 (prep.) samples aged at 363 K.

After 16 days of aging, there is no increase in the catalytic activity for the unlinked samples. On the other hand, in crosslinked samples after 16 days of aging a significantly higher reaction rate was observed.

Reaction rate, g/h-gcat 10⁻²

The reason for the increase in the reaction rate for 16 days aged and crosslinked samples is presently still unclear. If some unit cells would have had formed, one could suspect the increase in accessibility of acid sites with crosslinking the particles to be the reason of the increased activity. However, ¹³C MAS NMR analysis did not reveal any formation of MFI structure in the 16 days aged samples and thus further studies are needed to clarify this issue.

The mesopore area of the 16 days aged and crosslinked sample is 528 m²/g. where the 1 day aged and crosslinked sample has a mesopore area of 460 m²/g. The higher mesopore area of the 16 days aged sample might have improved the catalytic activity.

Many experiments were repeated several times starting from the synthesis of the materials, to check the reproducibility of the results. In case of the Silicalite-1 samples, relative experimental errors of the reaction rate are between 10 % and 25 %. When ZSM-5 (prep.) samples are tested starting from the synthesis, the relative differences in the reaction rates were up to 70 % in one or two cases. Thus, there is also the possibility that the unexplainable high reaction rate of 16 days aged and crosslinked sample could be due to experimental error.

4.4.3. The Effect of Linker Amount

Crosslinking has a large positive effect on the reaction under any conditions tested. The effect of linker amount is observed for both ZSM-5 (prep.) and Silicalite-1 samples and for both aging temperatures. Samples crosslinked with 0.65 mmol and 1.3 mmol of linker were tested and compared to the unlinked samples as well as to the commercial zeolite catalyst. The catalytic activities of Silicalite-1 samples are given in Figures 4.37 and 4.38.

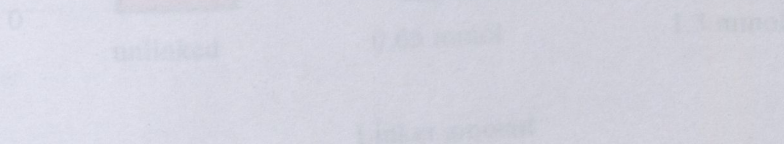


Figure 4.38. Reaction rates of Silicalite-1 samples aged at 363 K.

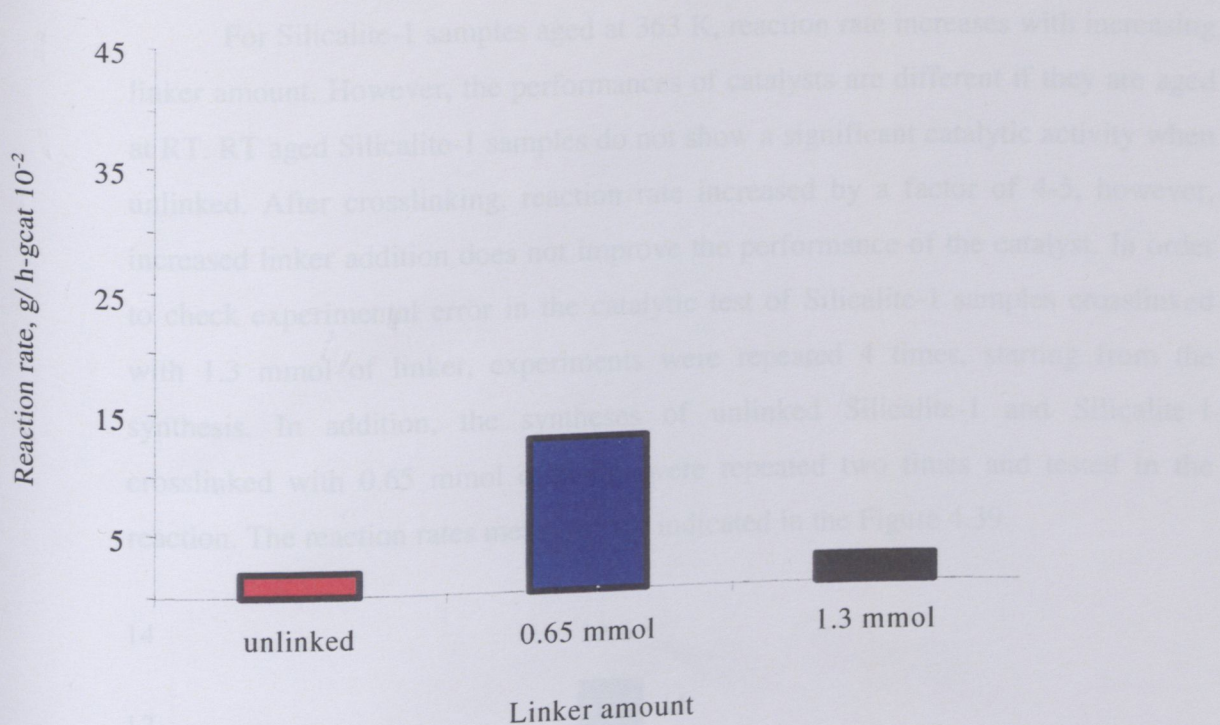


Figure 4.37. Reaction rates of Silicalite-1 samples aged at RT .

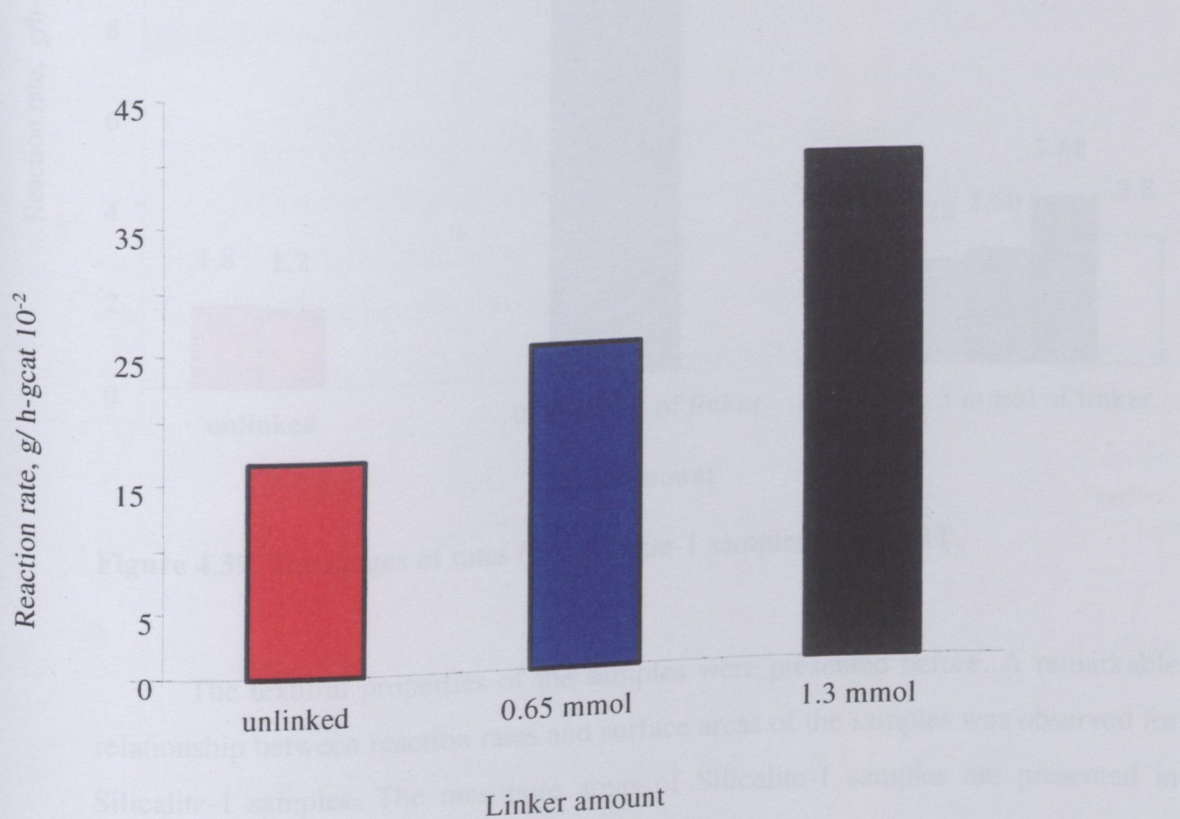


Figure 4.38. Reaction rates of Silicalite-1 samples aged at 363 K.

For Silicalite-1 samples aged at 363 K, reaction rate increases with increasing linker amount. However, the performances of catalysts are different if they are aged at RT. RT aged Silicalite-1 samples do not show a significant catalytic activity when unlinked. After crosslinking, reaction rate increased by a factor of 4-5, however, increased linker addition does not improve the performance of the catalyst. In order to check experimental error in the catalytic test of Silicalite-1 samples crosslinked with 1.3 mmol of linker, experiments were repeated 4 times, starting from the synthesis. In addition, the syntheses of unlinked Silicalite-1 and Silicalite-1 crosslinked with 0.65 mmol of linker were repeated two times and tested in the reaction. The reaction rates measured are indicated in the Figure 4.39.

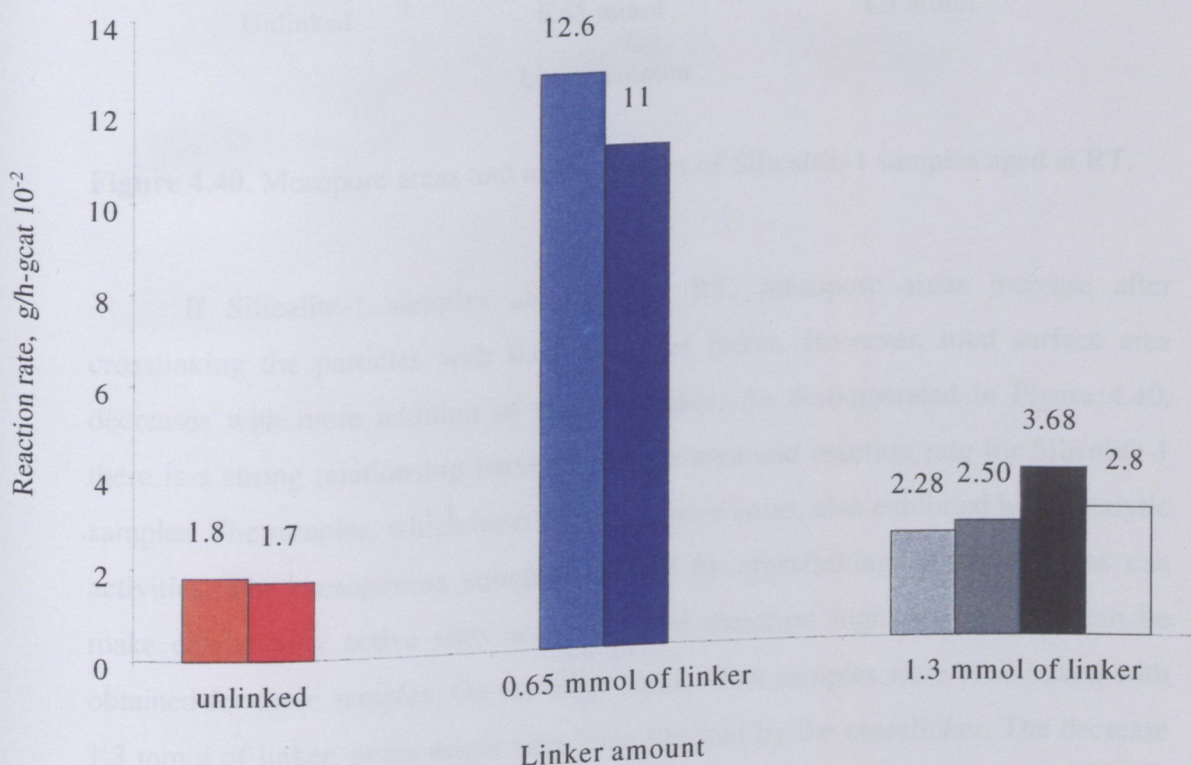


Figure 4.39. The ranges of rates for Silicalite-1 samples aged at RT.

