Identify Vicinal Silanols and Promote Their Formation on MCM-41 via Ultrasonic Assisted One-Step Room-Temperature Synthesis for Beckmann Rearrangement

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ABSTRACT Siliceous mesoporous MCM-41 materials were synthesized under ultrasonic treatment from 0.5 h to 3 h. The obtained U-[Si]MCM-41 catalysts were applied in the Beckmann rearrangement of cyclohexanone oxime (CHO) to *ε*-caprolactam (CPL). The ultrasonic treatment can increase of the pore wall thickness, while the density of surface SiOH groups increased slightly. Quantitative ^{1}H MAS NMR studies of the U-[Si]MCM-41 catalysts hint the presence of isolated and vicinal silanols. After dehydration at 393 K, ^{1}H MAS NMR signals of poly-hydrogen-bonded vicinal silanols occurred, which are strongly reduced after dehydration at 473 K. Correspondingly, a much higher conversion of CHO to CPL was observed for U-[Si]MCM-41 dehydrated at 393 K in comparison with those dehydrated at 473 K. This finding indicates poly-hydrogen-bonded SiOH groups can promote the reaction, and improve the catalytic performance of siliceous catalytic materials in the Beckmann rearrangement of CHO in an energy economic way at suitable activation temperature.

KEYWORDS mesoporous MCM-41; ultrasonic treatment; Beckmann rearrangement; surface sites; solid-state NMR spectroscopy.

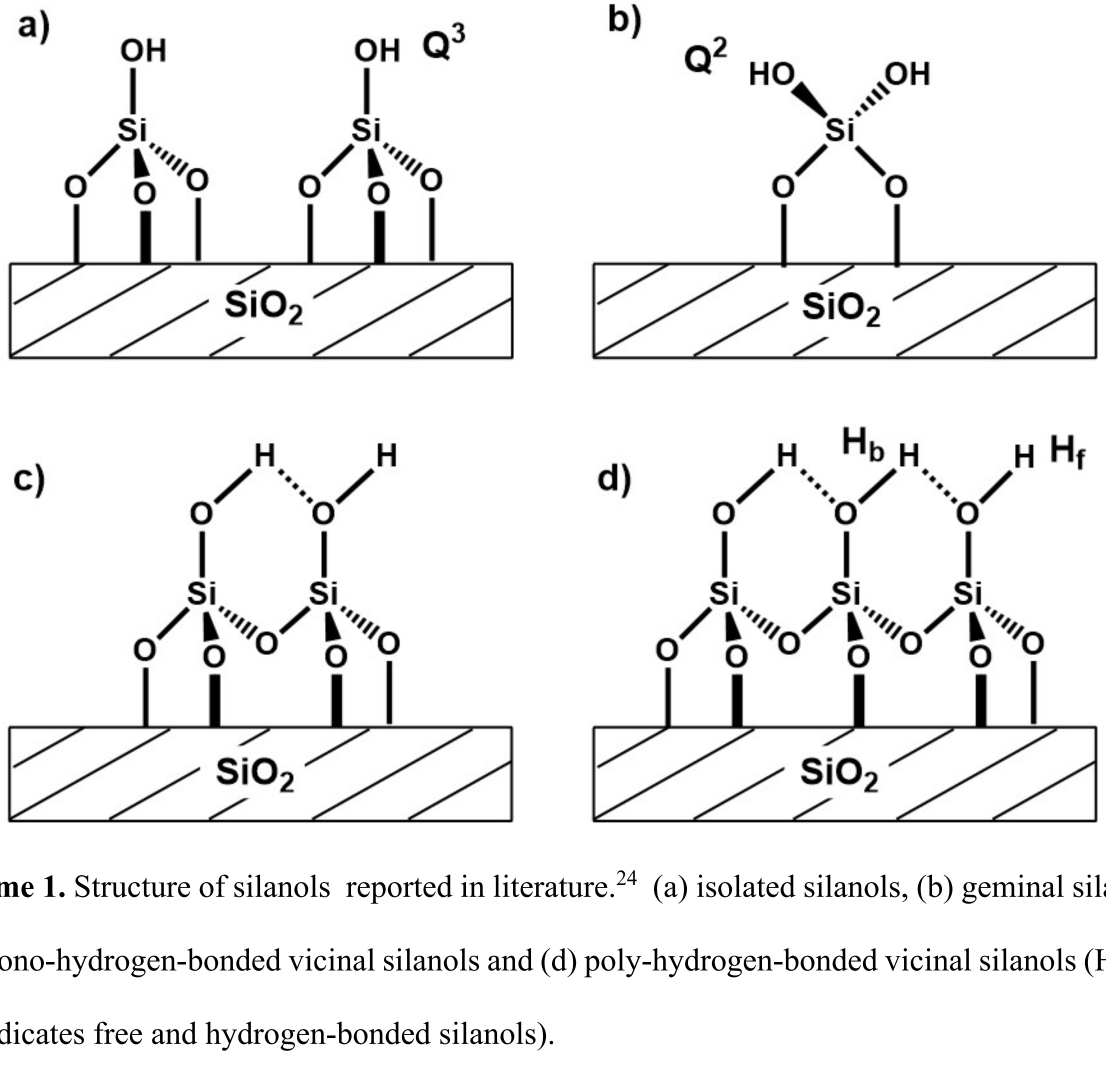
1. INTRODUCTION

In the industrial production of synthetic fibres, plastics and resins, e.g. Nylon-6, ε-caprolactam (CPL) is a key intermediate.[1-3] Globally, the annual production of CPL is around 4.5 billion kilograms.[4] Most of the CPL is produced by the Beckmann rearrangement of cyclohexanone oxime (CHO) using concentrated sulfuric acid in a large scale.[5,6] However, inherent disadvantages of this process result from the hazardous and corrosive nature of the catalyst, the energy consumption, and the stoichiometric amounts of ammonium sulfate formed as a by-product due to the neutralization of sulfuric acid by ammonia. Therefore, recent studies focus on the development of suitable solid catalysts for the efficient production of CPL from CHO via a green process.[7-9]

