

# Arenesulfonic acid functionalized mesoporous silica as a novel acid catalyst for the liquid phase Beckmann rearrangement of cyclohexanone oxime to $\epsilon$ -caprolactam

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## Abstract

Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam was performed in liquid phase for the first time on arenesulfonic acid-functionalized SBA-15 (SBA-ar-SO<sub>3</sub>H) mesoporous silica with different loadings of the acid. The catalysts were prepared via co-condensation of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) and tetraethyl orthosilicate (TEOS) in the presence of Pluronic 123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) and characterized by XRD, N<sub>2</sub> adsorption–desorption, TGA, EA and acid–base titration method. The oxime conversion and selectivity to  $\epsilon$ -caprolactam were found to increase with the loading of arene-SO<sub>3</sub>H groups. The influences of solvent and reaction temperature on the rearrangement of oxime in the liquid phase were examined. The oxime rearrangement and hydrolysis were proposed to be catalyzed on different active sites of –SO<sub>3</sub>H and Si–OH, respectively. The catalytic activity of SBA-ar-SO<sub>3</sub>H was also compared with the activities of other solid acid catalysts such as propylenesulfonic acid-functionalized SBA-15, H-ZSM-5, H-mordenite, Al-MCM-41 and Al-SBA-15. The results revealed that SBA-ar-SO<sub>3</sub>H has higher catalytic activity and lactam selectivity.

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**Keywords:** Beckmann rearrangement; Cyclohexanone oxime;  $\epsilon$ -Caprolactam; SBA-15; Arenesulfonic acid

## 1. Introduction

The importance of the Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam, which is a valuable starting material for the manufacture of nylon fibers and resins, has been widely documented in the literature [1–3]. Current commercial processes for this reaction, however, require the use of oleum or sulfuric acid as a reaction medium [4]. That causes problems in product separation, corrosion hazard of the reactor and the large amount of ammonium sulfate formed as by-product. The environmental regulations and process safety continue to drive the industry to develop solid acids to replace liquid acid processes. In the past two decades, various solid catalysts have been applied to the Beckmann rearrangement of cyclohexanone oxime [5–11], especially the zeolite catalysts

for vapor-phase reactions. However, the vapor-phase Beckmann rearrangement reaction over solid acid catalysts is usually carried out at temperatures higher than 250 °C, and still rapid catalyst deactivation is encountered due to the coke formation and irreversible adsorption of the basic reaction products [12,13]. In contrast, the solid/liquid phase catalytic system appears to be more promising, where the reaction can proceed at a moderate temperature and the catalyst deactivation is minimized due to the presence of solvent.

Acidic zeolites have been widely studied in the synthesis of fine chemicals due to their high surface area and confined domains [14–17]. However, their uses are often restricted by the small pore diameter of less than 1 nm. For reactions performed in the liquid phase, the reaction substrates and products need to diffuse rapidly towards and away from the catalytic active sites. The discovery of mesoporous molecular sieves of M41S family has attracted much attention of many research groups because these

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materials are likely to offer improved reaction activity in the conversion of larger substrate molecules in their well-defined channels with narrow pore size distribution [18,19]. In 1998, another family of mesoporous silica, named SBA-15, of hexagonal-ordered pore structure was synthesized using amphiphilic triblock copolymers as pore-directing agents [20]. The SBA-15 mesoporous silica has received great attention since then because of its larger pore diameter and better hydrothermal stability in comparison to MCM-41, its analog in the M41S family. However, in spite of these materials having larger pore dimensions, the acidity of mesoporous materials like Al-MCM-41 and Al-SBA-15, is much weaker than that of microporous zeolites [21]. In order to overcome this drawback, ordered sulfonic-acid modified mesoporous silica has been prepared either via post-grafting technique or through one-pot synthesis [22–29]. The purpose of this study is to reveal the catalytic performance of the arene-sulfonic acid-functionalized SBA-15 in the liquid phase Beckmann rearrangement of cyclohexanone oxime to caprolactam.

## 2. Experimental

### 2.1. Sample preparation

Arene-sulfonic acid-functionalized SBA-15 materials (abbreviated as SBA-ar-SO<sub>3</sub>H) were prepared by one-pot synthesis, referred to Ref. [23]. Four grams of Pluronic 123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>,  $M_{av}$  = 5800, Aldrich) was dissolved in 125 g of 1.9 M HCl solution at room temperature. After TEOS (Aldrich) was added, the resultant solution was equilibrated at 40 °C for 45 min for pre-hydrolysis, and then CSPTMS (Gelest) and H<sub>2</sub>O<sub>2</sub> were slowly added into the solution. The molar composition of the mixture was (1- $x$ ) TEOS: $x$  CSPTMS: $3x$  H<sub>2</sub>O<sub>2</sub>:5.8 HCl:0.017 P123:165 H<sub>2</sub>O, where  $x$  varied from 0 to 0.15. The resultant mixture was stirred at 40 °C for 20 h and then transferred to a polypropylene bottle and reacted at 100 °C for 24 h under static conditions. The solid product was recovered by filtration and dried at room temperature overnight. The template was removed from the as-synthesized material by refluxing in ethanol for 24 h (1.5 g of as-synthesized material per 400 ml of ethanol). Finally, the material was filtered, washed several times with water and ethanol and dried at 50 °C.