The textural properties of the samples were presented before. A remarkable relationship between reaction rates and surface areas of the samples was observed for Silicalite-1 samples. The mesopore areas of Silicalite-1 samples are presented in Figure 4.40 together with the rates.

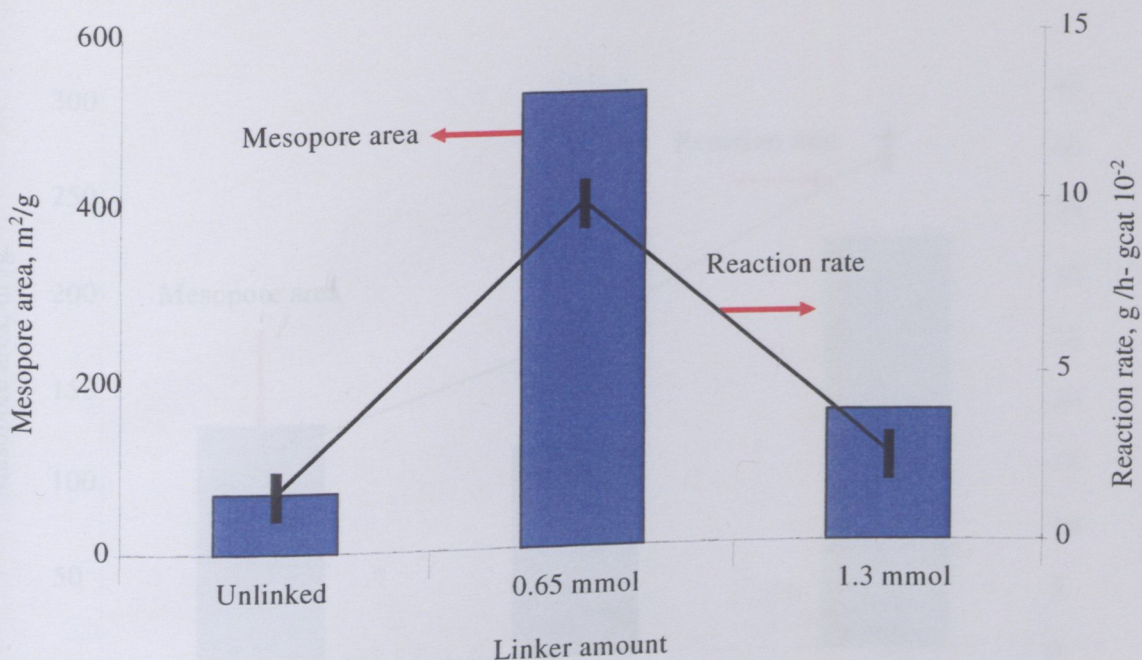


Figure 4.40. Mesopore areas and reaction rates of Silicalite-1 samples aged at RT.

If Silicalite-1 samples are aged at RT, mesopore areas increase after crosslinking the particles with 0.65 mmol of linker. However, total surface area decreases with more addition of silicone linker. As demonstrated in Figure 4.40, there is a strong relationship between surface area and reaction rate for Silicalite-1 samples. The samples, which have high mesopore areas, also exhibited high catalytic activities. The mesoporous structure created by crosslinking of the particles can make catalytically active sites accessible and therefore high reaction rate can be obtained for these samples. On the other hand, when samples were crosslinked with 1.3 mmol of linker, pores might have been blocked by the crosslinker. The decrease in the mesopore areas along with the decrease in the reaction rates can be explained by pore blockage.

Silicalite-1 samples are crystalline and catalytically active even before crosslinking if they are aged at 363 K. For Silicalite-1 samples aged at 363 K, a direct proportionality was observed between reaction rate and mesopore area. Especially, when the linker amount was increased to 1.3 mmol, mesopore areas and the reaction rates of the samples increased.

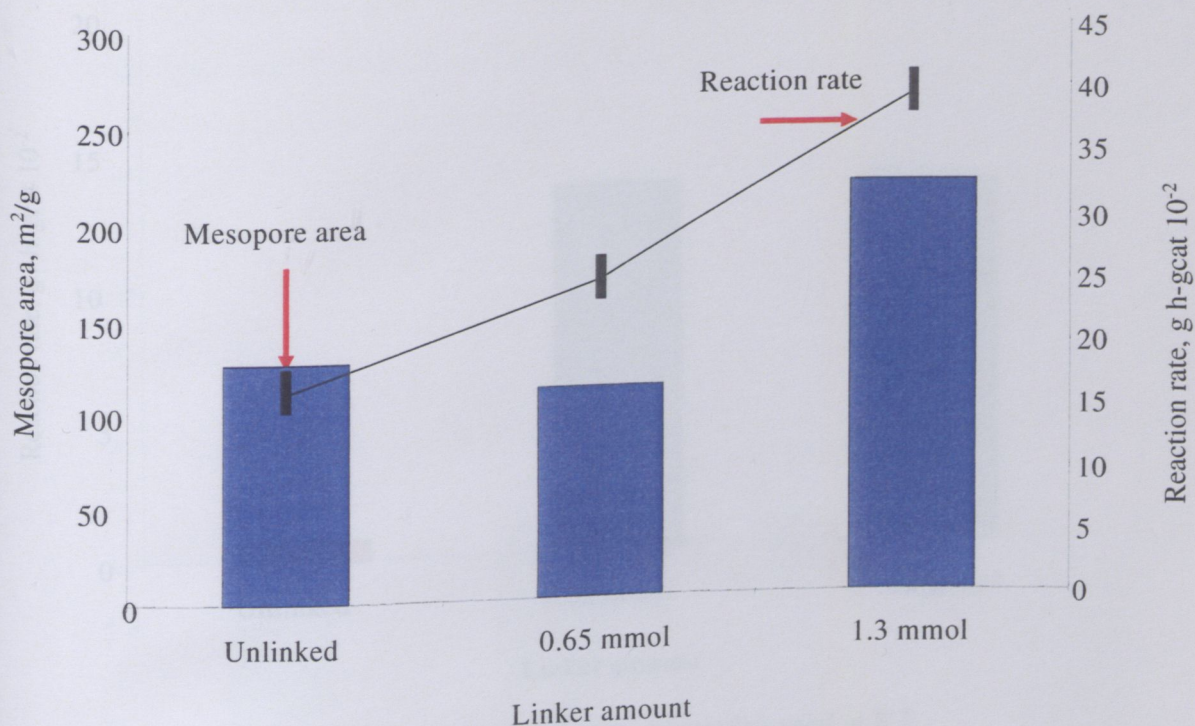


Figure 4.41. Mesopore areas and reaction rates of Silicalite-1 samples aged at 363 K.

For ZSM-5 (prep.) samples, the linker amount effect was different than for Silicalite-1. The results are presented in Figure 4.42 and 4.43. Unlinked ZSM-5 (prep.) samples are inactive in the reaction even when they are aged at higher temperature. It was already mentioned that ZSM-5 (prep.) samples, which are used in this reaction, are not crystalline. Thus, low catalytic activity is expected for these samples. After crosslinking a drastic increase in the reaction rate is obvious for both RT and high temperature aged samples. However, after adding 1.3 mmol of linker, the reaction rate does not increase further.

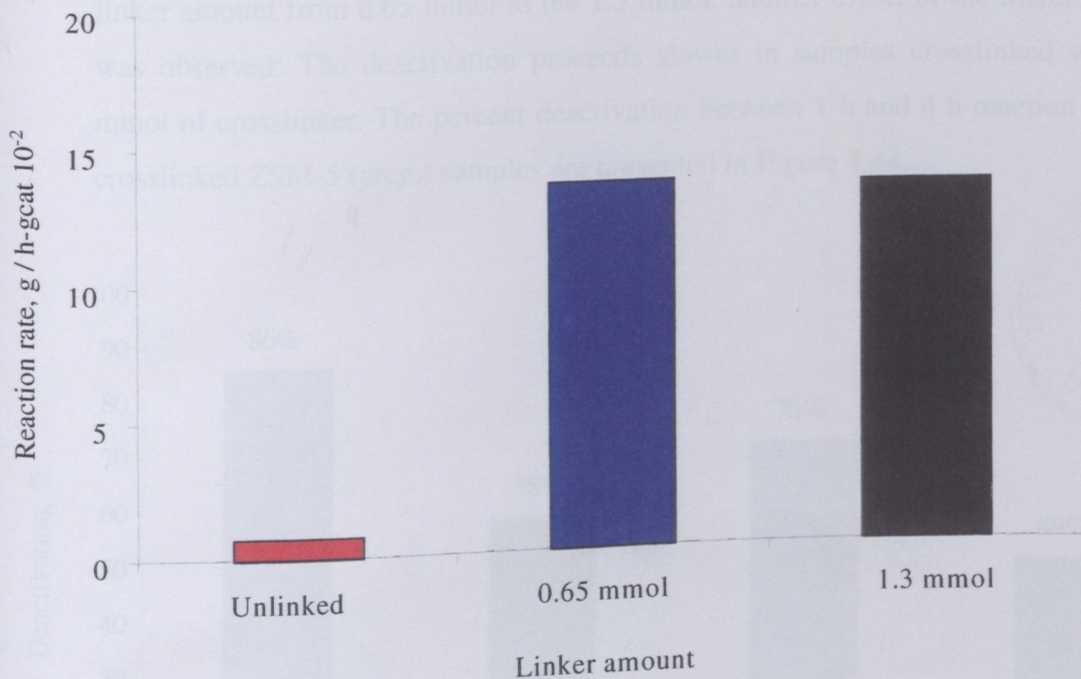


Figure 4.42. Reaction rates of ZSM-5 (prep.) samples aged at RT.

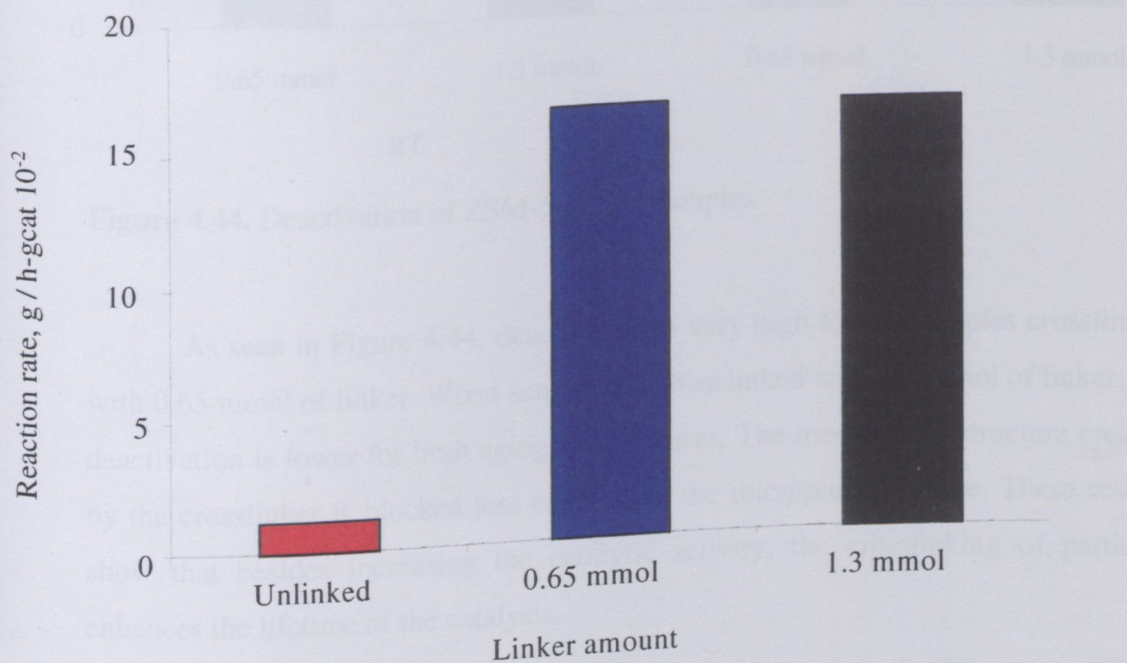


Figure 4.43. Reaction rates of ZSM-5 (prep.) samples aged at 363 K.