Various zeolites and mesoporous silica-alumina materials have been applied for this purpose as solid catalysts.[10-19] Zeolites containing weak Brønsted acid sites have been observed to catalyze the Beckmann rearrangement of CHO, however, their industrial application suffered from the rapid catalyst deactivation and the high reaction temperature (> 573 K) for the CPL desorption.[20,21] Surface silanol groups (SiOH) having much weaker acid strength than bridging OH groups (Si(OH)Al) in zeolites are able to catalyze the Beckmann rearrangement of CHO. Solid catalysts with silanol groups as active sites exhibit a suitable deactivation resistance and a high CPL selectivity in the vapor-phase Beckmann rearrangement of CHO.[14, 22] Therefore, silicalite-1 exclusively containing SiOH groups as catalytically active surface sites was found to be one of the best catalysts for this reaction.[6, 23]

Surface SiOH groups have been classified into three major types (Scheme 1): a) isolated silanols ($Si(OSi)_3OH$, Q^3); b) geminal silanols ($Si(OSi)_2(OH)_2$, Q^2); and c) and d) vicinal silanols (hydrogen-bonded Q^3, Q^2, or combinations).[24] The acid strength of silanols depends on the number of OH groups connected to one silicon center, i.e. a higher acid strength was found for Q^3 than for

Q^2 species, as indicated by the p*K*a value of 2.0 to 4.5 and 8.2 to 8.5, respectively.[25-27] When silanols are hydrogen-bonded, the acid strength of the free hydroxyl proton (H_f) in vicinal silanols can be enhanced in comparison to the hydrogen-bonded proton (H_b).[28,29] In the FTIR spectra of CO-loaded catalysts, this effect can lead to a larger shift Δ*v* of the OH vibrations of vicinal silanol groups (105 cm^{-1}) compared with isolated silanol groups (90 cm^{-1}).[30] Therefore, investigate the effect of various SiOH groups and obtain the optimal acidity on surface is prerequisite for the development of new catalysts with an enhanced performance in the Beckmann rearrangement of CHO to CPL.



Scheme 1. Structure of silanols reported in literature.[24] (a) isolated silanols, (b) geminal silanols, (c) mono-hydrogen-bonded vicinal silanols and (d) poly-hydrogen-bonded vicinal silanols (H_f and H_b indicates free and hydrogen-bonded silanols).

The formation of silanol groups on siliceous mesoporous MCM-41 materials ([Si]MCM-41), possessing larger surface area and pore size (1.5-5 nm) than zeolites, can be flexibly controlled and tuned. Earlier investigations demonstrated that MCM-41 materials have a high potential as catalysts in the Beckmann rearrangement of CHO.[13,31,32] MCM-41 materials can promote the diffusion of reactants due to their mesopores, yield CPL at moderate reaction temperatures of 373 K to 403 K, and are characterized by a low catalyst deactivation in the liquid phase.[13, 32] Generally, MCM-41 materials are prepared via a surfactant-directed formation of the mesoporous structure from the hydrolyzed silicon precursors, followed by a condensation between neighboring silanols to form the silica framework.[33,34] With an ultrasonic enhanced synthesis, the condensation rate and final connectivity between neighboring SiOH groups can be influenced,[35,36] resulting in a larger pore wall thickness (higher stability), and a lower energy and time consumption than the classic hydrothermal synthesis (room temperature *vs*. 333 to 423 K, 3 to 6 h *vs*. 1 to 6 days for the synthesis).[34,37,38]

Considering the above-mentioned properties of [Si]MCM-41, this material is interesting for developing optimized solid catalysts for the Beckmann rearrangement of CHO to CPL as presented in this work. By solid-state NMR spectroscopy, the various types of silanol groups generated in the [Si]MCM-41 particles, their density and strength were investigated. Furthermore, based on the catalytic results, the thermal treatment of the [Si]MCM-41 materials was found to be a key parameter for improving these mesoporous solids as catalysts in the Beckmann rearrangement of CHO to CPL.

2. Experimental Section

2.1. Catalyst preparation. The materials used for the synthesis, such as aqueous solution of NH_4OH (25%), tetraethylorthosilicate (TEOS, 100%) and hexadecyl trimethylammonium chloride solution (CTACl, 25%) were all obtained from Sigma-Aldrich. The preparation method was similar as described in our earlier work.[39] For the typical synthesis of [Si]MCM-41, ammonium hydroxide solution, CTACl, TEOS in a volume ratio of 1:1:1 were added to 500 ml demineralized water and completely mixed with the assistance of an ultrasonic bath (300 W and 40 kHz) at room temperature. After sonicated for 0.5 h, 1 h, 2 h and 3 h, the resulting solids were collected by filteration, washed with demineralised water, and then dried in an oven at 353 K. The final [Si]MCM-41 materials were obtained after the as-synthesized products were calcined at 823 K with a heating rate of 1 K min^{-1} in the presence of static air for 6 h. The obtained samples were assigned U-[Si]MCM-41_X, where X = 0.5, 1, 2 and 3 corresponds to the ultrasonic irradiation time in hours.

2.2. Characterization of the textural and morphological properties. Small-angle X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM) were employed to characterize the structure and morphology of the different U-[Si]MCM-41 materials under study. X-ray diffraction was performed on a Siemens D5000 with Cu-Kα radiation in the range of 2-10° and with scanning steps of 0.02°. SEM images were recorded on a Field Emission Scanning Electron Microscopy (FESEM), Zeiss Ultra+. TEM images were obtained by using a Philips CM120 BioFilter microscope utilizing samples that were mounted on a carbon coated copper grid by drying a droplet of a suspension of the ground sample in ethanol. The surface area, average pore size, and total pore volume of the U-[Si]MCM-41 materials were determined by N_2 adsorption/desorption isotherms. An amount of 50 mg of each sample was degassed at 423 K for 12 h under vacuum before the measurements and then recorded at 77 K using an Autosorb IQ-C equipment.

