



Acidity enhanced [Al]MCM-41 via ultrasonic irradiation for the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam



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ABSTRACT

Using solid acid catalysts to replace liquid acids in the liquid-phase Beckmann rearrangement of cyclohexanone oxime (CHO) into ϵ -caprolactam (CPL) is crucial for the environmentally friendly production of synthetic fibers, such as Nylon-6. In this work, we prepared aluminum-containing MCM-41 catalysts under ultrasonic irradiation with various Si/Al ratios for this purpose. Quantitative ¹H MAS NMR investigations show that ultrasonic irradiation significantly promotes the formation of active Brønsted acid sites (BAS) on the [Al]MCM-41 catalysts up to 8 times higher than those prepared at the same conditions without ultrasonic irradiation, and up to 12 times higher BAS density than those reported in the literatures. The catalytic performance of [Al]MCM-41 catalysts can be strongly improved with increasing the BAS density, particularly to the ratio of BAS/(weakly acidic SiOH groups). Moreover, [Al]MCM-41 catalysts dehydrated at 393 K obtained two time higher CHO conversion and CPL yield than that dehydrated at 473 K. Hydrogen-bonded water molecules retained at low dehydration temperature may block surface SiOH groups and promote the reaction process. With higher BAS density resulting from ultrasonic irradiation, [Al]MCM-41 catalyst (Si/Al = 10) in this work obtained the highest CPL yield among all [Al]MCM-41 materials reported for liquid-phase Beckmann rearrangement up to now. Finally, the reusability of [Al]MCM-41 catalyst was tested and no significant activity loss can be observed after five reaction cycles.

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1. Introduction

Beckmann rearrangement of cyclohexanone oxime (CHO) into ϵ -caprolactam (CPL), a key industrial intermediate of 4.5 million tons produced annually, is of great importance in the manufacturing of synthetic fibers and resins, such as Nylon-6 [1]. The production of CPL is currently dominated by concentrated sulfuric acid in large scale [2,3]. To replace the harmful and corrosive liquid acids, recent works has focused on the development of environmentally friendly solid acids for the efficient production of CPL in a green chemical process.

A major industrial strategy is to develop solid acids for the liquid-phase Beckmann rearrangement [4–17]. It can produce CPL at moderate temperature (373–403 K) with less catalyst deactivation [8,18], and has the flexibility to replace homogeneous catalyst in existing plants, in comparison to that in the vapor-phase

[19–24]. Crystalline zeolites and mesoporous silica-alumina (e.g. [Al]MCM-41), providing Brønsted acid sites (BAS) with easily tunable properties, are the most popular solid acid catalysts. Surface BAS are active sites to initialize the reaction via N-protonation to form an intermediate via a 1,2-H shift and dehydration, followed by rearrangement into the desired CPL [25], where higher BAS strength can promote the N-protonation [26]. However, the strong BAS on zeolites facilitate the formation of CPL at low temperature (<373 K) but require high temperature for the desorption of CPL (523–623 K) from active sites [27], resulting in lower CPL selectivity and fast catalyst deactivation [10,28]. Using a solvent (e.g. Bezonitrile (PhCN)) with suitable polarity and basicity can enhance the catalytic activity and prevent catalyst deactivation [8,11,18]. Moreover, poisoning strong BAS and Lewis acid sites (LAS) via pre-adsorption of guest molecules (e.g. H₂O and PhCN) can significantly improve the catalytic performance of zeolite (e.g. HUSY) in the Beckmann rearrangement of CHO [9,11].

Alternatively, [Al]MCM-41 materials possess BAS with relative weak acid strength compared to zeolite are favoured in Beckmann

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rearrangement reactions [8,21–23]. It exhibits better catalytic performance than that of H-Beta zeolite with a CHO conversion of 50.6% vs. 41% and CPL selectivity of 89.1% vs. 86.3% [8]. Moreover, the catalytic performance of [Al]MCM-41 in the Beckmann rearrangement is significantly improved with decreasing Si/Al from 26.5 to 12 [8]. This is because BAS on [Al]MCM-41 are generated by Al species incorporated into the silica framework and flexibly coordinated to neighboring SiOH groups, where a higher Al content may promote the formation of BAS. It directs the current efforts to improve the catalytic performance of [Al]MCM-41 by introducing more Al species into the silica framework.

MCM-41 materials prepared by classic hydrothermal methods is often time and energy consuming (1–7 days at 333–423 K) [29–32]. Recently, the rapid room-temperature synthesis of MCM-41 has been introduced to prepare these materials in hours at milder conditions [25,33–39]. Quantitative ^1H NMR spectroscopy shows the BAS density on [Al]MCM-41 strongly increased from 0.013 to 0.121 mmol/g with decreasing Si/Al ratio from 50 to 15 [25]. These surface acidic OH groups are widely accepted to be generated by Al located in the vicinity of surface SiOH groups, well known as tetrahedrally coordinated aluminum (Al^{IV}) species [25,40,41]. However, the conventional hydrothermal and sol-gel techniques with distinct inhomogeneity can result in Al species polymerized together (e.g. the different hydrolysis velocity of precursors) [42,43], and lower the density of BAS on [Al]MCM-41.