Although there is no further increase in the reaction rate with increasing the linker amount from 0.65 mmol to the 1.3 mmol, another effect of the linker amount was observed: The deactivation proceeds slower in samples crosslinked with 1.3 mmol of crosslinker. The percent deactivation between 1 h and 4 h reaction time of crosslinked ZSM-5 (prep.) samples are presented in Figure 4.44.

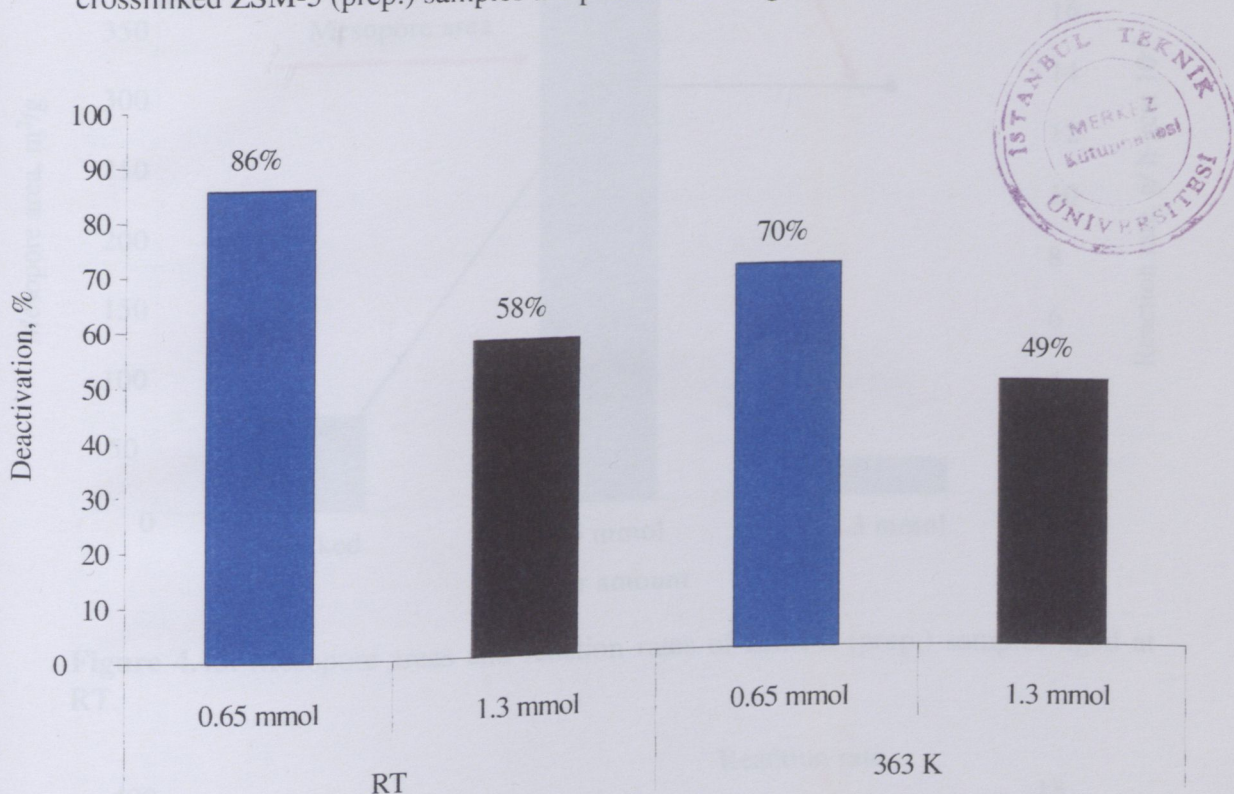


Figure 4.44. Deactivation of ZSM-5 (prep.) samples

As seen in Figure 4.44, deactivation is very high for the samples crosslinked with 0.65 mmol of linker. When samples are crosslinked with 1.3 mmol of linker, the deactivation is lower for both aging temperatures. The mesoporous structure created by the crosslinker is blocked less easily than the micropore structure. These results show that besides increasing the catalytic activity, the crosslinking of particles enhances the lifetime of the catalysts.

The relation between mesopore areas and reaction rates is different for ZSM-5 (prep.) samples than it is for Silicalite-1 samples. There is no clear relation between reaction rates and mesopore areas for ZSM-5 (prep.) samples, when they are calcined and acid treated (CAT) or calcined and ion exchanged (CIE) before the catalytic test. On the other hand, for the samples, which are acid treated without calcination

(UAT), the relationship between reaction rates and the mesopore areas is obvious. Reaction rates (UAT) and mesopore areas of ZSM-5 (prep.) samples are presented in Figures 4.45 and 4.46 together with the rates.

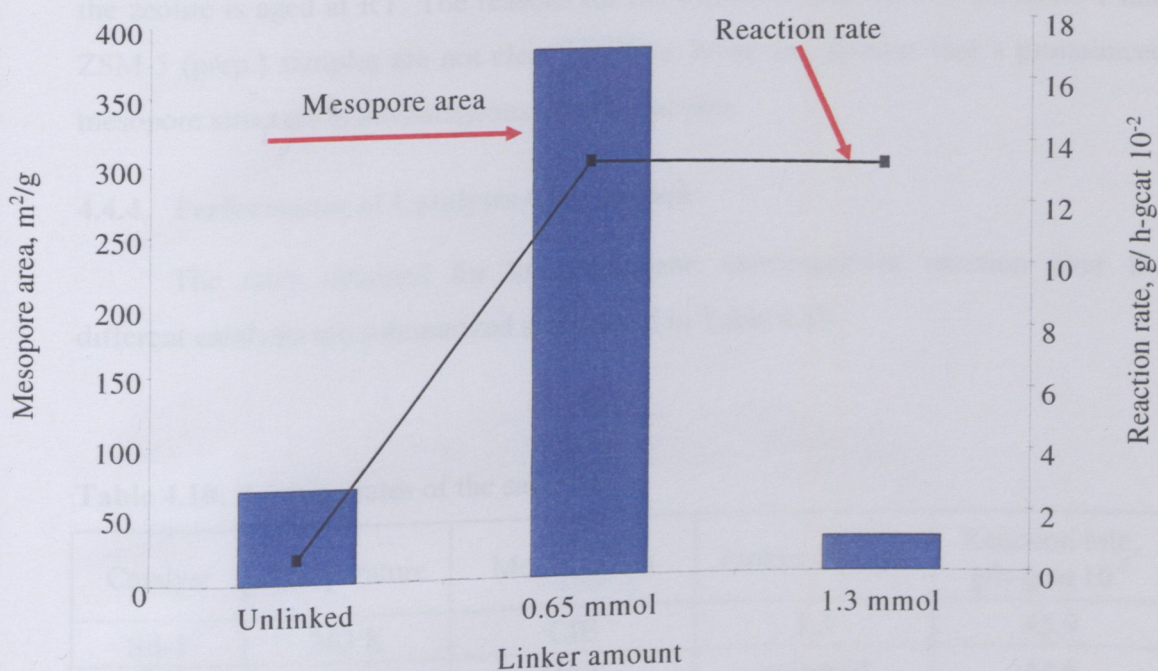


Figure 4.45. Mesopore areas and reaction rates of ZSM-5 (prep.) samples aged at RT.

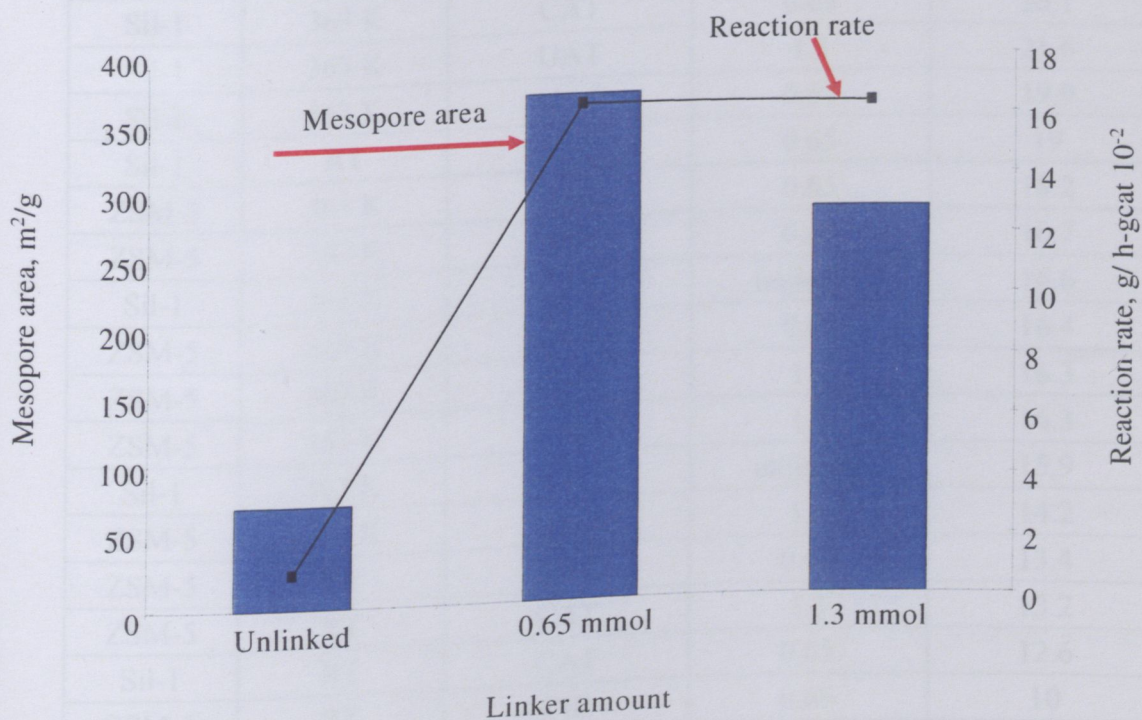


Figure 4.46. Mesopore areas and reaction rates of ZSM-5 (prep.) samples aged at 363 K.

As seen from the Figures above, for both aging temperatures, the reaction rates and mesopore areas increase after crosslinking with 0.65 mmol of linker. For the samples with 1.3 mmol of linker, the mesopore areas decrease, especially when the zeolite is aged at RT. The reasons for the different behaviors of Silicalite-1 and ZSM-5 (prep.) samples are not clear yet. It is, however, obvious that a pronounced mesopore structure is advantageous for the reaction.

4.4.4. Performance of Catalysts-Comparison

The rates obtained for the Beckmann rearrangement reaction over the different catalysts are summarized and ranked in Table 4.10.

Table 4.10. Reaction rates of the samples

Catalyst	Temperature	Modification	Linker amount	Reaction rate, g/h-gcat 10 ⁻²
Sil-1	363 K	CIE	1.3	45.9
Sil-1	363 K	UAT	unlinked	42.6
Sil-1	363 K	CAT	1.3	39.4
Sil-1	363 K	CIE	0.65	27.3
Sil-1	363 K	CAT	0.65	25.1
Sil-1	363 K	UAT	1.3	21.6
Sil-1	363 K	UAT	0.65	19.9
Sil-1	RT	CIE	0.65	19
ZSM-5	363 K	UAT	0.65	18.2
ZSM-5	363 K	CIE	0.65	16.7
Sil-1	363 K	CAT	unlinked	16.6
ZSM-5	363 K	CAT	0.65	16.4
ZSM-5	363 K	CAT	1.3	16.3
ZSM-5	363 K	CIE	1.3	16.3
Sil-1	363 K	CIE	unlinked	15.9
ZSM-5	363 K	UAT	1.3	14.2
ZSM-5	RT	CAT	0.65	13.4
ZSM-5	RT	CAT	1.3	13.2
Sil-1	RT	CAT	0.65	12.6
ZSM-5	RT	CIE	0.65	10

Tablo 4.10.(cont.)