2.3. Solid-state NMR spectroscopy. Priority to ^{29}Si MAS NMR investigations, all samples were fully hydrated by exposure to the saturated vapor of a 1 M aqueous $Ca(NO_3)_2$ solution at ambient temperature overnight in a desiccator. The ^{29}Si MAS NMR spectra were recorded using a 7 mm MAS NMR probe on a Bruker Avance III 400 WB spectrometer at the resonance frequency of 79.5 MHz and with the sample spinning rate of 4 kHz. Single-pulse $\pi/2$ excitation and high-power proton decoupling with the recycle delay of 20 s were applied with 3600 scans for each spectrum.[40]

Before the ^{1}H MAS NMR experiments, the samples were dehydrated in glass tubes under vacuum at a pressure of less than 10^{-2} bar at 393 K, 473 K, or 723 K for 12 h. The ^{1}H MAS NMR studies of the samples dehydrated at 393 K and 473 K were carried out on a Bruker Avance III 700 spectrometer at the resonance frequency of 700.4 MHz with the sample spinning rate of 14 kHz using 2.5 mm MAS NMR rotors. These spectra were recorded after single-pulse $\pi/2$ excitation with a repetition time of 5 s. The samples dehydrated at 723 K were utilized for the loading with 70 mbar of CD_3CN (99.96 atom % D, Aldrich Chemistry) on a vacuum line, followed by an evacuation at room temperature for 10 min to remove weakly physisorbed probe molecules. The ^{1}H MAS NMR investigations of these samples were carried out using a 4 mm MAS NMR probe on a Bruker Avance III 400 WB spectrometer at the resonance frequency of 400.1 MHz with the sample spinning rate of 8 kHz. The spectra were recorded after single-pulse $\pi/2$ excitation with a repetition time of 20 s and 40 scans. The quantitative evaluation of the spectra was performed using the Bruker software WINNMR and WINFIT.

2.4. Catalytic studies. The Beckmann arrangement of CHO to CPL was carried out in a four-necked-round bottom flask equipped with a reflux condenser. The U-[Si]MCM-41 catalysts (50 mg) were given in a flask being an oil bath and dehydrated in flow nitrogen gas (200 to 250 mL min^{-1}) at temperatures of 393 K or 473 K for 12 h. After cooling down, a mixture of CHO (50 mg) and benzonitrile (PhCN, 10 mL) was injected into the flask and stirred during the reaction at 473 K for 7 h. The reaction products were analyzed using a gas chromatograph Shimadzu GCMS-QP2010 Ultra equipped with a Rtx-5MS capillary column (30 m × 0.25 mm × 0.25 μm) connected with a mass spectrometer for the qualitative analysis, as well as a RTX-5 capillary column (30 m × 0.32 mm × 3 μm) connected with a GC-FID detector for the quantitative analysis. The conversion of CHO (C_{CHO}) and yield of CPL (Y_{CPL}) was calculated by:

$$C_{\mathrm{CHO}}\ (\%) = 100 \times [(\mathrm{CHO})_0 - (\mathrm{CHO})] / (\mathrm{CHO})_0 \qquad (2)$$

$$Y_{\mathrm{CPL}}\ (\%) = 100 \times (\mathrm{i}) / (\mathrm{CHO})_0 \qquad (1)$$

where (i) is the molar concentration of the product CPL and $(\mathrm{CHO})_0$ and (CHO) corresponding to the molar concentrations of CHO before and after the reaction, respectively.

3. Results and Discussion

3.1. Physical characterization. The structure of the U-[Si]MCM-41 materials was investigated by small-angle ($2\theta = 1.5$–10^{o}) X-ray diffraction (Fig. 1). A strong d(100) reflection and two weak d(110) and d(200) reflections hint at the hexagonal long range order of the samples under study, as typically reported for MCM-41materials.[39,40] With increasing ultrasonic irradiation times of 0.5 h to 3 h (Fig. 1a-d), the three reflections became more narrow and the weak reflections were strongly enhanced. This indicates that the hexagonal structure of the U-[Si]MCM-41 materials was improved and well-constructed with increasing ultrasonic irradiation time.

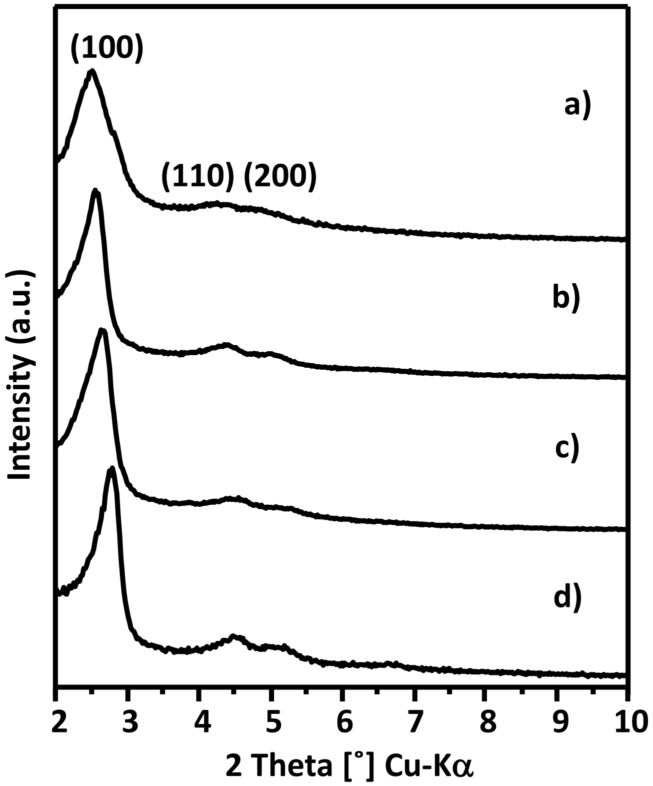


Figure 1. Small-angle XRD patterns of the U-[Si]MCM-41 materials obtained for different ultrasonic irradiation times of 0.5 h (a), 1 h (b), 2 h (c) and 3 h (d).

The nitrogen adsorption/desorption isotherms and the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curves of the U-[Si]MCM-41 materials are shown in Fig. 2. The mesopore systems of all U-[Si]MCM-41 samples were confirmed by type IV isotherms.[41] The corresponding pore size distributions (Fig. 2, insets) are narrow for all [Si]MCM-41 materials under study.

