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Active sites on SBA-15 in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam

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Abstract

Modified SBA-15 materials were studied as catalysts in the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. Their combined micropore and mesopore system allows the investigation of the influence of pore dimensions, acid site concentration and strength, and location on the catalytic activity. A treatment utilizing H_2SO_4 allows to study the contribution of silanol groups as potential catalytically active sites in mesopores and micropores independent of one another. Applying ^{29}Si solid-state NMR and DRIFTS experiments using a probe molecule, surface and in-wall silanol groups can be discriminated and quantified, making analysis correlating location, acidity, and catalytic activity possible. Combining all results leads to conclusions concerning the location of the catalytic reaction, the nature of the catalytic active sites, and their properties, which provides a basis for a rational optimization of catalysts.

Keywords: SBA-15; Catalysis; Beckmann rearrangement; Silanol group; DRIFT

1. Introduction

The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam is an important process step in the production of polyamide 6, better known under the trade name nylon. On an industrial scale, the reaction is carried out mainly in liquid phase, catalyzed by stoichiometric amounts of concentrated sulfuric acid and oleum. Besides the significant corrosion potential, the main drawback of the liquid-phase reaction results from neutralization of the sulfuric acid with ammonia, leading to ammonium sulfate as a byproduct in amounts as high as 1.9 tons per ton of product [1] over the whole process. Obviously, there is a strong driving force for the development of alternative routes, aiming at more economic and environmentally friendly processes. Consequently, gas-phase reactions using solid acid catalysts have been investigated. Early studies showed such diverse materials as tungsten oxide [2], tantalum oxide [3], titanium oxide [4], and boron-alumina [4] to be active for the reaction, but also revealed rapid deactivation. More recent studies have focused mainly on zeolites as solid acid catalysts in the Beckmann rearrangement and on the influence of their acid strength as well as the optimization of reaction conditions, including solvents, temperature, and pressure.

Although zeolite structure and composition can be controlled over a very wide range, no agreement has been reached with respect to the location of the catalytically active sites. Sato et al. [5] observed a connection between external surface area and catalytic activity along with evidence for a reaction occurring mainly on the outer surface. Camblor et al. [6] found internal silanols of Beta zeolites to be more active in the liquid-phase reaction. Variation of the crystal size by the group of Hölderich et al. [7,8] confirmed increasing activity with decreasing crystal size, with decreasing crystal size in concert with increasing external surface area. Weitkamp et al. [1] proved that the diffusion of cyclohexanone oxime as well as ε-caprolactam in the pore system of an MFI-type zeolite is possible, and Yashima et al. [9] found the selectivity to ε-caprolactam to be dependent on the pore size of zeolites. Nevertheless, the location of

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the catalytically active sites remains a matter of debate, even though substantial evidence points toward a reaction occurring on or close to the external surface [5]. In an earlier study, we investigated colloidal Silicalite-1 crystals [10] with a maximum external surface area. To maintain the high surface area [11] and avoid agglomeration, a cross-linking procedure has been applied, using a silicone linker as spacer to connect the colloidal crystals to form a network. The strong correlation between catalytic activity and mesoporosity induced us to further investigate the location of the catalytically active sites using a different silica material with combined micropore and mesopore system and a somewhat regular but not crystalline structure. Thus, we studied SBA-15, an ordered mesoporous silica material with combined micropore and mesopore system. In one earlier study [12], SBA-15 was used in this reaction in liquid phase in comparison with a number of other, more acidic catalysts; however, the activity observed for SBA-15 in that work was comparably low.

The mesopores in SBA-15, each surrounded by a corona of micropores, are arranged in a two-dimensional hexagonal structure. In contrast to zeolite materials, SBA-15 has amorphous pore walls. The aging temperatures allow control over mesopore size and micropore volume. We investigated two different aging temperatures and applied a method for stepwise template removal, recently reported by Yang et al. [13,14]. Applying this method, the catalytic activity of silanol groups in the micropores and mesopores can be studied independently of one another. Therefore, the template is first removed exclusively from the mesopores via ether cleavage using sulfuric acid. Subsequently, the mesopore surface can be hydrophobized using a trimethylsilylation agent, which reacts with the catalytically active silanol groups, followed by low-temperature calcination to remove the template from the micropore region (Fig. 1). ^{29}Si solid-state NMR spectroscopy of the different pretreated SBA-15 materials allows quantification of the silanol concentration. Discrimination of surface and in-wall silanol groups (those occluded in the walls), as well as silanols on the micropore or mesopore surface, becomes possible. These investigations allowed us to draw further conclusions on the dependence of the location of the active sites on the resulting catalytic activity in the Beckmann rearrangement reaction. Additional studies using IR spectroscopy with adsorbed probe molecules were aimed at understanding the requirements with respect to acidity of active sites. Applying DRIFTS experiments with toluene as the probe molecule, we were able to determine differences in the acid strength of silanols depending on their location. Combining the results of these studies gives a deeper understanding of the structural needs, which may allow optimization of catalyst materials for the Beckmann rearrangement of cyclohexanone oxime, in terms of ideal pore structure and nature of the acid sites.