Catalyst	Temperature	Modification	Linker amount	Reaction rate, g/h-gcat 10^{-2}
Sil-1	RT	UAT	0.65	10
ZSM-5	RT	CIE	1.3	9.4
ZSM-5	RT	UAT	0.65	8.3
ZSM-5	RT	UAT	1.3	7.65
Sil-1	RT	CIE	1.3	3.5
Sil-1	RT	UAT	unlinked	2.9
Sil-1	RT	CIE	unlinked	2.5
Sil-1	RT	UAT	1.3	2.5
Sil-1	RT	CAT	1.3	2.28
Sil-1	RT	CAT	unlinked	2.1
ZSM-5	363 K	CIE	unlinked	0.8
ZSM-5	RT	CAT	unlinked	0.76
ZSM-5	RT	CIE	unlinked	0.47
ZSM-5	RT	UAT	unlinked	0.43
ZSM-5	363 K	CAT	unlinked	0.43
ZSM-5	363 K	UAT	unlinked	0.23

As seen in Table 4.10, aging temperature has a significant effect on reaction rate. The highest reaction rates were measured for samples aged at 363 K, especially for Silicalite-1 samples. Unlinked samples had consistently low activity, which could be strongly improved by crosslinking the particles. Modifications, such as acid treatment or calcination, do not have any important effect on the reaction rate.

The catalysts were compared for their performances, with a commercial ZSM-5 sample, as well as with a crosslinked Aerosil (Aerosil 380, Degussa AG). The measurements performed with crosslinked Aerosil samples are considered as blank experiments since Aerosil is an amorphous, small particle, nonporous silica. These experiments therefore allow to study the linker effect, with no zeolitic units present. The results are presented in Figure 4.47.

In Figure 4.47, several catalyst samples are compared. A crosslinker amount of 0.65 mmol was used in all cases.

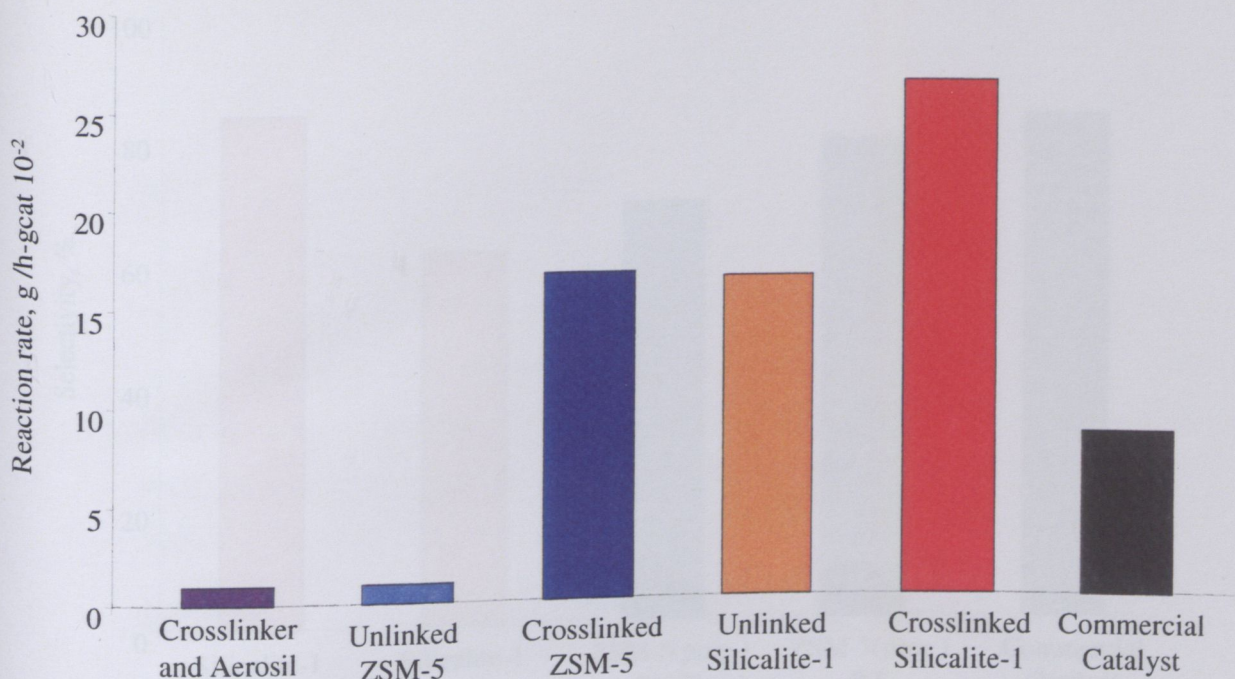


Figure 4.47. Catalytic activities of samples-comparison.

Crosslinked Aerosil did not exhibit any significant activity in comparison to the other samples. This confirms that the crosslinker has no catalytic activity on its own. The increase in the reaction rate for the linked samples, therefore, cannot be explained by the catalytic activity of the crosslinker. The micro-mesoporous structure created by crosslinking and the enhanced accessibility of acid centers should instead be considered as the reason for the improved catalytic performance.

All the crosslinked samples aged at 363 K showed a higher catalytic activity than commercial ZSM-5. The Silicalite-1 sample aged at 363 K showed the highest activity of all samples. It should be noted, though, that the commercial ZSM-5 was not a catalyst sample optimized for the Beckmann rearrangement.

The selectivities of unlinked samples are given in Figure 4.48. The commercial ZSM-5 and the Silicalite-1 sample aged at 363 K showed the highest product selectivities. In contrast, for Silicalite-1 samples aged at RT, a relatively low selectivity was obtained. ZSM-5 (prep.) samples exhibited a higher selectivity when aged at RT.

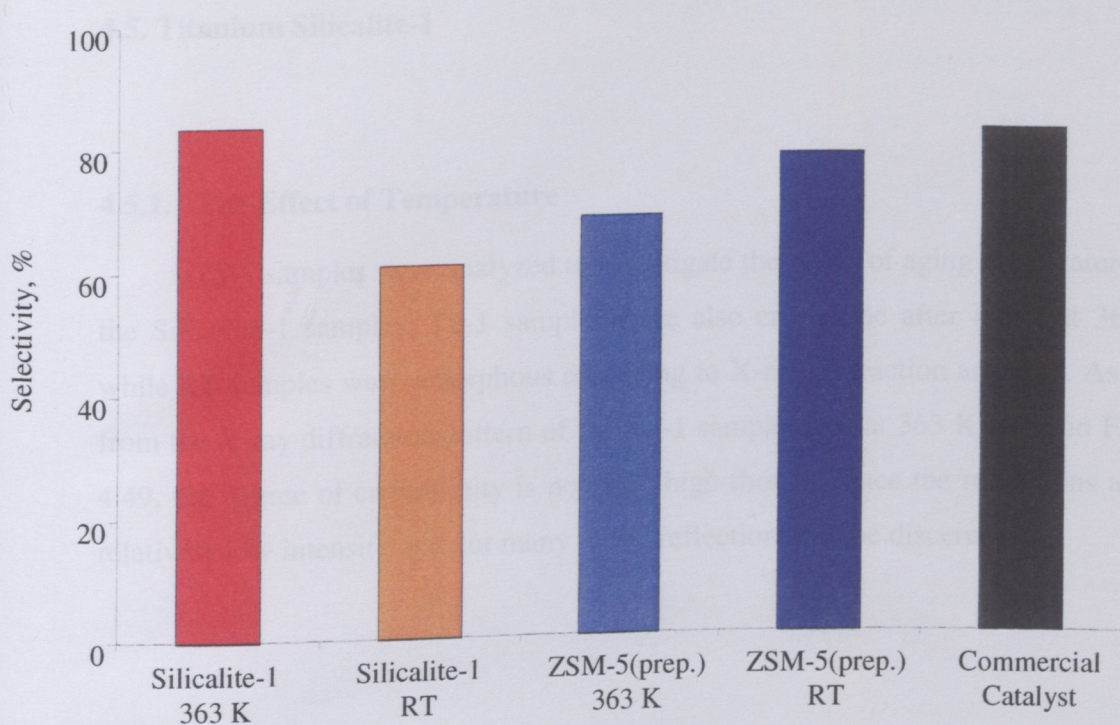


Figure 4.48. Selectivities of unlinked samples.

Selectivity values of about 80% were obtained, which is lower than those reported in the literature. In this study, toluene was chosen as the solvent. It is known (70) that the selectivity of the catalysts is high when polar solvents such as methanol or ethanol are used. The relatively lower selectivities obtained may be due to the nonpolar solvent used in this study. Hence, it may be possible to improve the selectivities via the choice of solvent.

200-212 nm is directly correlated to framework Ti, whereas the appearance of the band above 280 nm is an indication for extra framework titanium species (82).

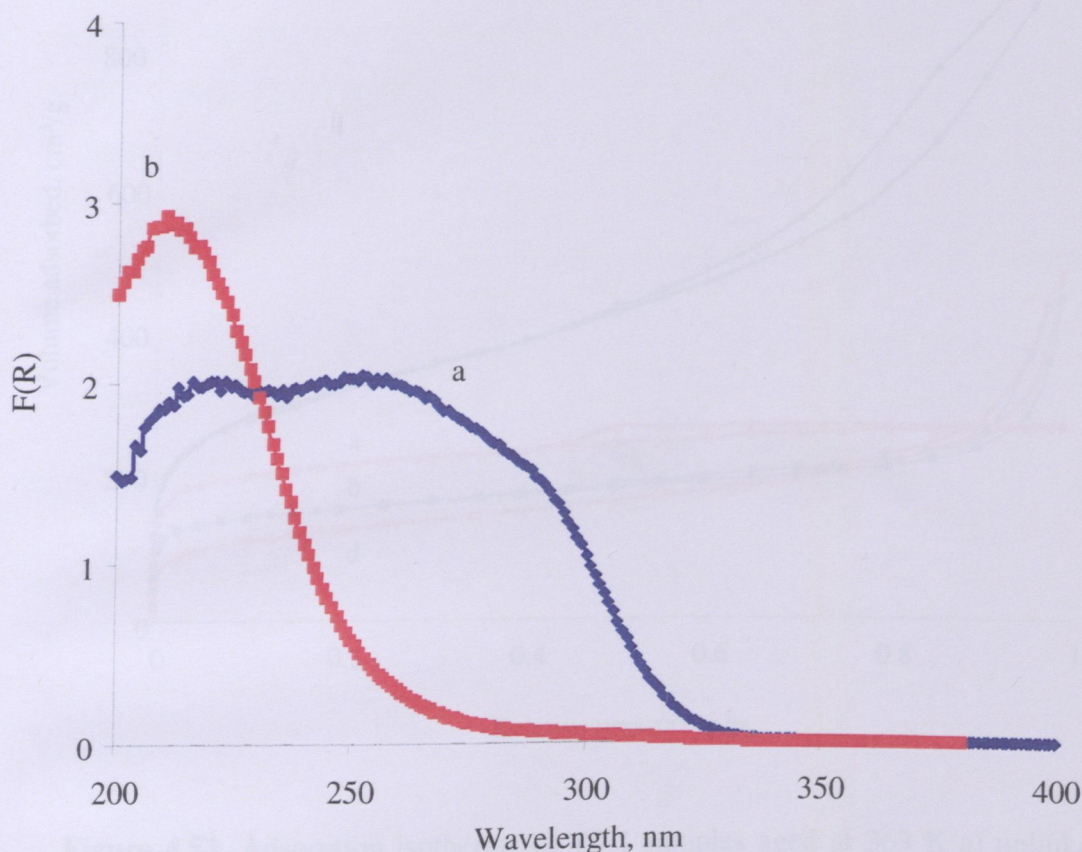


Figure 4.50. DRUV spectra for unlinked TS-1 samples aged at a) RT, b) 363 K.

The results show that (Figure 4.50), TS-1 samples have a high amount of extra framework titanium when aged at RT. After aging samples at 363 K for 24 hours, the absorption at about 260-280 nm, indicative of the octahedral position of titanium species disappears.