The structure data obtained by XRD and the results of the nitrogen adsorption/desorption experiments are summarized in Table 1. The pore wall thickness of the U-[Si]MCM-41 materials of 1.2 to 1.6 nm, as estimated from the difference between the unit cell parameter a_0 and the pore size D, is significantly larger than that reported in the literature (ca. 1 nm).[39, 42] Hence, the ultrasonic irradiation during the synthesis leads to the formation of thicker pore walls and enhances the mechanical strength of the obtained U-[Si]MCM-41 materials. Furthermore, the increasing pore wall thickness from 1.2 to 1.6 nm with increasing ultrasonic irradiation time from 0.5 h to 3 h are well in line with the improved hexagonal structure of the U-[Si]MCM-41 materials as observed via XRD.

Table 1. Structural and textural properties of [Si]MCM-41 materials under study: d(100)-spacing, unit cell parameter a0, BET surface areas, total pore volume, average pore size, and pore wall thickness. And the number of SiOH groups.

Catalyst	$d_{(100)}{}^{a}$ / nm	$a_0{}^{b}$ / nm	$A_{BET}{}^{c}$ / m^2/g	V^c / cm^3/g	D^c / nm	Pore wall thickness / nm
[Si]MCM-41_0.5	3.5	4	1228	0.728	2.3	1.3
[Si]MCM-41_1	3.46	4	1171	1.130	2.8	1.2
[Si]MCM-41_2	3.45	4	1120	0.741	2.4	1.6
[Si]MCM-41_3	3.3	3.8	1013	0.829	2.2	1.6

[a] d_{100}-spacing was determined using the $d(100)$ reflection ($2d\sin\theta = \lambda$, $\lambda = 0.1542$ nm). [b] The hexagonal unit cell parameter $a_0 = (2/\sqrt{3})d_{100}$, which represents the distance between two neighboring pores. [c] Specific surface areas (A_{BET}), total pore volume (V) and average pore size (D) were determined by BET analysis of nitrogen adsorption-desorption isotherms.

3.2. Solid-state NMR spectroscopic investigations. ^{29}Si MAS NMR spectroscopy has been used to study the silicon coordination inside the framework of the U-[Si]MCM-41 materials (Fig. 3). The signals at ca. δ_{29Si} = -110 and -102 ppm in Figures 3a to 3d were attributed to Q^4 ($Si(OSi)_4$) and Q^3 ($Si(OSi)_3OH$) species, respectively, while the small hump at δ_{29Si} = -92 ppm was assigned to Q^2 ($Si(OSi)_2(OH)_2$) species. Q^4 species represent completely condensed silicon atoms at tetrahedral positions, while one and two hydroxyl groups are bounded at the silicon atoms in the case of Q^3 and Q^2 species, respectively. The $Q^4/(Q^3 + Q^2)$ ratio is often utilized to quantify the condensation degree of silica frameworks.[38] Upon determining the contents of the different Q^n (n

= 0-4) species by an evaluation of the ^{29}Si MAS NMR spectra of the different U-[Si]MCM-41 materials (Fig. 3a-d bottom), $Q^4/(Q^3 + Q^2)$ ratios of 1.6 to 2.1 were obtained. This is much higher than that of [Si]MCM-41 ($Q^4/(Q^3 + Q^2) = 1.4$) prepared without ultrasonic irradiation.[36, 39, 43] Particularly, the $Q^4/(Q^3 + Q^2)$ ratio of U-[Si]MCM-41_1 is 26 % higher than that of the [Si]MCM-41 material synthesized under the same conditions, however, without ultrasonic irradiation.[39] Clearly, ultrasonic irradiation during the synthesis promotes the condensation of silicon precursors, in a good agreement with thicker pore wall.