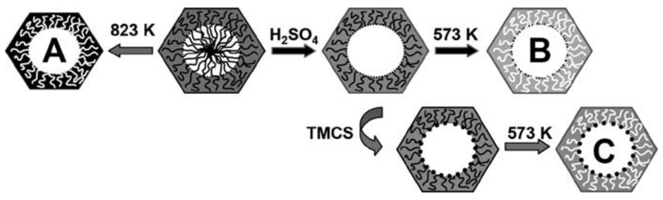

Fig. 1. Template removal and surface modification scheme of SBA-15: (A) calc. 823 K, (B) H_2SO_4-treated, calc. 573 K, (C) H_2SO_4-treated, trimethylsilylated mesopores, calc. 573 K.

2. Experimental

The procedure for synthesizing ordered mesoporous silica (SBA-15) followed the method described by Ryoo et al. [15]. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($EO_{20}PO_{70}EO_{20}$) copolymer Pluronic P123 was used as the structure-directing agent. To prepare the synthesis solution with a molar composition of $0.16P123{:}9.54SiO_2{:}950H_2O{:}5.12$ HCl, the template was dissolved in water and HCl was added. The mixture was heated to 308 K, followed by addition of TEOS under vigorous stirring. After stirring for 24 h at 308 K, the synthesis solution was aged for another 24 h at 333 or 373 K, respectively. The precipitate was filtered and dried without washing at 363 K for 24 h. Template removal was facilitated using ethanol extraction; therefore, 10 g of the sample was suspended in 500 ml of EtOH containing 0.01 mol HCl. After being stirred for 30 min, filtered, and washed with acetone, the sample was dried again at 363 K for 24 h. For cleaving the template to generate exclusively mesopores, 10 g of solid was mixed with 600 g 48% H_2SO_4 solution and refluxed at 368 K for 18 h. The mixture was cooled, decanted twice, and filtered. The solid was washed with water until the eluent was neutral, then washed with acetone and dried at 363 K for 24 h. Opening of the micropores could be accomplished by heating the acid-treated sample to 573 K in air for 3 h at a heating rate of 2 K/min [13,14]. Samples with hydrophobized mesopore surface were prepared using the acid-treated sample, in which the micropores were still blocked. The sample was reacted with trimethylchlorosilane (TMCS) to functionalize the accessible mesopore surface. To achieve this, 1.5 g of the acid-treated sample was stirred in 100 ml of toluene for 30 min, after which 8 ml of TMCS was added. After stirring for another 24 h, the sample was filtered, washed, and calcined at 573 K to remove the template from the micropores as described above. For comparison, as-synthesized material was calcined at 823 K. The sample was calcined in two steps, first for 3 h at 453 K using a heating rate of 5 K/min to dry the material, followed by heating at a rate of 1 K/min to 823 K for 6 h. To distinguish surface silanol groups from those hidden in the walls, SBA-15 aged at 333 and 373 K, calcined at 823 K or acid-treated and low-temperature-calcined, was fully hydrophobized, as shown in Fig. 2. To achieve this, 1 g of each sample, degassed overnight at 473 K, was stirred in 30 ml of toluene for 15 min, followed by addition of 3 ml trimethylsilylimidazole (TMSI) in which the imidazole, as a better leaving group, enhances surface coverage [16]. Cross-checking with samples hydrophobized with TMCS instead revealed insignificantly increased catalytic activity—$<10\%$ higher—compared with samples hydrophobized with TMSI. After stirring for 24 h at 273 K under reflux, the samples were filtered, washed with pentane, and dried at 363 K overnight. To ensure a complete reaction, this procedure was performed twice.