4.5.2. The Effect of Linker Amount

The effect of linker amount was investigated for TS-1 samples. Adsorption isotherms for TS-1 samples, aged at 363 K, are given in Figure 4.51. The adsorption isotherm for the sample crosslinked with 1.3 mmol of linker is different from the others in some ways. The amount of adsorbed N_2 is very high and a sharp increase after $p/p_0=0.1$ was obtained, which can be attributed to the occurrence of significant mesoporosity in this sample.

The samples have micropore volumes of about $0.18 \text{ cm}^3/\text{g}$, which is a hint towards the Silicalite-1 structure (77). Only for the sample prepared with the highest linker concentration, the micropore volume decreased. Some decrease in the micropore volumes and areas with increasing linker amount should be expected due to decreasing zeolite fraction in the samples. The sample crosslinked with 1.3 mmol of linker is an exception not only in this sense, but also due to its very high mesoporosity, as mentioned above.

The effect of linker amount was also observed clearly in DRUV analyses of the TS-1 samples. The results are shown in Figure 4.52.

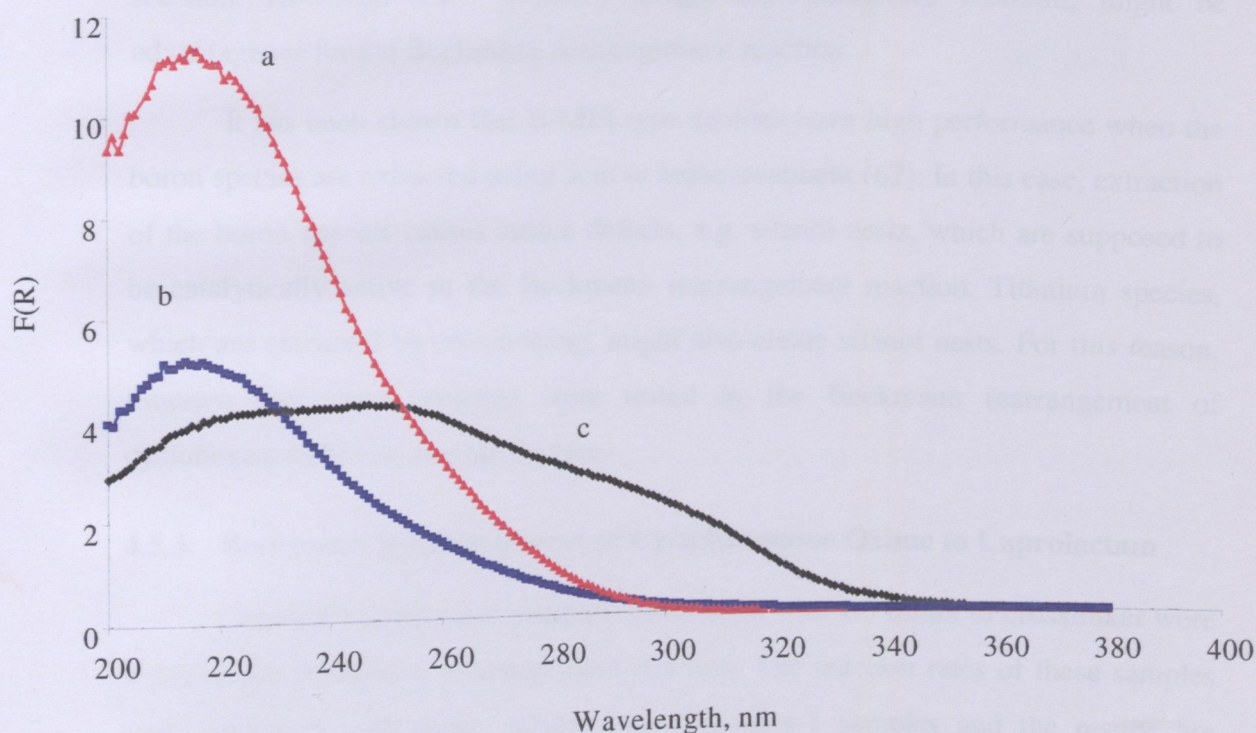


Figure 4.52. UV analyses of TS-1 samples prepared with different amounts of linker a) unlinked, b) 0.65 mmol, c) 1.3 mmol.

For unlinked samples, and samples linked with 0.65 mmol of linker, only tetrahedral titanium species could be detected as evidenced by the absorption around 200-220 nm. However, when 1.3 mmol of linker was added, one more shoulder

appeared at approximately 280-300 nm, which is attributed to octahedral titanium species.

When samples are crosslinked in the synthesis solution HCl is produced as a result of the linking reaction. The increase in the linker amount results in an increase in the concentration of the HCl. The high linker concentration in the synthesis solution can thus cause an extraction of titanium species from the structure depending on the linker concentration.

It is known that for the epoxidation of propene tetrahedral titanium species are favorable. Therefore, crosslinked samples, especially those crosslinked with 1.3 mmol of crosslinker, are not expected to show a high catalytic activity in this reaction. However, TS-1 samples, having extraframework titanium, might be advantageous for the Beckmann rearrangement reaction.

It has been shown that B-MFI type zeolites have high performance when the boron species are extracted using acid or basic treatment (62). In this case, extraction of the boron species causes lattice defects, e.g. silanol nests, which are supposed to be catalytically active in the Beckmann rearrangement reaction. Titanium species, which are extracted by crosslinking, might also create silanol nests. For this reason, titanium Silicalite-1 samples were tested in the Beckmann rearrangement of cyclohexanone oxime to caprolactam.

4.5.3. Beckmann Rearrangement of Cyclohexanone Oxime to Caprolactam

Unlinked samples and samples crosslinked with 1.3 mmol of crosslinker were tested in the Beckmann rearrangement reaction. The reaction rates of these samples were compared with those observed for Silicalite-1 samples and the results are presented in Figure 4.53.

Another advantage of the TS-1 samples was that the reaction rate increased for both Silicalite-1 and TS-1 samples. The contribution of crosslinking was much higher for TS-1 samples. Samples crosslinked with 1.3 mmol of linker, did not lose catalytic activity even after 4 hours time on stream. The deactivation rates, compared with Silicalite-1 and ZSM-5 samples, are presented in Figure 4.54. The reaction rate of the crosslinked TS-1 sample decreased only by 4.7 % after 4 hours, where the corresponding values for ZSM-5 and Silicalite-1 samples were 48.5 % and 48.6 %, respectively.

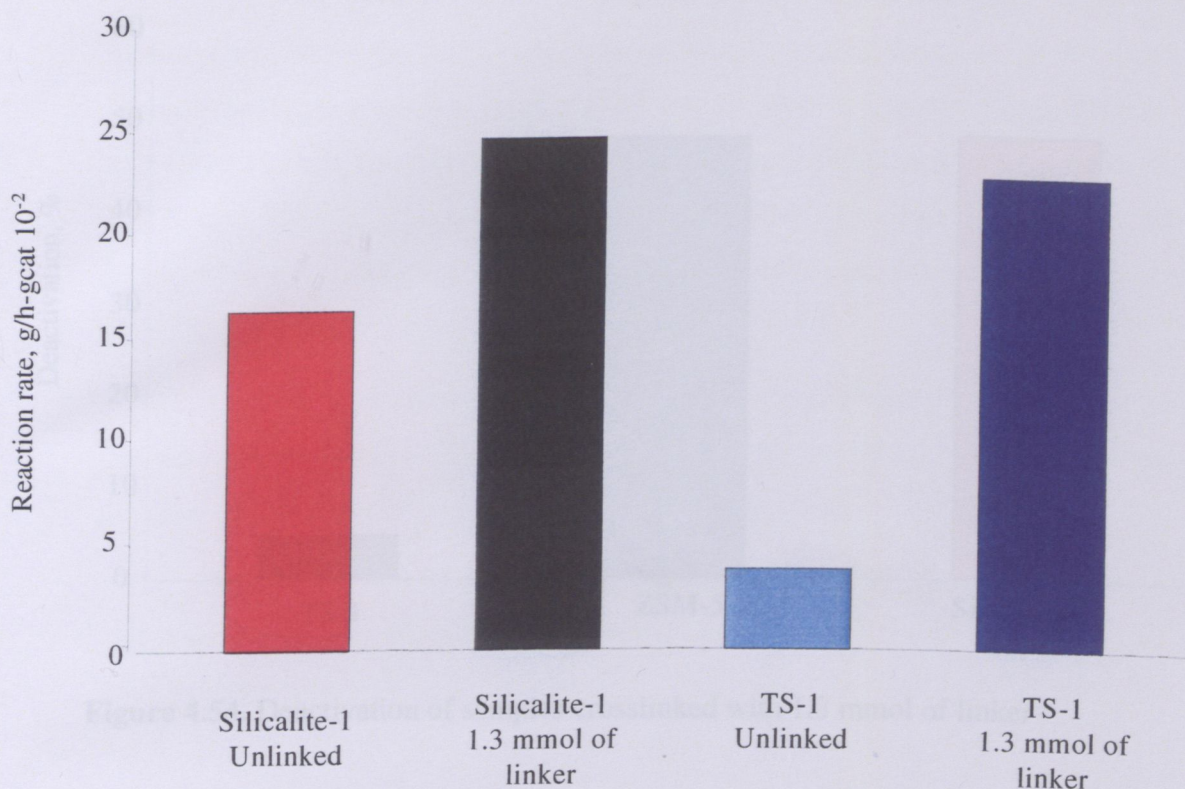


Figure 4.53. Reaction rates of Silicalite-1 and TS-1 samples.

Unlinked TS-1 samples were less active in comparison to unlinked Silicalite-1 samples. After crosslinking, however, the reaction rate increased for both Silicalite-1 and TS-1 samples. The contribution of crosslinking was much higher for TS-1.

Although crosslinked TS-1 samples exhibited similar activity as Silicalite-1 samples, another advantage of crosslinked TS-1 samples was observed. TS-1 samples, which were crosslinked with 1.3 mmol of linker, did not lose catalytic activity even after 4 hours time on stream. The deactivation rates, compared with Silicalite-1 and ZSM-5 samples, are presented in Figure 4.54. The reaction rate of the crosslinked TS-1 sample decreased only by 4.7 % after 4 hours, where the corresponding values for ZSM-5 and Silicalite-1 samples were 48.5 % and 48.6 %, respectively.

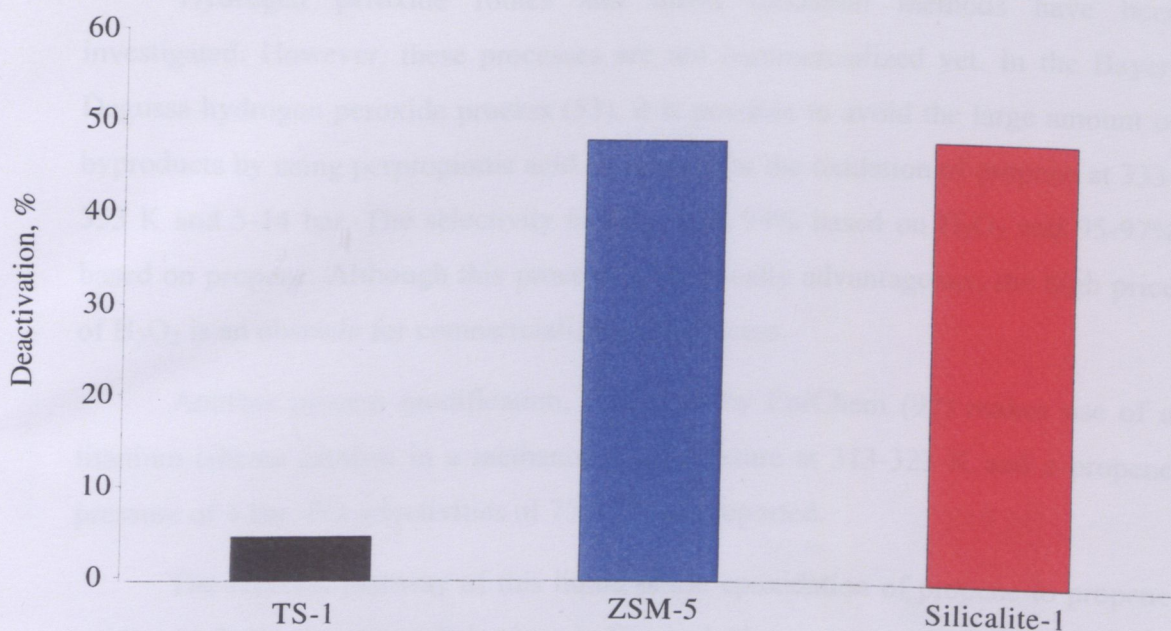


Figure 4.54. Deactivation of samples crosslinked with 1.3 mmol of linker

The catalyst life is longer when 1.3 mmol of linker is used to crosslink ZSM-5 (prep.) and Silicalite-1 samples. However, the deactivation rates of ZSM-5 and Silicalite-1 samples prepared with 1.3 mmol of linker are still 10 times higher than that of the TS-1 sample. In order to clarify this difference, detailed analyses should be made and catalysts should be tested for longer times on stream.