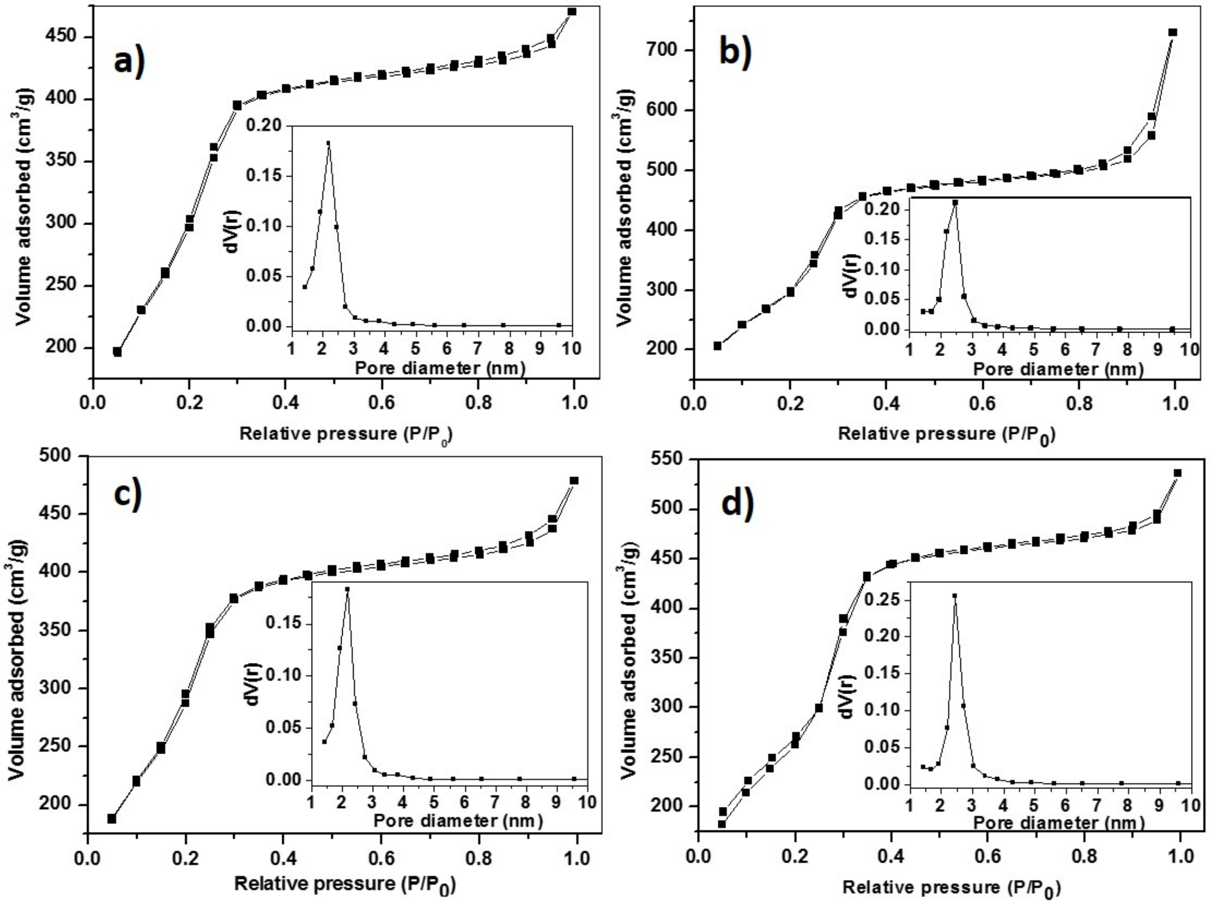


Figure 2. Nitrogen adsorption/desorption isotherms and pore size distributions of U-[Si]MCM-41_0.5 h (a), U-[Si]MCM-41_1 h (b), U-[Si]MCM-41_2 h (c) and U-[Si]MCM-41_3 h (d).

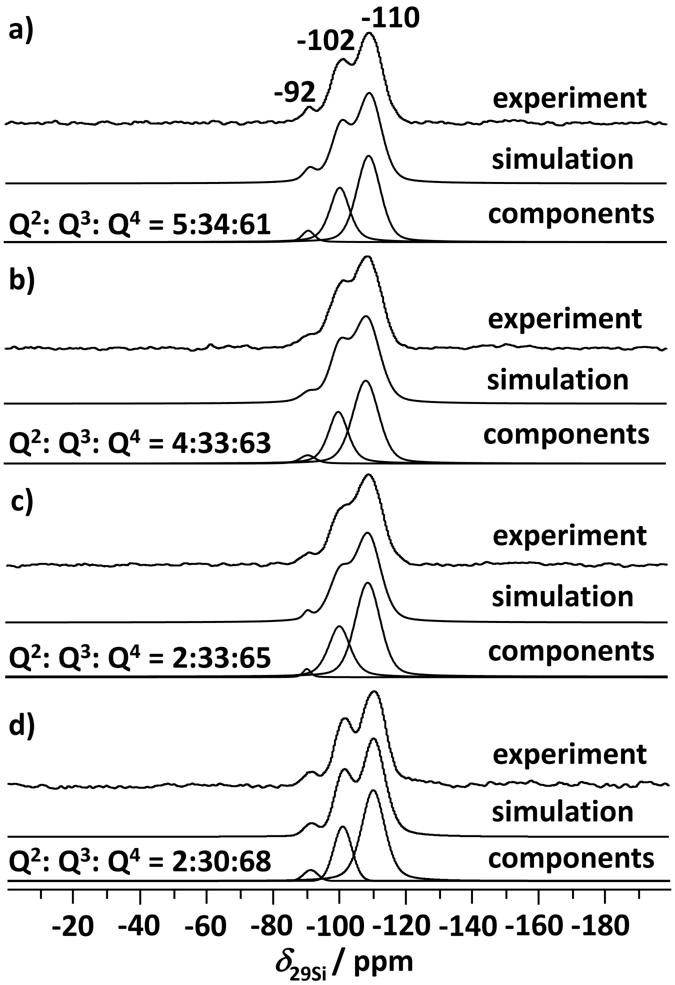


Figure 3. ^{29}Si MAS NMR spectra of U-[Si]MCM-41 samples obtained for different ultrasonic irradiation times of 0.5 h (a), 1 h (b), 2 h (c) and 3 h (d).

Generally, Q^3 species ($Si(OSi)_3OH$) are considerred as catalytically active sites for Beckmann rearrangement.[23] ^{1}H MAS NMR spectroscopy is a suitable method for determining the density of these surface sites.[44] Often, liquid-phase Beckmann rearrangement is carried out at reaction temperatures of $T \leq 473$ K. The catalysts applied for the Beckmann rearrangement in the present work were dehydrated at 393 K and 473 K. By ^{1}H MAS NMR spectroscopy of U-[Si]MCM-41 catalysts pretreated at the same temperatures, the effect of these dehydration procedures on the hydroxyl coverage was investigated.