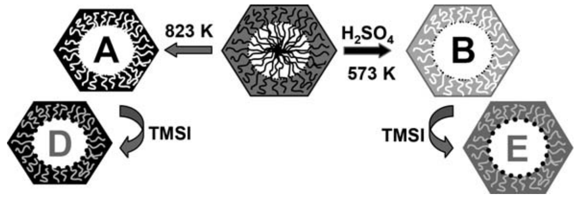

Fig. 2. Surface hydrophobization of micropores and mesopores using TMSI: (D) for silica calcined before at 823 K and (E) for acid-treated and 573 K calcined samples.

2.1. *Vapor-phase Beckmann rearrangement reaction*

The Beckmann rearrangement reaction of cyclohexanone oxime to ε-caprolactam was carried out as a vapor-phase reaction using a continuous-flow reactor at atmospheric pressure and 553 K. A 200-mg catalyst sample, pelletized and ground to a particle size fraction of 250–500 µm, together with 2 g of quartz sand, were packed as a catalyst bed. Before the catalytic activity was measured, the samples were activated overnight in the reactor under air flow at 573 K. Before the reaction, the gas flow was switched to nitrogen as the carrier gas, and the reactor was cooled to 553 K. Cyclohexanone oxime dissolved in toluene (to give a molar ratio of 26.5) was fed to the reactor using a HPLC pump. Adjusting the vapor pressure of cyclohexanone oxime to 2.2 kPa, a WHSV of 1.95 $g_{oxime}\,g_{cat}^{-1}\,h^{-1}$ was reached. The effluent was condensed, and three fractions of 5 min each were collected after 1 h (55, 60, 65 min) and after 4 h (275, 280, 285 min) to determine catalytic activity. (If not stated otherwise, the catalytic activities reported herein refer to 1 h on stream.) The catalytic activity and selectivity of all samples were determined by analyzing the condensate by gas chromatography using a flame ionization detector (Agilent Technology 6890N).

3. Characterization

SBA-15 was characterized using nitrogen sorption isotherms recorded with a Quantachrome Nova 3200E instrument. Before the measurements, all samples were pretreated overnight at 473 K under vacuum. Surface areas, pore volumes, and pore dimensions were determined with the NLDFT equilibrium model (N_2 at 77 K on silica) implemented in the NovaWin software package (Quantachrome Instruments). ^{29}Si MAS NMR measurements were carried out on a Bruker Avance 500WB spectrometer with a spinning rate of 10 kHz. Molar fractions of Q^2-, Q^3-, Q^4-, and M-groups were determined from ^{29}Si MAS NMR Spectra. Silanol concentrations were calculated by dividing the molar fraction of the respective silicon species by the molar weight of the sample (determined as sum of molar weights and fractions of the different silicon species). Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Nicolet Magna 500 using a high-temperature reaction cell (Harrick). Samples were pretreated overnight in the reaction cell at 473 K under nitrogen flow. Reference spectra were recorded at room temperature under nitrogen flow with 5000 scans. To study the interaction with toluene, toluene was evaporated and passed over the sample with nitrogen as the carrier gas. The spectra were recorded after 4 h of equilibration and recalculated using the Kubelka–Munk equation.

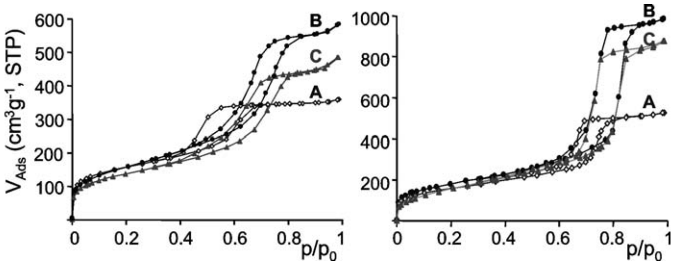

Fig. 3. N_2 sorption isotherms of SBA-15 aged at 333 K (left) or 373 K (right): (A) calc. 823 K, (B) H_2SO_4-treated, calc. 573 K, (C) H_2SO_4-treated, trimethylsilylated mesopores, calc. 573 K.