4.5.4. Epoxidation of Propene to Propene Oxide with Hydrogen Peroxide

Propene oxide (PO) is one of the important intermediates in chemical industry. It is the starting material for a broad spectrum of products including polymers (polyurethans, polyesters), oxygenated solvents (propylene glycol ethers) and industrial fluids (polyglycols).

PO is commercially manufactured by the chlorohydrin process or indirect epoxidation of propene in liquid phase. Since both processes are influenced economically and ecologically by the wastewater and byproduct problems, current research has focused on another safe and economical and ecologically sound production method.

Hydrogen peroxide routes and direct oxidation methods have been investigated. However, these processes are not commercialized yet. In the Bayer-Degussa hydrogen peroxide process (53), it is possible to avoid the large amount of byproducts by using perpropionic acid. It is used for the oxidation of propene at 333-353 K and 5-14 bar. The selectivity is more than 94% based on H_2O_2 and 95-97% based on propene. Although this process is technically advantageous, the high price of H_2O_2 is an obstacle for commercializing the process.

Another process modification, published by EniChem (92) makes use of a titanium silicate catalyst in a methanol-water mixture at 313-323 K and a propene pressure of 4 bar. PO selectivities of 75-97 % are reported.

The reaction pathway of this liquid phase epoxidation of propene to propene oxide with hydrogen peroxide is given in Figure 4.55.

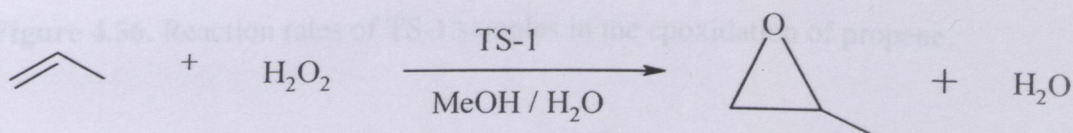


Figure 4.55. Epoxidation of propene to propene oxide with hydrogen peroxide.

The disadvantages of the liquid phase reaction, such as the costs of manufacturing, the difficulties in the separation of the product, and the danger of explosion directed research towards another solution, namely the gas phase reaction. The TS-1 samples were tested in the gas phase epoxidation of propene. Hydrogen peroxide was fed into the reactor after total evaporation of 50 wt % H_2O_2 solutions at 373 K in a specially designed and passivated vaporizer. Nitrogen was used as carrier gas. The reaction conditions for the epoxidation of propene with hydrogen peroxide are given in another study (85). The results are presented in Figure 4.56.

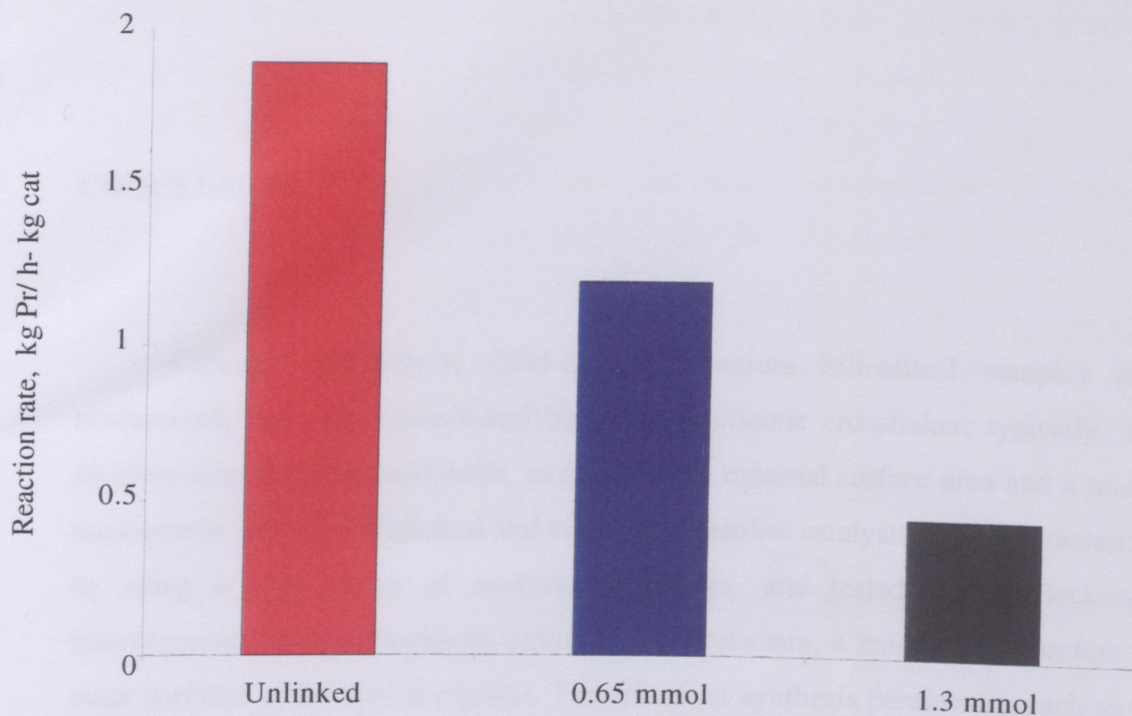


Figure 4.56. Reaction rates of TS-1 samples in the epoxidation of propene.

The TS-1 samples are active, but appreciably less so than conventional TS-1, which has a reaction rate around 3 kg propene / h kg cat (85). The reaction rate decreases with increasing linker amount. That the fraction of Titanium Silicalite-1 in the sample decreases as the amount of linker increases, may explain the lower reaction rates observed for the crosslinked samples.

CONCLUSION

Colloidal Silicalite-1, ZSM-5, and Titanium Silicalite-1 samples were synthesized, and were crosslinked by using a silicone crosslinker, typically, 1,7-dichloro-octamethyl-tetrasiloxane, to create more external surface area and a micro-mesoporous structure. Unlinked and crosslinked zeolite catalysts, were characterized by using a wide range of analysis techniques, and tested in the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam, a reaction that prefers the outer surfaces of the zeolite crystals. The effects of synthesis parameters, such as the aging time, aging temperature, and the amount of linker, on the activities of the catalyst samples for the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam were examined.

Crosslinking of the particles created additional mesoporosity, which could be observed by using N_2 adsorption analysis. A Type I isotherm was obtained for all unlinked samples, while linking resulted in a sharp increase between $p/p_0=0.4$ and $p/p_0=0.6$, indicating that mesoporosity was created by crosslinking.

^{29}Si MAS NMR analysis also showed evidence for crosslinking. The intensities of the Q^2 and Q^3 groups decreased, while the intensity of Q^4 groups increased after crosslinking. Two new lines were observed at -18 ppm and -22 ppm, which were attributed to the T-groups in the silicone linker.

All ZSM-5 samples were amorphous, including those aged for up to 16 days at 363 K, while Silicalite-1 samples aged at 363 K for 24 h were crystalline according to XRD, TEM, and ^{13}C MAS NMR analyses. ZSM-5 samples were termed as ZSM-5 (prep.), indicating that they were prepared from a solution which would result in the formation of ZSM-5 crystals under suitable conditions.

The effect of linker amount was investigated at three levels, a low (0.65 mmol), a medium (1.3 mmol) and a high (2.6 mmol) amount of linker addition. For Silicalite-1 samples aged at 363 K, micropore areas decreased and mesopore areas

increased with increasing linker amount. On the other hand, adsorption behaviour was different for Silicalite-1 and ZSM-5 (prep.) samples aged at RT. Extremely high total adsorbed volumes were observed when the samples were crosslinked with medium amount of linker. On the other hand, when the samples were crosslinked with 1.3 mmol of linker, micropore and mesopore areas decreased.

In all cases, the crosslinked materials were found to have substantially better catalytic performance than the non-crosslinked samples and than a commercial ZSM-5 catalyst (ALSI-PENTA® SH-27, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 23-27$). About tenfold increase of the caprolactam yield was typical for many of the crosslinked colloidal zeolites, and typically, the crosslinked materials performed better than the commercial ZSM-5.

Aging temperature had a positive effect on the catalytic performances of all materials. Regarding the amount of linker addition, while the use of a low level of linker (0.65 mmol) for crosslinking substantially increased the reaction rates of the ZSM-5 (prep.) samples, which did not show any activity when unlinked, increasing the linker amount (1.3 mmol) did not increase the reaction rates further. However, another advantage of using a high amount of linker was noticed. The catalyst lifetimes of the ZSM-5 (prep.) samples, which were crosslinked with 1.3 mmol of linker, were substantially improved. The deactivation was 86 % after 4 h time on stream for the sample prepared with 0.65 mmol of linker and only 58 % for the sample prepared with 1.3 mmol of linker. The catalyst lifetime is known to be a critical criterion for catalysts to be used in the Beckmann rearrangement reaction.

The best performance was obtained by the catalysts prepared by crosslinking of Silicalite-1 aged at 363 K. A strong relationship was observed between mesopore areas and reaction rates of Silicalite-1 samples aged at this temperature. Reaction rate increased parallel to the increase in the mesopore area. Reaction rates were related to the mesopore areas for the samples aged at room temperature too. The only difference between the samples aged at 363 K and room temperature was in their behaviour when linked with high amounts of linker. For the samples aged at 363 K, mesopore areas and the reaction rates of the samples continued to increase at high linker amounts, while for those aged at room temperature, mesopore area and reaction rate started to decrease when a certain level of linker amount was exceeded.

The relationship between rates and mesopore areas was less clear for ZSM-5 (prep.) samples. There was only a clear trend for the samples which had been acid treated without calcination (UAT). In this case, reaction rates and mesopore areas increased after crosslinking up to a certain amount (0.65 mmol) of linker usage. When the linker amount was further increased (1.3 mmol), reaction rates remained almost constant and mesopore areas decreased for both aging temperatures.

Aerosil crosslinked using the same linker did not exhibit any activity in the Beckmann reaction, indicating that the crosslinker had no catalytic activity on its own and that all catalytic activity originated from the zeolite surfaces.

TS-1 samples were also tested in the Beckmann rearrangement reaction of cyclohexanone oxime to caprolactam. For this purpose, unlinked samples and samples crosslinked with 1.3 mmol of linker were studied. The unlinked TS-1 sample did not show any significant activity. However, after crosslinking the reaction rate increased. Furthermore, the sample deactivation was considerably lower for the crosslinked TS-1 sample in comparison to any of the other materials studied. The TS-1 sample deactivated by only 4.7 % after 4 hours on stream, while the activity of the ZSM-5 (prep.) and Silicalite-1 samples dropped by 48-80 % under the same conditions.

The selectivity toward caprolactam varied for the different materials, but was mostly above 65 %. The higher reactivity of the crosslinked materials was attributed to improved mass transfer and a high concentration of readily accessible catalytic sites on or close to the external surfaces of the colloidal zeolite particles.