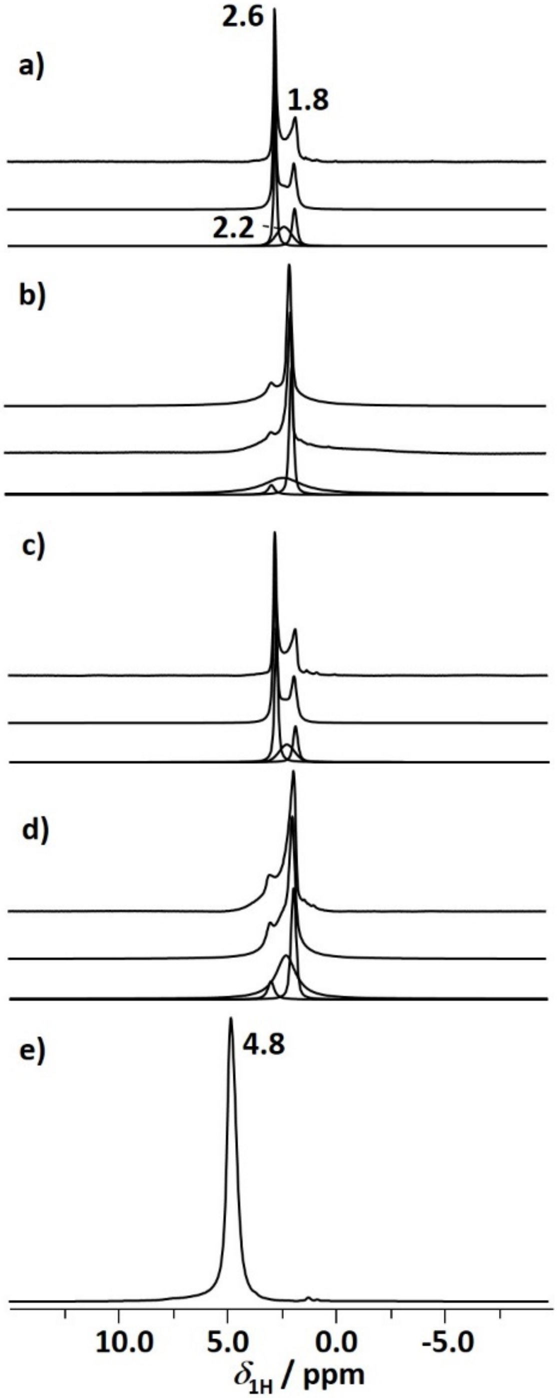


Figure 4. ^{1}H MAS NMR spectra U-[Si]MCM-41_0.5 (a, b) and U-[Si]MCM-41_3 (c, d) dehydrated at 393 K (a, c) and 473 K(b, d), and of fully hydrated U-[Si]MCM-41_3 (e), recorded at 700 MHz.

In Figure 4, the ^1H MAS NMR spectra of the U-[Si]MCM-41 materials synthesized with the shortest (0.5 h: U-[Si]MCM-41_0.5) and longest (3 h: U-[Si]MCM-41_3) ultrasonic irradiation times and after dehydration at 393 K (Figs. 4a and 4c) and 473 K are shown (Figs. 4b and 4d). Furthermore, as an example, Figure 4e shows the spectrum of a fully hydrated sample, in this case of the fully hydrated U-[Si]MCM-41_3. This ^1H MAS NMR spectrum consists of a strong signal at δ_{1H} = 4.8 ppm due to bulk water in the mesopores of the MCM-41 structure. Comparison of the spectrum in Figure 4e with those obtained for samples dehydrated at 393 K indicates a complete removal of the bulk water already after the above-mentioned thermal treatment, which agrees well with literature data.[45] After dehydration the U-[Si]MCM-41 materials at 393 K, the ^1H MAS NMR spectra in Figures 4a and 4c are dominated by signals at δ_{1H} = 1.8 ppm and 2.6 ppm. Furthermore, simulation of these spectra hint at the presence of an additional broad and weak signal at δ_{1H} = 2.2 ppm (Figs. 4a and 4c, bottom). The ^1H MAS NMR spectra in Figures 4b and 4d show that an increase of the dehydration temperature to 473 K is accompanied by a strong decrease of the signal at 2.6 ppm, while the signals at 1.8 and 2.2 ppm are nearly unchanged in their intensity.

According to literature,[44] ^1H MAS NMR signals of siliceous catalysts in the range of δ_{1H} = 1.2 to 2.6 ppm are assigned to surface SiOH groups. Because of the low contents of the ^{29}Si MAS NMR signals due to Q^2 ($Si(OSi)_2(OH)_2$) species in Figure 3, the ^1H MAS NMR signals must be mainly caused by isolated and vicinal SiOH groups, respectively, i.e. originated by Q^3 ($Si(OSi)_3OH$) species.[46] As hydrogen-bonded silanols observed in pure silica,[47] the signal at 2.6 ppm has been assigned to poly-hydrogen-bonded vicinal silanols, since the OH-OH conenction can shifted the ^1H chemical shift to low fields.[48] Further investigations on U-[Si]MCM-41 at higher dehydration temperature were applied. At 463 K < T < 673 K, dehydroxylation between neighboring SiOH groups is carried out,[24] reducing the number of poly-hydrogen-bonded vicinal

SiOH groups as observed with U-[Si]MCM-41 when dehydrated at 473 K (Fig. 4d and d). Upon dehydrated under T > 673 K, surface vicinal SiOH groups can be further dehydrated and dissociated,[24] which significantly increased the density of isolated SiOH groups (δ_{1H} = 1.8 ppm) with the disappearance of signal at δ_{1H} = 2.6 ppm in U-[Si]MCM-41 dehydrated at 723 K (in Supporting Information Fig. S1 and Table S1). For the detailed SiOH densities and numbers of strongly physisorbed water molecules, see Table 2.

Table 2. Densities of isolated SiOH ($SiOH^{isol}$) and mono- and poly-hydrogen-bonded vicinal SiOH ($SiOH^{mono}$ and $SiOH^{poly}$) groups. Determined by ^1H MAS NMR spectroscopy (Fig. 4) of the U-[Si]MCM-41_0.5 and U-[Si]MCM-41_3 materials after dehydration at 393 K and 473 K.

Catalyst	Dehydration temperature / K	$SiOH^{isol}$ 1.8 ppm^b mmol/g	$SiOH^{mono}$ 2.2 ppm^b mmol/g	$SiOH^{poly}$ 2.6 ppm^b mmol/g
U-[Si]MCM-41_0.5	393	0.23	0.31	0.46
U-[Si]MCM-41_0.5	473	0.24	0.33	0.01
U-[Si]MCM-41_3	393	0.21	0.29	0.55
U-[Si]MCM-41_3	473	0.23	0.31	0.11

To clarify, whether the different durations of the ultrasonic irradiation during the synthesis of the U-[Si]MCM-41 materials led to changes in the acid strength of the surface OH groups, ^1H MAS NMR spectroscopic studies of dehydrated samples before and after adsorption of the weak base acetonitrile-d3 (CD_3CN) were performed.[47, 49] For demonstrating the results of these investigations, Figures 5a-d show the ^1H MAS NMR spectra of U-[Si]MCM-41 materials, recorded before (bottom) and after (top) adsorption of CD_3CN. Comparison of these spectra results in a low-field shift of the SiOH signals at δ_{1H} = 1.8 to 2.2 ppm to a position at 4.8 ppm. These values correspond to an adsorbate-induced resonance shift $\Delta\delta_{1H}$ of ca. 3.0 ppm, which is typical for SiOH groups interacting with CD_3CN.[49] This adsorbate-induced resonance shift $\Delta\delta_{1H}$ is due to the formation of hydrogen bonds (O–H---N) between the surface SiOH groups and the adsorbate molecules (CD_3CN) and correlates with the acid strength of the involved hydroxyl protons.[45, 50] The $\Delta\delta_{1H}$ values of ca. 3.0 ppm were observed for all U-[Si]MCM-41 samples under study and hint at a similar weak acid strength for all these catalysts.