Table 1
Surface areas, pore volumes and pore dimensions of SBA-15 calcined at 823 K (A) or acid-treated and calcined at 573 K (B)

	Specific surface area (m^2/g)	Mesopore diameter (nm)	Pore volume (cm^3/g)
	SBA-15 aged at 333 K		
Calc. 823 K (A)	504.2	6.1	0.53
H_2SO_4, calc. 573 K (B)	673.4	7.0	0.93
	SBA-15 aged at 373 K		
Calc. 823 K (A)	563.7	8.2	0.90
H_2SO_4, calc. 573 K (B)	692.4	9.4	1.47

4. Results and discussion

Nitrogen sorption isotherms in Fig. 3 show that SBA-15 aged at 333 K exhibited higher micropore volumes, while the samples aged at 373 K had larger mesopore areas and larger pore dimensions. SBA-15 calcined at 823 K (A) exhibits a small hysteresis shifted to the left, indicating that shrinkage of the structure occurs during the thermal treatment and that the mesopore volume is decreased. Sulfuric acid-treated and low-temperature-calcined samples (B) show high nitrogen uptake in the mesopore region together with larger mesopore diameters, which can be attributed to the higher degree of condensation achieved during the acid treatment, thus avoiding further shrinkage of the structure. In addition, the low-temperature calcination helps maintain the pore system. Table 1 summarizes the textural data for the various pretreated SBA-15 materials. The isotherms of samples with trimethylsilylated mesopore surface (C) retain the sharp hysteresis at high relative pressure and high nitrogen uptake, confirming the absence of pore-blocking effects.

The ^{29}Si MAS NMR spectrum of SBA-15 calcined at 823 K (A) exhibits a broad resonance over the whole range for Q^2, Q^3, and Q^4 silicon atoms (Fig. 4). Sulfuric acid-treated and low-temperature-calcined samples (B) show three distinguishable resonances at −88, −98, and −109 ppm, with the greatest intensity for Q^3 and Q^4 silicon atoms. Hydrophobization (C) results in an additional resonance at −18 ppm, which can be assigned to the silicon atom from TMCS. Together with this resonance arising, the intensities for Q^2 and Q^3 groups decrease as the surface reaction with TMCS, consuming silanols, proceeds. Nonetheless, a fraction of remaining Q^2 and Q^3 groups cannot be avoided, even in the case of trimethylsilylation of the whole surface, including micropores and mesopores. These remaining silanol groups are either located inside the pore walls and hence are inaccessible for any reaction or located on the surface, where steric constraints hinder their consumption. ^{29}Si NMR spectroscopy allows quantification of the number of silanol groups, which are most probably the catalytically active sites [17]. However, quantification of Q^2, Q^3, and Q^4 takes all silicon atoms into consideration, regardless of their location on the micropore and mesopore surface or their incorporation in the pore walls. To refer catalytic activity to the silanol concentration, discrimination between surface and in-wall silanols is necessary, because only surface silanols can act as active sites. Investigation of SBA-15 with trimethylsilylated mesopore surface gives access to the silanol concentration on the micropore surface together with those hidden in the walls. ^{29}Si NMR of SBA-15 with a fully trimethylsilylated surface gives information about the number of silanols incorporated in the pore walls (assuming the absence of nonreacting sites due to steric constraints). This has to be done for each sample separately (Fig. 5), because different aging temperatures and either calcination at 823 K or acid treatment and low-temperature calcination yield materials that differ greatly in terms of wall thickness, surface area, and degree of condensation. The determination of surface silanols becomes possible by correlation of each sample with its corresponding hydrophobized form (Table 2), resulting in four hydrophobized reference samples, SBA-15 aged at 333 K and 373 K, either calcined at 823 K (D) or acid-treated and low-temperature-calcined (E).

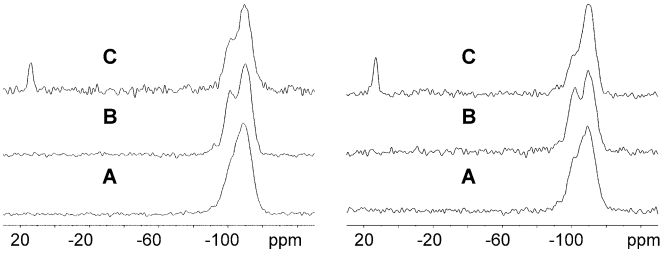

Fig. 4. ^{29}Si MAS NMR of SBA-15 aged at 333 K (left) and 373 K (right): (A) calc. 823 K, (B) H_2SO_4-treated, calc. 573 K, (C) H_2SO_4-treated, trimethylsilylated mesopores, calc. 573 K.