In conclusion, crosslinking of zeolite particles has been shown in this study to be useful for the preparation of improved catalysts for Beckmann rearrangement reaction. The crosslinking procedure can be subject to further investigations. Materials, which have high micropore areas as well as high mesopore areas, could also be applied to other catalytic applications in the future.

- [11] Sato, H., Hirose, K., Kitamura, M., Nakamura, Y., 1989, Vapor Phase Beckmann Rearrangement over High-Silicious ZSM-5, *Stud.Surf.Sci.Catal.*, **49**, 1213-1222.
- [12] Mao, D., Lu, G., Chen, Q., Xia, Z., Zhang, Y., 2001, Catalytic Performance of B_2O_3/TiO_2-ZrO_2 for Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime: the Effect of Boric Loading, *Catal.Lett.*, **77**, 119-124.

REFERENCES

- [13] Ichihashi, H., Sato, H., 2001, The Development of New Heterogeneous Catalytic Processes for the Production of Epsilon-Caprolactam, *Appl.Catal. A*, **221**, 359-366.
- [1] Ågren, P., Thomson, S., Ilhan, Y., Zibrowius, B., Schmidt, W., Schüth, F., 2002, Chemical Linking of MFI Type Colloidal Zeolite Crystals, *Stud.Surf.Sci.Catal*, **142**, 159-166.
- [2] Ravishankar, R., Kirschhock, C.E.A., Schoeman, B.J., Devos, D., Grobet, P.J., Jacobs, P.A., Martens, J.A., 1999, Synthesis, Isolation and Characterization of Nano-Powder of Silicalite-1 Type Molecular Sieves, in M.M.J. Treacy Marcus, B.K., Bisher, M.E., *Proceedings of the 12th Zeolite Conference* MRS, Pennsylvania, 1825-1832.
- [16] Yashima
- [3] Mintova, S., Bein, T., 2001, Nanosized Zeolite, Films for Vapor Sensing Applications, *Micropor.Mesopor.Mat.*, **50**, 159-166.
- [4] Tsay, C.S., Chang, A.S.T., 1998, The Synthesis of Colloidal Zeolite TPA-Silicalite-1, *Micropor.Mesopor. Mat.*, **26**, 89-99.
- [18] Magnesia
- [5] Zhang, W., Han, X., Liu, X., Ba, X., 2001, The Stability of Nanosized H-ZSM-5 Zeolite; A High Resolution Solid-State NMR Study, *Micropor.Mesopor.Mat.*, **50**, 13-23.
- [19] Robinson
- [6] Schoeman, B.J., Sterte, J., Otterstedt, J.E., 1993, Synthesis and Size Tailoring of Colloidal Zeolite Particles, *J.Chem.Soc.Chem.Comm.*, **12**, 994-995.
- [20] Zhang, X., Li, L., Martín-Aranda, R., Yeung, K.L., 2004, An
- [7] Schoeman, B.J., Sterte, J., Otterstedt, J.E., 1994, Colloidal Zeolite Suspensions, *Zeolites*, **14**, 110-116.
- [26] Zhang, X., Li, L., Martín-Aranda, R., Yeung, K.L., 2004, An
- [8] Ravishankar, R., Kirschhock, C.E.A., Knops-Gerrits, P.P., Feijen, E.J.P., Grobet, P.J., Vanoppen, P., De Schroyer, F.C., Mieke, G., Fuess, H., Schoeman, B.J., Jacobs, P.A., Martens, J.A., 1999, Characterization of Nanosized Material Extracted from Clear Suspensions for MFI Zeolite Synthesis, *J.Phys.Chem.*, **103**, 4960-4964.
- [22] Dyer, A.
- [9] Knight, C.T.G., Kinrade, S.D., 2002, Comment on "Identification of precursor species in the formation of MFI zeolite in the TPAOH-TEOS- H_2O system", *J.Phys.Chem.B.*, **106**, 3329-3332.
- [24] Yashima
- [10] Kragten, D.D., Fedeyko, J.M., Sawant, K.R., Rimer, J.D., Vlachos, D.G., Lobo, R.F., Tsapatsis, M., 2003, Structure of the Silica Phase Extracted from Silica/(TPA)OH Solutions Containing Nanoparticles, *J.Phys.Chem.B.*, **107**, 10006-10016.
- [25] Kallipour

- [11] Sato, H., Hirose, K., Kitamura, M., Nakamura, Y., 1989, Vapor Phase Beckmann Rearrangement over High-Silicious ZSM-5, *Stud.Surf.Sci.Catal.*, **49**, 1213-1222.
- [12] Mao, D., Lu, G., Chen, Q., Xie, Z., Zhang, Y., 2001, Catalytic Performance of B_2O_3/TiO_2-ZrO_2 for Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime; the Effect of Boria Loading, *Catal.Lett.*, **77**, 119-124.
- [13] Ichihashi, H., Sato, H., 2001, The Development of New Heterogeneous Catalytic Processes for the Production of Epsilon-Caprolactam, *Appl.Catal. A.*, **221**, 359-366.
- [14] Kim, S.J., Kim, M.H., Ko, Y., Seo, G., Uh, Y.S., 2001, Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime over Tantalum Pillared Magadiite, *Stud.Surf.Sci.Catal.*, **135**, 23-P-18.
- [15] Ichihashi, H., 2003, Vapor Phase Beckman Rearrangement over a High Silica MFI Zeolite, *Stud.Surf.Sci.Catal.*, **145**, 73-78.
- [16] Yashima, T., Miura, K., Komatsu, T., 1994, Beckmann Rearrangement of Cyclohexanone Oxime on the External Surface of Zeolite Crystals *Stud.Surf.Sci.Catal.*, **84**, 1897-1904.
- [17] Käth, H., Gläser, R., Weitkamp, J., 2000, Beckmann Rearrangement of Cyclohexanone Oxime to Epsilon-Caprolactam on Zeolites with MFI Structure, *Chem.Ing.Tech.*, **72**, 400-403.
- [18] Magnoux, P., Misk, M., Joly, G., Jullian, S., Guisnet, M., 1997, Composition. Location, Modes of Formation and of Removal of Coke Deposited on a 5A Adsorbent, *Stud.Surf.Sci.Catal.*, **105**, 1835-1842.
- [19] Robinson, S.M., Arnold, W.D., Byers, C.H., 1994, Mass-Transfer Mechanisms for Zeolite Ion-Exchange in Waste-Water Treatment, *AIChE Journal*, **40**, 2045-2054.
- [20] Zhang, X.F., Lai, E.S.M., Martin-Aranda, R., Yeung, K.L., 2004, An Investigation of Knoevenagel Condensation Reaction in Microreactors Using a New Zeolite Catalyst, *Appl.Catal.A.*, **261**, 109-118.
- [21] Schoonover, M.W., Cohn, M.J., 2000, New Materials Discovery for Industrial Applications, *Top. Catal.*, **13**, 367-372.
- [22] Dyer, A., White, K.J., 1999, Cation Diffusion in the Natural Zeolite Clinoptilolite, *Thermochim. Acta.*, **341**, 341-348.
- [23] Lovallo, M.C., Tsapatsis, M., 1996, Preferentially Oriented Submicron Silicalite Membranes, *AIChE Journal*, **42**, 3020-3029.
- [24] Valtchev, V., Schoeman, B.J., Hedlund, J., Mintova, S., Sterte, J., 1996, Preparation and Characterization of Hollow Fibers of Silicalite-1, *Zeolites*, **17**, 408-415.
- [25] Kalipcilar, H., Gade, S.K., Noble, R.D., Falconer, J.L., 2002, Synthesis and Separation Properties of B-ZSM-5 Zeolite Membranes on Monolith Supports, *J.Membr.Sci.*, **210**, 113-127.

- [26] Yeom, Y.H., Wen, B., Sachtler, W.M.H., Weitz, E., 2004, NO_x Reduction from Diesel Emissions over a Nontransition Metal Zeolite Catalyst, A Mechanistic Study Using FTIR Spectroscopy, *J.Phys.Chem.B.*, **108**, 5386-5404.
- [27] Cho, G., Lee, J.S., Glatzhofer, D.T., Fung, B.M., Yuan, W.L., O'Rear, E.A., 1999, Ultra-Thin Zeolite Films Through Simple Self-Assembled Processes, *Adv.Mater.*, **11**, 497-499.
- [28] Holmberg, B.A., Wang, H.T., Norbeck, J.M., Yan, Y.S., 2003, Controlling Size and Yield of Zeolite Y Nanocrystals Using Tetramethylammonium Bromide, *Micropor.Mesopor.Mat.*, **59**, 13-28.
- [29] Cambor, M.A., Corma, A., Mifsud, A., Perez-Pariente, J., Valencia, S., 1997, Synthesis of Nanocrystalline Zeolite Beta in the Absence of Alkali Metal Cations, *Stud.Surf.Sci.Catal.*, **105**, 341-348.
- [30] Schoeman, B.J., Sterte, J., Otterstedt, J.E., 1994, The Synthesis of Colloidal Zeolite Hydroxysodalite Sols by Homogeneous Nucleation, *Zeolites*, **14**, 208-216.
- [31] Persson, A.E., Schoeman, B.J., Sterte, J., Otterstedt, J.E., 1994, The Synthesis of Discrete Colloidal Particles of TPA-Silicalite-1, *Zeolites*, **14**, 557-567.
- [32] Persson, A.E., Schoeman, B.J., Sterte, J., Otterstedt, J.E., 1995, Stable Suspensions of Discrete Colloidal Zeolite ZSM-5 Crystals, *Zeolites*, **15**, 611-619.
- [33] Moor, P., Beelen, P., Van Santen, R., 1997, SAXS/WAXS Study on The Formation of Precursor and Crystallization of Silicalite, *Microporous Materials*, **9**, 117-130.
- [34] Mintova, S., Olson, N.H., Valtchev, V., Bein, T., 1999, Mechanism of Zeolite a Nanocrystal Growth from Colloids at Room Temperature, *Science*, **283**, 958-960.
- [35] Mintova, S., Valtchev, V., 1999, Synthesis of Nanosized FAU-type Zeolite, *Stud.Surf.Sci.Catal.*, **125**, 141-148.
- [36] Mintova, S., Petkov, N., Karaghiosoff, K., Bein, T., 2002, Crystallization of Nanosized MEL-Type Zeolite from Colloidal Precursors, *Mater.Sci.Eng., C*, **19**, 111-114.
- [37] Mintova, S., Olson, N.H., Senker, J., Bein, T., 2002, Mechanism of the Transformation of Silica Precursor Solutions into Si-MFI Zeolite, *Angew.Chem.Int.Ed.*, **41**, 2558-2561.
- [38] Mintova, S., Valtchev, V., Bein, T., 2003, Formation of Colloidal Molecular Sieves, Influence of Silica Precursor, *Colloids Surf. A*, **217**, 153-157.
- [39] Burkett, S.L., Davis, M.E., 1994, Mechanism of Structure in the Synthesis of Si-ZSM-5, An Investigation by Intermolecular ¹H-²⁹Si CP MAS NMR, *J.Phys.Chem.*, **98**, 4647-4653.