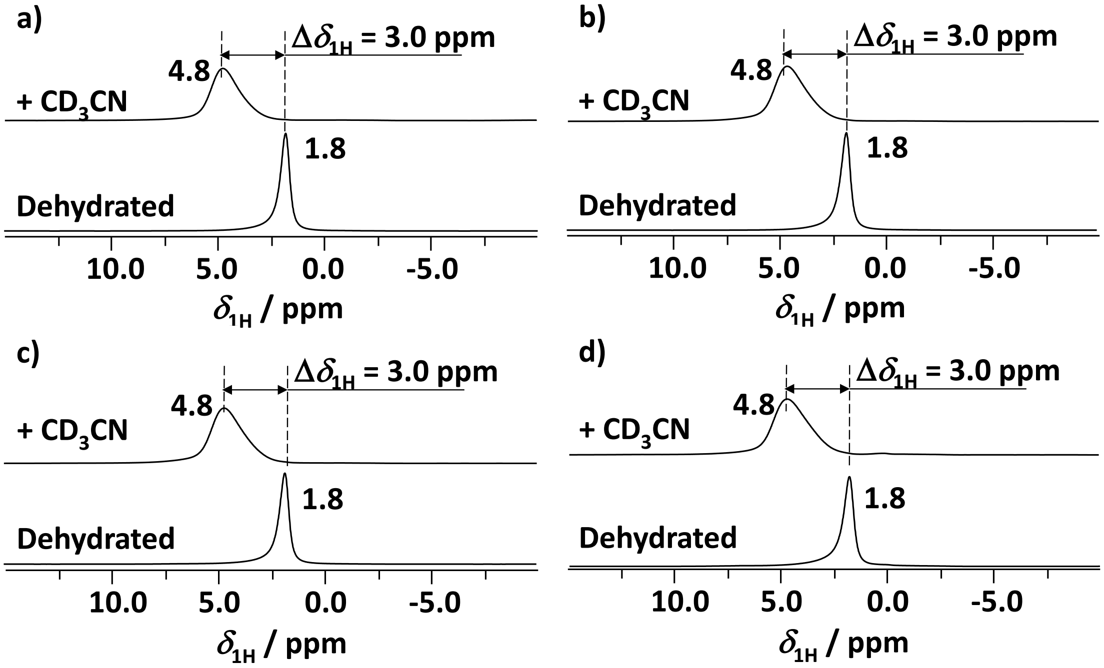


Figure 5. ^{1}H MAS NMR spectra of dehydrated U-[Si]MCM-41_0.5 (a), U-[Si]MCM-41_1 (b), U-[Si]MCM-41_2 (c) and U-[Si]MCM-41_3 (d) reordered before (bottom) and after (top) loading with CD_3CN.

Summarizing can be stated that an increased duration of the ultrasonic irradiation during the synthesis of the U-[Si]MCM-41 materials under study is accompanied only by a weak decrease of the SiOH densities (Table 2). Furthermore, for the catalysts prepared with ultrasonic irradiation times of 0.5 to 3.0 h, a similar weak acid strength was observed (see Fig. 5). The most interesting result of the solid-state NMR investigations, on the other hand, is the presence of poly-hydrogen-bonded vicinal silanols. These sites remains on the U-[Si]MCM-41 surface still after dehydration at 393 K, while these surface sites are almost disappeared after dehydration at 473 K, which may influence the cyclohexanone oxime conversion.

3.3. Beckmann rearrangement of cyclohexanone oxime (CHO) to ε-caprolactam (CPL). The Beckmann rearrangement of CHO to CPL was carried out in PhCN at 473 K for 7 h on U-[Si]MCM-41 catalysts dehydrated at 393 K and 473 K. The CHO conversions and the yields of CPL are summarized in Table 3. Interestingly, the CHO conversions of 14.1 % to 20.4 % and the CPL yields of 4 % to 6.4 %, obtained with the U-[Si]MCM-41 catalysts dehydrated at 473 K, were much lower than those obtained with these catalysts dehydrated at 393 K (CHO conversions of 47 % to 55 % for and CPL yields of 8.7 % to 17.6 %).

Table 3. Results of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam on the U-[Si]MCM-41_x catalysts (x: duration of ultrasonic irradiation) under study, dehydrated at 393 K and 473 K.[a]

	Dehydration at 393 K		Dehydration at 473 K	
	C_{oxime} %	Y_{ε} %	C_{oxime} %	Y_{ε} %
[Si]MCM-41_0.5	47.0	8.7	15.7	4
[Si]MCM-41_1	51.9	13.7	27.0	5.7
[Si]MCM-41_2	53.4	10.4	20.4	4.3
[Si]MCM-41_3	55.0	17.6	14.1	6.4