It has been reported previously [44–47] that ultrasonic enhanced techniques can result in sonochemical effects in liquid for continuous formation and growth of particles, implosive collapse of bubbles, and the sonochemical reactions at the interfacial region can introduce physicochemical change and enhance the liquid-solid mass transfer. These properties are able to homogeneously disperse silica oligomers in the mixture for efficient fabrication of [Si]MCM-41 with small particle size and a higher condensation degree [48]. In the preparation of MCM-41 with high titanium content, ultrasonic irradiation promotes the re-dispersion and condensation of inorganic species, resulting in titanium homogeneously distributed into the MCM-41 framework [49]. Similarly, the ultrasonic irradiation assisted sol-gel method is promising to improve the dispersion and condensation of Al into [Al]MCM-41 framework, and thus, promote the formation of BAS on the [Al]MCM-41 surface.

In this work, [Al]MCM-41 has been prepared at room temperature under ultrasonic irradiation. The mesoporous structure and texture of materials obtained have been studied by XRD and N_2 adsorption/desorption. The local structure and surface acid sites have been characterized by solid-state NMR spectroscopy. Quantitative ^1H MAS NMR spectroscopy shows that [Al]MCM-41 prepared with ultrasonic irradiation exhibits up to 8 times enhanced density of BAS. These [Al]MCM-41 materials were used as catalyst for the Beckmann rearrangement of CHO. A lower activation temperature was found to improve the catalytic performance of [Al]MCM-4. It is hypothesized that residual water molecules poison the strong sites on the surface.

2. Materials and methods

2.1. Catalyst preparation

All chemicals used for the [Al]MCM-41 synthesis, such as ammonium hydroxide solution (28% NH_3 in H_2O), tetraethylorthosilicate (TEOS, >98%), hexadecyltrimethylammoniumchloride solution (CTACl, purum, ~25% in H_2O), and aluminum sulfate octadecahydrate (>98%) were obtained from Sigma-Aldrich. The preparation method is similar to that described in our earlier work [25]. For a typical preparation of [Al]MCM-41, CTACl, an ammo-

nium hydroxide solution, TEOS in a volume ratio of 1:1:1 in 500 ml demineralized water and a certain amount of aluminum sulfate octadecahydrate calculated based on Si/Al ratios were mixed under vigorous stirring at room temperature. Then the resulting mixture was immediately subjected to sonication at room temperature for 1 h in an ultrasonic bath with a power of 300 W and ultrasonic frequency of 40 kHz. The resulting solid was filtered and washed with distilled water and then dried in an oven at 353 K. Finally, the obtained MCM-41 materials were calcined at 823 K with a heating rate of 1 K/min in the presence of static air for 6 h. The nomenclature of [Al]MCM-41 is defined as U-[Al]MCM-41/x, where U represents ultrasonic irradiation and x is the Si/Al ratios of 10, 20, 30, 40 and 50.

2.2. Characterization of textural and morphological properties

2.2.1. XRD characterization

Small-angle X-ray diffraction (XRD) studies were performed on a Siemens D5000 with $\text{Cu-K}\alpha$ radiation in the range of 2–10°, and with scanning steps of 0.02°.

2.2.2. BET measurements

The surface area, average pore size, and total pore volume of the MCM-41 materials were determined by N_2 adsorption/desorption isotherms on an Autosorb IQ-C system. 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.

2.3. Solid-state NMR investigation

Prior to ^{27}Al and ^{29}Si MAS NMR investigations, all samples were fully hydrated by exposure to the saturated vapor of $\text{Ca}(\text{NO}_3)_2$ solution at ambient temperature overnight in a desiccator. Before the ^1H and ^{13}C MAS NMR experiments, the samples were placed in glass tubes and dehydrated at 723 K for 12 h under a pressure of less than 10^{-2} bar. The dehydrated samples were sealed in the glass tubes or directly loaded with ammonia or acetone- $2-^{13}\text{C}$ (99.5% ^{13}C -enriched, Sigma-Aldrich) on a vacuum line. Subsequently, the loaded samples were evacuated at 393 K for 1 h (for ammonia) or at room temperature for 2 h (for acetone) to remove weakly physisorbed molecules. Subsequently, the samples were transferred into the MAS NMR rotors under dry nitrogen gas inside a glove box.

^1H , ^{27}Al , and ^{13}C MAS NMR investigations were carried out on a Bruker Avance III 400 WB spectrometer at resonance frequencies of 400.1, 104.3, and 100.6 MHz, respectively, and with the sample spinning rate of 8 kHz using 4 mm MAS rotors. The spectra were recorded after single-pulse $\pi/2$ and $\pi/6$ excitation with repetition times of 20 s and 0.5 s for studying ^1H and ^{27}Al nuclei, respectively. Quantitative ^1H MAS NMR measurements were performed using a zeolite H,Na-Y (35% ion-exchanged) as an external intensity standard. ^{13}C cross-polarization (CP) MAS NMR spectra were recorded with a contact time of 4 ms and the repetition time of 4 s. The ^{29}Si MAS NMR measurements were performed on the same spectrometer using a 7 mm MAS NMR probe 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 a recycle delay of 20 s were applied [50].

2.4. Catalytic reaction

The obtained U-[Al]MCM-41 catalysts were tested in the Beckmann rearrangement of CHO to CPL. The reaction was carried out in a four-necked-round bottom flask equipped with a reflux condenser. Prior to reaction, the U-[Al]MCM-41 catalysts (50 mg) were pre-loaded in the flask and dehydrated in nitrogen gas flow

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