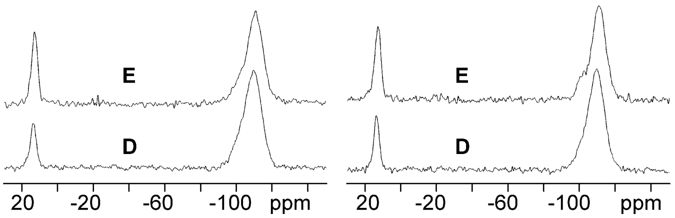

Fig. 5. ^{29}Si MAS NMR of SBA-15 aged at 333 K (left) and 373 K (right): (D) calc. 823 K, fully trimethylsilylated surface, (E) H_2SO_4-treated, calc. 573 K, fully trimethylsilylated surface.

SBA-15 was tested in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. The results are presented in Fig. 6. Samples aged at 333 or 373 K, respectively, show comparable productivity, indicating a minor influence of aging temperature. The productivity of sulfuric acid-treated and low-temperature-calcined samples (B) is superior to that of the samples calcined at 823 K (A). Interestingly, the activity of SBA-15 materials reaches values similar to the highest ones measured for cross-linked Silicalite-1 [10], for which up to 3.5 $\mathrm{mmol_{capr}\,g_{cat}^{-1}\,h^{-1}}$ could be reached. Consequently, the high activity of SBA-15 materials emphasizes that crystallinity of the silica structure is no prerequisite for high activity in Beck-

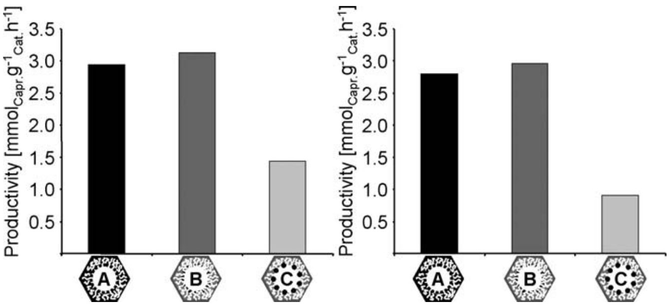

Fig. 6. Catalytic activity of SBA-15 aged at 333 K (left) and 373 K (right): (A) calc. 823 K, (B) H_2SO_4-treated, calc. 573 K, (C) H_2SO_4-treated, trimethylsilylated mesopores, calc. 573 K.

Table 2
Total and surface silanol concentration in different pretreated SBA-15 materials

	Q^2 (%)	Q^3 (%)	Q^4 (%)	M (%)	Total silanol (mmol/g)	Surface silanols (mmol/g)[a]	Silanol number (1/nm^2)
			SBA-15 aged at 333 K				
Calc. 823 K (A)	4	29	67		5.8	2.8	3.29
H_2SO_4, calc. 573 K (B)	4	35	61		6.7	4.0	3.58
H_2SO_4, TMCS, 573 K (C)	3	32	65	8	5.6	2.8	
Calc. 873 K, TMSI (D)	2	19	79	16	3.1		
H_2SO_4, calc. 573 K, TMSI (E)	3	18	79	26	2.7		
			SBA-15 aged at 373 K				
Calc. 873 K (A)	5	32	63		6.6	3.7	3.92
H_2SO_4, calc. 573 K (B)	5	38	57		7.5	5.4	4.66
H_2SO_4, TMCS, 573 K (C)	5	25	70	11	4.6	2.5	
Calc. 823 K, TMSI (D)	2	18	80	19	2.9		
H_2SO_4, calc. 573 K, TMSI (E)	1	16	83	32	2.1		

[a] Although trimethylsilylation of the surface aims at a complete consumption of all surface silanols, a small fraction of silanol groups may still be present on the surface due to steric hindrance, but was neglected for the calculations of the surface silanol concentration.

Table 3
Catalytic activity after 1 h on stream (a) related to the catalyst weight and (b) normalized to surface silanols determined from ^{29}Si NMR