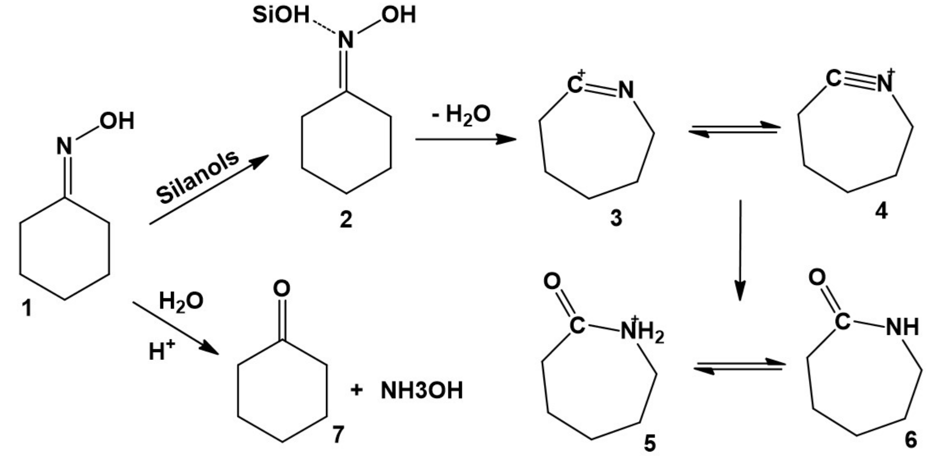
[a] Conversion of cyclohexanone oxime (50 mg) in PhCN (10 ml) using a 50 mg catalyst at 473 K for 7 h to yield ε-caprolactam.

U-[Si]MCM-41_0.5 and U-[Si]MCM-41_3 catalysts exhibited similar isolated (δ_{1H} = 1.8 ppm) and mono-hydrogen-bonded vicinal (δ_{1H} = 2.2 ppm) silanol groups after the same dehydration temperature at 393 or 473 K as shown in Table 2. The significant difference is the amount of poly-hydrogen-bonded SiOH groups (0.46 and 0.01 mmol/g for U-[Si]MCM-41_0.5 vs. 0.55 and 0.11 mmol/g for U-[Si]MCM-41_3 dehydrated at 393 K and 473 K, respectively, which strongly depends on the condensation degree of silicon species as shown in Fig. 3). These different contents of poly-hydrogen-bonded SiOH groups are accompanied by CPL yields, which are for U-[Si]MCM-41_3 about twice of those for U-[Si]MCM-41_0.5 after the same dehydration temperature, and about twice of those for the same catalyst, but comparing the samples dehydrated at 393 K and 473 K.

According to Scheme 2,[51] surface SiOH groups promote the dehydration of CHO to form the intermediate **3** (more stable in form **4)**, which is subsequently transferred into the intermediate **5** by addition of H_2O. Finally, the product **6** is formed by deprotonation. The water elimination (from intermediates **2** to **3**) and water addition (from intermediates **3** and **4** to **5**) is the key step to drive Beckmann rearrangement. Poly-hydrogen-bonded SiOH groups exhibit relative higher strength in comparison with isolated silanols[30] are proposed to promote the reaction. Moreover, the nearest-neighboring isolated silanols (perhaps vicinal silanols) exhibit higher affinity to water in comparison with isolated silanols.[52] In this case, vicinal silanols can help to stabilize water molecule in the local structure, which can facilitate water added back to intermediates in an efficient way.

Further reducing the dehydration temperature (< 393 K) of U-[Si]MCM-41 was investigated, which may result in a large amount of mobile water molecules on surface.[24, 45, 53-54] When fully hydrated U-[Si]MCM-41_3 with a strong water signal at δ_{1H} = 4.7 ppm (Fig. 4e) was employed, a

CHO conversion of 45.3 % and a CPL yield of 3.1 % were obtained with, much less than that obtained by sample dehydrated at 393 K without mobile water molecules (55 % and 17.6 %). These mobile water are considered to block surface sites, and resulted in the hydrolysis of CHO to cyclohexanone,[13] a major by-product observed here.



Scheme 2. Proposed mechanism of Beckmann rearrangement of CHO to yield CPL.[51]

Finally, the reusability of the U-[Si]MCM-41 catalysts was tested with U-[Si]MCM-41_3 using the standard conditions specified in Table 1. After each test, the used catalyst was recovered by calcined in air at 823 K. Recycling the catalyst five times did not lead to a significant loss of activity (kept at ca. 55-58 %) and selectivity to lactam (22-24 %). This indicates U-[Si]MCM-41 catalysts are highly stable under current conditions for Beckmann rearrangement.

The catalytic activity obtianed here is not as active as those obtained with metal-doped MCM-41 and zeolites, and metal-organic-framework catalsyts, which possess much higher acid stregnth compared to U-[Si]MCM-41 catalysts.[13, 55-57] However, this work introduced a simple method to enhance the catalytic performance via optimising dehdyration temperature. The active sites identified here is also important to improve the catalytic performance of siliceous catalysts that are used in Beckmann rearrangment of CHO to CPL industrially.

4. Conclusions

In this work, U-[Si]MCM-41 materials have been successfully synthesized at room temperature under ultrasonic irradiation. Pore wall thickness (1.2 to 1.6 nm) was significantly enhanced by the higher condensation degree of U-[Si]MCM-41 framework ($Q^4/(Q^3 + Q^2)$ ratio of 1.6 to 2.1) than those prepared without ultrasonic irradiation ($Q^4/(Q^3 + Q^2) = 1.4$). The SiOH densities were determined by quantitative ^{1}H MAS NMR spectroscopy of samples dehydrated at different temperatures. Three types of silanol groups, including isolated SiOH, mono- and poly-hydrogen-bonded SiOH groups was identified and quantified by using ^{1}H MAS NMR spectroscopy.

Poly-hydrogen-bonded SiOH groups with relative higher strength than isolated silanols,[30] may promote the Beckmann rearrangement of CHO to CPL. Increasing dehydration temperature from 393 K to 473 K can strongly decrease the content of poly-hydrogen-bonded SiOH groups on U-[Si]MCM-41 materials by dehydroxylation and dissociation. It leads to a 2.2 to 2.8 times higher CPL yield of U-[Si]MCM-41 catalysts dehydrated at 393 K than those dehydrated at 473 K. Therefore, this work provides new insights in parameters, which could help to improve the catalytic performance of mesoporous siliceous materials in the Beckmann rearrangement of CHO to CPL, such as by optimizing the preparation conditions, surface silanol groups and the catalyst pretreatment.

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H MAS NMR (Fig. S1), quantitative results of silanol groups (Table S1)

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Notes

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