- [40] Burkett, S.L., Davis, M.E., 1995, Mechanism of Structure in the Synthesis of Pure-Silica Zeolites; 1. Synthesis of TPA/Si-ZSM-5, *Chem. Mater.*, **7**, 920-928.
- [41] Tsay, C.S., Chang, A.S.T., 1998, The Synthesis of Colloidal Zeolite TPA-Silicalite-1, *Micropor. Mesopor. Mat.*, **26**, 89-99.
- [42] Zhang, W., Han, X., Liu, X., Ba, X., 2001, The Stability of Nanosized H-ZSM-5 Zeolite; a High Resolution Solid-State NMR Study, *Micropor. Mesopor. Mat.*, **50**, 13-23.
- [43] Kirschhock, C.E.A., Ravishankar, R., Verspeurt, F., Grobet, P.J., Jacobs, P.A., Martens, J.A., 1999, Identification of Precursor Species in the Formation of MFI Zeolite in the TPAOH-TEOS-H₂O System, *J. Phys. Chem. B.*, **103**, 4965-4971.
- [44] Kirschhock, C.E.A., Ravishankar, R., VanLooveren, L., Jacobs, P.A., Martens, J.A., 1999, Mechanism of Transformation of Precursors into Nanoslabs in the Early Stages of MFI and MEL Zeolite Formation from TPAOH-TEOS-H₂O and TBAOH-TEOS-H₂O Mixtures, *J. Phys. Chem. B.*, **103**, 4972-4978.
- [45] Kirschhock, C.E.A., Ravishankar, R., Jacobs, P.A., Martens, J.A., 1999, Aggregation Mechanism of Nanoslabs with Zeolite MFI-Type Structure, *J. Phys. Chem. B.*, **103**, 11021-11027.
- [46] Aguado, J., Serrano, D.P., Sotelo, J.L., Van Grieken, R., Escada, J.M., 2001, Influence of the Operating Variables on the Catalytic Conversion of a Polyolefin Mixture over HMCM-41 and Nanosized HZSM-5, *Ind. Eng. Chem. Res.*, **40**, 5696-5704.
- [47] Aerts, A., van Isacker, A., Huybrechts, W., Kremer, S.P.B., Kirschhock, C.E.A., Collignon, F., Houthoofd, K., Denayer, J.F.M., Baron, G.V., Marin, G.B., Jacobs, P.A., Martens, J.A., 2004, Decane Hydroconversion on Bifunctional Zeogrid and Nano-zeolite Assembled from Aluminosilicate Nanoslabs of MFI Framework Type, *Appl. Catal. A.*, **257**, 7-17.
- [48] *Chemical Week*, 23, September 8, 1999
- [49] Dahlhoff, G., Niederer, J.P.M., Hölderich, W.F., 2001, epsilon-Caprolactam: New by-product Free Synthesis Routes, *Catal. Rev.-Sci. Eng.*, **43**, 381-441.
- [50] EniChem, Sumitomo in Caprolactam Venture, 2000, *Chem. Eng. News*, October 23, 18.
- [51] Van Savage, E., Sumitomo EniChem to Build a Plant Featuring New Caprolactam Process-Brief Article, *Chemical Market Reporter*, 2000, 16,1.
- [52] Ritz, J., Fuchs, H., Kieczska, H., Moran, W.C., 2001, Caprolactam, In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th Ed., Bailey, J.E et al. Eds., VCH, Weinheim.
- [53] Weissermel, K., Arpe, H.-J., 1997, Industrial Organic Chemistry, VCH Publishers, Inc., New York.

- [54] Kob, N., Drago, R.S., 1997, Catalysis of the Formation of Epsilon-Caprolactam from Cyclohexanone Oxime by Tungsten Oxide Solid Acids, *Catal.Lett.*, **49**, 229-234.
- [55] Ushikubo, T., Wada, K., 1994, Vapor-Phase Beckmann Rearrangement over Silica-Supported Tantalum Oxide Catalysts, *J.Catal.*, **148**, 138-148.
- [56] Sharghi, H., Sarvari, M.H., 2003, Titanium oxide (TiO₂) Catalysed one-Step Beckmann Rearrangement of Aldehydes and Ketones in Solvent Free Conditions, *J.Chem.Res.*, **3**, 176-178.
- [57] Albers, P., Seibold, K., Haas, T., Prescher, G., Hölderich, W.F., 2003, SIMS/XPS Study on the Deactivation and Reactivation of B-MFI Catalysts Used in the Vapour-Phase Beckmann Rearrangement, *J.Catal.*, **176**, 561-568.
- [58] Dahlhoff, G., Eickelberg, W., Hölderich, W.F., 2001, Recent Developments in the Catalyst Regeneration for the Beckmann Rearrangement of Cyclohexanone Oxime to epsilon-Caprolactam, *Stud.Surf.Sci.Catal.*, **139**, 335-342.
- [59] Ichihashi, H., Kitamura, M., 2002, Some Aspects of the Vapor Phase Beckmann Rearrangement for the Production of epsilon-Caprolactam over High Silica MFI Zeolites, *Catal.Today*, **73**, 23-28.
- [60] Corma, A., Garcia, H., Primo, J., Sastre, E., 1991, Beckmann Rearrangement of Cyclohexanone Oxime on Zeolites, *Zeolites*, **11**, 593-597.
- [61] Heitmann, G.P., Dahlhoff, G., Hölderich, W.F., 1999, Catalytically Active Sites for the Beckmann Rearrangement of Cyclohexanone Oxime to epsilon-Caprolactam, *J.Catal.*, **186**, 12-19.
- [62] Heitmann, G.P., Dahlhoff, G., Niederer, J.P.M., Hölderich, W.F., 2000, Active Sites of a [B]-ZSM-5 Zeolite Catalyst for the Beckmann Rearrangement of Cyclohexanone Oxime to Caprolactam, *J. Catal.*, **194**, 122-129.
- [63] O'Sullivan, P., Forni, L., Hodnett, B.K., 2001, The Role of Acid Site Strength in the Beckmann Rearrangement, *Ind.Eng.Chem.Res.*, **40**, 1471-1475.
- [64] Dai, L.X., Koyama, K., Miyamoto, M., Tatsumi, T., 1999, Highly Selective Vapor Phase Beckmann Rearrangement over H-USY Zeolites, *Appl.Catal. A.*, **189**, 237-242.
- [65] Ouyang, K.H., Chen, C.W., Ko, A.N., 2001, Synthesis of epsilon-Caprolactam from Cyclohexanone Oxime Using Zeolites H beta, HZSM-5, and Alumina Pillared Montmorillonite, *J.Chin.Chem.Soc.*, **48**, 137-144.
- [66] Takahashi, T., Nasution, M.N.A., Kai, T., 2001, Effects of Acid Strength and Micro Pore Size on Epsilon-Caprolactam Selectivity and Catalyst Deactivation in Vapor Phase Beckmann Rearrangement over Acid Solid Catalysts, *Appl.Catal. A.*, **210**, 339-344.

- [67] Takahashi, T., Kai, T., Nasution, M.N.A., 1995, Catalyst Deactivation of High Silica Metallosilicates in Beckmann Rearrangement of Cyclohexanone Oxime, *Stud.Surf.Sci.Catal.*, **97**, 431-436.
- [68] Takahashi, T., Nishi, M., Tagawa, Y., Kai, T., 1995, Catalyst Deactivation of High-Silica HZSM-5 in the Beckmann Rearrangement Reaction of Cyclohexanone Oxime, *Micropor.Mesopor.Mat.*, **3**, 467-471.
- [69] Dai, L.X., Iwaki, Y., Koyama, K., Tatsumi, T., 1997, Development of Advanced Zeolite Catalysts for the Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime, *Appl.Surf.Sci.*, **121**, 335-338.
- [70] Komatsu, T., Maeda, T., Yashima, T., 2000, Kinetic study on the Effect of Solvent in 'Vapor-Phase' Beckmann Rearrangement of Cyclohexanone Oxime on Silicalite-1, *Micropor.Mesopor.Mat.*, **35**, 173-180.
- [71] Yashima, T., Oka, N., Komatsu, T., 1997, Vapor phase Beckmann Rearrangement of Cyclohexanone Oxime on the Zeolite Catalysts, *Catal.Today.*, **38**, 249-253.
- [72] Kim, M.H., Ko, Y., Kim, S.J., Uh, Y.S., 2001, Vapor Phase Beckmann Rearrangement of Cyclohexanone Oxime over Metal Pillared Ilerite, *Appl.Catal.A.*, **210**, 345-353.
- [73] Hölderich, W.F., Röseler, J., Heitmann, G., Liebens, A.T., 1997, The Use of Zeolites in the Synthesis of Fine and Intermediate Chemicals, *Catal.Today.*, **37**, 353-366.
- [74] Cambor, M.A., Corma, A., Garcia, H., Semmer-Herledan, V., Valencia, S., 1998, Active Sites for the Liquid-Phase Beckmann Rearrangement of Cyclohexanone. Acetophenone and Cyclododecanone Oximes, Catalyzed by Beta Zeolites, *J.Catal.*, **177**, 267-272.
- [75] Barrett, E.P., Joyner, L.G., Halenda, P.P., 1951, The Determination of Pore Volume and Area Distributions in Porous Substances I, Computations from Nitrogen Isotherms, *J.Am.Chem.Soc.*, **73**, 373-380.
- [76] Sing, K.S.W., Everett, D.H., Moscou, L., Pierrotti, R.A., Roquerol, J., Siemieniwska, T., 1985, IUPAC Recommendations, *Pure Appl. Chem.*, **57**, 603-619.
- [77] Rouquerol, F., Rouquerol, J., Sing, K., 1999, Adsorption by Powders and Porous Solids; Principles, Methodology and Applications, Academic Press, San Diego.
- [78] De Boer, L.P., Van Der. Zondervan, G.J., 1965, Studies on Pore Systems in Catalysts, VII. Description of the Pore Dimensions of Carbon Blacks by the T Method, *J.Catal.*, **4**, 649-653.
- [79] Crawford, S.M.N., Houston, J.R., 2003, ²⁹Si MAS NMR and XRD Studies of Solid State Cation Migration through Zeolite Materials, *Abstract of Papers - American Chemical Society*, **225**, 414-422.

- [80] Fejes, P., Lazar, K., Marsi, I., Rockenbauer, A., Korecz, L., Nagy, J.B., Perathoner, S., Centi, G., 2003, Isomorphously Substituted Fe-ZSM-5 Zeolites as Catalysts Causes of Catalyst Ageing as Revealed by X-band EPR, Mossbauer and ^{29}Si MAS NMR spectra, *Appl.Catal.A.*, **252**, 75-90.
- [81] Engelhardt, G., Michel, D., 1987, High Resolution Solid State NMR of Silicates and Zeolites, Wiley, Chichester.
- [82] Vayssilov, G.H., 1997, Structural and Physicochemical Features of Titanium Silicalites, *Catal.Rev. -Sci.Eng.*, **39**, 209-251.
- [83] Kawai, T., Tsutsumi, K., 1998, Evaluation of the Secondary Pore Structure of Hydrothermally- and Acid-Treated Faujasite Type Zeolites, *Adsorption*, **4**, 225-231.
- [84] Kawai, T., Tsutsumi, K., 1999, A Study on the Surface Silanol Groups Developed by Hydrothermal and Acid Treatment of Faujasite Type Zeolites, *J. Colloid.Interface Sci.*, **212**, 310-316.
- [85] Kruppa, T.M., *PhD Thesis in prep.*, Bochum University, Bochum, Germany
- [86] Kruppa, T.M., 2003, Gas Phase Epoxidation of Propene with Hydrogen Peroxide. *Europa Cat-VI, The European Catalysis Forum*, Innsbruck, Austria, August 31- September 04.
- [87] Li, Q.H., Mihailova, B., Creaser, D., Sterte, J., 2001, Aging Effects on the Nucleation and Crystallization Kinetics of Colloidal TPA-Silicalite-I, *Micropor.Mesopor.Mat.*, **43**, 51-59.
- [88] Schmidt, W., personal communication.
- [89] Reding, G., Maurer, T., Kraushaar-Czarnetzki, B., 2003, Comparing Synthesis Routes to Nano-Crystalline Zeolite ZSM-5, *Micropor.Mesopor.Mat.*, **57**, 83-92.
- [90] Li, Q.H., Creaser, D., Sterte, J., 2002, An Investigation of the Nucleation/Crystallization Kinetics of Nanosized Colloidal Faujasite Zeolites, *Chem.Mater.*, **14**, 1319-1324.
- [91] Bell, A.T., 1999, NMR Applied to Zeolite Synthesis, *Colloids.Surf. A.*, **158**, 221-234.
- [92] Clerici, M.G., Bellussi, G., Romano, U., 1991, Synthesis of propylene oxide from propylene and hydrogen peroxide catalyzed by titanium silicalite, *J.Catal.*, **129**, 159-167

RESUME

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