	Productivity ($\text{mmol}_{\text{capr}}\ \text{g}_{\text{cat}}^{-1}\ \text{h}^{-1}$)	Productivity ($\text{mol}_{\text{capr}}\ \text{mol}_{\text{Si–OH}}^{-1}\ \text{h}^{-1}$)
	SBA-15 aged at 333 K	
Calc. 823 K (A)	2.94	1.07
H_2SO_4, calc. 573 K (B)	3.13	0.78
H_2SO_4, TMCS, 573 K (C)	1.44	0.51
Calc. 823 K, TMSI (D)	0.50	
H_2SO_4, 573 K, TMSI (E)	0.38	
	SBA-15 aged at 373 K	
Calc. 823 K (A)	2.80	0.76
H_2SO_4, calc. 573 K (B)	2.96	0.55
H_2SO_4, TMCS, 573 K (C)	0.91	0.36
Calc. 823 K, TMSI (D)	0.39	
H_2SO_4, 573 K, TMSI (E)	0.27	

mann rearrangement. Samples with hydrophobized mesopore surface (C) have significantly lower productivity, corresponding to their lower surface silanol concentration. Nonetheless, the residual activity of SBA-15 with hydrophobized mesopore surface in the reaction indicates that the catalytic reaction takes place on both micropore and mesopore surfaces.

Combining measured productivities of the SBA-15 samples with the number of surface silanol groups from ^{29}Si NMR measurements, it becomes possible to determine the intrinsic productivity of the surface silanols (Table 3). High-temperature-calcined (A) on the one hand, and acid-treated, low-temperature-calcined samples (B) on the other hand show high intrinsic activities per silanol. The treatment at higher temperature leads to silanol condensation and thus a reduced number of silanol groups. The remaining silanol groups, however, have superior activity, indicating that other properties besides silanol concentration are crucial for high activity. Samples with trimethylsilylated mesopore surface (C) exhibit lower intrinsic activities. Because the modification leads predominately to reaction of mesopore silanols, the intrinsic activity thus determined is strongly related to micropore silanols. Consequently, the greatest contribution to catalytic activity seems to come from mesopore silanols. Other factors may influence the observed productivities as well, including mass transfer limitations for the reaction in the micropores and lower reagent concentrations in the trimethylsilylated and thus the hydrophobic pore system. Nonetheless, the location of the silanol groups seems to have an impact on the measured productivity. Alternatively, the reactivity in the micropores may be altered by different constrains on the educt molecule and/or the transition state in the micropore compared with the mesopore.

Another factor assumed to have an influence on the activity of the silanol groups is their acidity. Condensation by calcination at 823 K will not necessarily result in the same surface reactions as acid treatment and low-temperature calcination. Hence, the remaining silanol groups may have different chemical and geometrical environments. This could result in different acid strength, which in turn would influence their activity in the Beckmann rearrangement. Some studies indicate an optimum acidity to reach a high intrinsic activity [18]; that is, sites should not be too weak but also not too strong. We performed DRIFTS measurements to assess the acidity of the silanol groups of the different samples. Direct observation of the OH-stretching vibrations and correlation of the position of the absorption band with acidity is known to possibly lead to erroneous results, and thus we studied the interaction with weakly basic probe molecules. The shift of the silanol band position after adsorption of the probe molecule is a good measure of the acidity of the groups [19]. The most commonly used probe molecule for investigating acidity, pyridine, is a too strong a base, so full proton transfer occurs and no shift in the OH band position can be observed. Hydrocarbons, on the other hand, are rather weak bases and hence are more suitable for the study of shifts in the OH-stretching bands. Consequently, we used toluene as the acidity probe. The interaction of SBA-15 with toluene results for both the high-temperature (A) and the acid-treated and low-temperature-calcined samples (B), in a shift of 138 cm^{-1} to lower frequencies, if the parent material had been synthesized at 333 K (Fig. 7). For the parent sample aged at 373 K that was then acid-treated and low-temperature-calcined (B), the shift was just slightly lower with 134 cm^{-1}. In contrast, the samples with hydrophobized mesopore surface (C) exhibit a lower shift of 120 cm^{-1} for SBA-15 aged at 333 K and of only 91 cm^{-1} for SBA-15 aged at 373 K. Comparing these results with the measured intrinsic activity based on the number of surface silanol groups (Table 4), it becomes obvious that catalytic activity and acid strength are in good agreement. Samples revealing the maximum shift were also found to exhibit superior intrinsic activity. Therefore, not only the location, but also the acidity of the silanol groups seem to be crucial for the catalytic activity, and the interplay between both factors will determine the overall performance of ordered mesoporous silica in the Beckmann rearrangement. However, the silanols with the lower acidity are located predominantly in the micropores, so that these two factors are correlated.

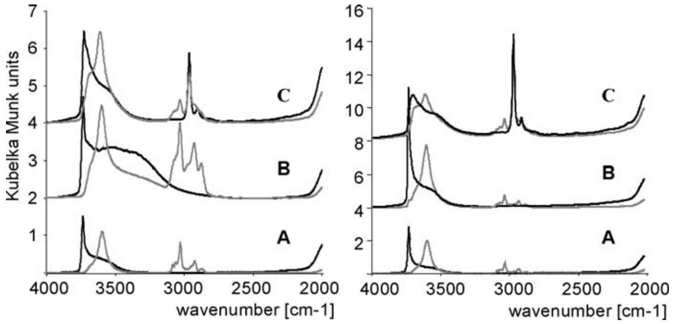

Fig. 7. DRIFT spectra of SBA-15 aged at 333 K (left) and 373 K (right), before (black) and after (grey) probing with toluene: (A) calc. 823 K, (B) H_2SO_4-treated, calc. 573 K (left: offset 2 KM units, right: 4 KM units), (C) H_2SO_4-treated, trimethylsilylated mesopores, calc. 573 K (left: offset 4 KM units and right: 8 KM units).

SBA-15 with fully trimethylsilylated surface (D, E) shows no shift or a very small shift of the silanol frequency when toluene is adsorbed, which is in line with the notion that all accessible silanol groups are capped, and only those buried in the walls remain. Catalytic activity does not completely drop to zero but does drop to low values (Table 3). This residual

Table 4
Intrinsic catalytic activity and shift of the silanol signal using toluene as probe molecule in DRIFT measurements

	Productivity × 10^1 ($\text{mol}_{\text{capr}}\,\text{mol}^{-1}_{\text{Si–OH}}\,\text{h}^{-1}$)	DRIFT shift (cm^{-1})
SBA-15 aged at 333 K		
Calc. 823 K (A)	10.70	138
H_2SO_4, calc. 573 K (B)	7.81	138
H_2SO_4, TMCS, 573 K (C)	5.09	120
SBA-15 aged at 373 K		
Calc. 823 K (A)	7.63	138
H_2SO_4, calc. 573 K (B)	5.52	134
H_2SO_4, TMCS, 573 K (C)	3.60	91

activity may be due to small amounts of surface silanols remaining intact, the concentration of which could be too low for detection with adsorbed toluene, or due to newly created surface silanols resulting from material defects. Interestingly, the selectivity over these samples increases to 70% for samples calcined at 823 K before the TMSI treatment (D), whereas the samples acid-treated and low-temperature-calcined before TMSI treatment (E) show selectivities reaching 90%. Furthermore, no deactivation of this residual activity was observed over 4 h. All other samples show pronounced deactivation of about 50% over this time. The reason for this behavior remains unclear.

5. Conclusion

SBA-15, a material with combined micropore and mesopore system but amorphous silica walls, was investigated as catalyst in the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. The material was pretreated to vary the silanol concentration and to cover silanols on the mesopore surface selectively, thus allowing independent investigation of catalytic activity in micropores and in mesopores. For all pretreatment conditions, high catalytic activity can be measured in the Beckmann rearrangement. The activity is very similar to that observed for the most active cross-linked, nanoparticulate zeolite samples studied earlier [9], proving that crystallinity of a silica is no prerequisite for high activity in this reaction. Acid-treated, low-temperature-calcined SBA-15 samples (B) exhibit the highest activities, corresponding to the very high total silanol concentration, whereas calcination at 823 K (A) leads to lower activity that can be attributed to fewer silanol groups in the samples. However, normalized to surface silanol concentration, the calcined samples show superior activity. Materials with trimethylsilylated mesopore surface (C) still exhibit catalytic activity, albeit at a lower level, emphasizing that both micropores and mesopores are involved in the catalysis. Correlation of catalytic activity and surface silanol concentration allows calculation of the intrinsic activity of the silanol groups. The results suggest that the contribution from acid sites in the mesopores to the catalytic activity is higher than that of the silanols in the micropores. Along with surface silanol concentration, catalytic activity is altered by the acidity of the silanol groups. DRIFTS analysis using toluene as the probe molecule gave evidence of a lower acid strength of the silanols in the micropores. Thus one may conclude that the medium acidity of silanols located in the mesopores is advantageous for the reaction studied. The location of the silanol groups in mesostructured SBA-15 silica thus influences its acid strength and, correspondingly, its reactivity in acid catalyzed reactions. This is an example of different chemical environments spatially separated on the nanometer length scale, which can and will be addressed by specific modification of parts of the surface.

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