Similarly, propylenesulfonic acid-functionalized SBA-15 (abbreviated as SBA-pr-SO<sub>3</sub>H) was synthesized via the co-condensation of mercaptopropyltrimethoxysilane (MPTMS) and TEOS according to the literature [22]. The molar composition of the mixture was 0.9 TEOS:0.1 CSPTMS:0.9 H<sub>2</sub>O<sub>2</sub>:5.8 HCl:0.017 P123:166 H<sub>2</sub>O.

Al-MCM-41 and Al-SBA-15 were prepared following the procedures described in the literature [30,31]. The Si/Al molar ratios were 32 and 60, respectively, as analyzed by energy dispersive X-ray spectroscopy (EDS). Ammonium mordenite with Si/Al molar ratio of 10 and ammonium

zeolite with Si/Al molar ratio of 115 were supplied by Advchem Laboratories Inc. Before being used as catalysts, they were converted to proton forms by calcination at 500 °C for 6 h.

### 2.2. Sample characterization

X-ray powder diffraction (XRD) data were obtained on a Panalytical X'Pert Pro diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at 45 kV and 40 mA. N<sub>2</sub> adsorption-desorption isotherms were carried out using MICROMERITICS TRISTAR 3000 at liquid nitrogen temperature. Before the measurements, the samples were degassed at 100 °C for 12 h. The specific surface areas were evaluated using Brunauer-Emmett-Teller (BET) method in the  $P/P^0$  range of 0.05–0.3. Pore size distribution curves were calculated using the desorption branch of the N<sub>2</sub> adsorption-desorption isotherms and the Barrett-Joyner-Halenda (BJH) method. Thermogravimetric analyses (TGA) were carried out on a Du Pont 951 thermogravimetric analyzer with a heating speed of 10 °C/min under air in a flow of 50 ml/min. Sulfur elemental analyses (EA) were performed on a Heraeus CHNS elemental analyzer. Ion-exchange capacities of the sulfonic acid-functionalized materials were determined using an aqueous solution of sodium chloride (NaCl, 2 M) as an exchange agent [23,32]. Solid of 0.05 g was added to NaCl aqueous solution. After equilibration, the resulting suspension was titrated potentiometrically by dropwise addition of 0.01 M NaOH aqueous solution.

### 2.3. Catalytic reaction

Cyclohexanone oxime and various organic solvents were supplied by Aldrich, Acros or Merck, and were used without further purification. Reactions were carried out under N<sub>2</sub> in a flask that was equipped with a reflux condenser and a magnetic stirrer. The reactor was placed in a thermostatic bath. In a typical experiment, 0.2 g of the solid catalyst was pre-refluxed with toluene for 2 h, then in situ dried in vacuum at 150 °C overnight to remove adsorbed moisture in the catalyst, then cooled to the required temperature, and finally a solution of 2 mmol cyclohexanone oxime in solvent was poured into the reactor and rapidly heated to the set reaction temperature under N<sub>2</sub>. The liquid products were separated from the reaction mixture with a filtering syringe and analyzed by using a Chrompak CP 9000 gas chromatograph (GC) equipped with 30 m  $\times$  0.32 mm RTX-50 capillary column and FID detector. Quantitative analysis was based on the area ratio of the standard mixtures containing known molar ratios of products and resultant. The concentrations of liquid products were corrected by addition of the percentage of each compound adsorbed by the catalyst. Reaction products were also identified by GC-mass spectrometry (HP5971 mass spectrometer connected with a 30 mm  $\times$  0.25 mm RTX-50 capillary column).

### 3. Results and discussion

#### 3.1. Catalyst characterization

Small angle X-ray powder diffraction patterns of extracted SBA-ar-SO<sub>3</sub>H with different acid loadings are shown in Fig. 1. All the samples with 5–15% arenesulfonic acid groups in the synthesis mixture have one very intense peak and two weak peaks indexed to (1 0 0), (1 1 0) and (2 0 0) diffractions, respectively, indicating that the prepared materials contained well-ordered hexagonal arrays of one-dimensional channel structure similar to that of pure siliceous SBA-15 [20]. Moreover, the diffraction peaks shift slightly toward lower  $2\theta$  angle as the sulfonic acid loading increases. In other words, the lattice expands when sulfonic acid-functionalized silane CSPTMS was introduced into the synthesis mixture. However, the intensity of the XRD peaks decreases and the higher order (1 1 0) and (2 0 0) diffractions are less resolved when the molar content of CSPTMS was raised to 15%. This phenomenon is explained by considering that the presence of CSPTMS would perturb the self-assembly of the surfactant and the silica precursors [23].

The physico-chemical and textural properties of the functionalized SBA-15 materials with different loadings of CSPTMS and several other porous acid catalysts are listed in Table 1. In comparison to that of pure siliceous SBA-15, the  $d_{100}$  spacing of arenesulfonic acid functionalized materials increases while the surface area and pore volume decrease with the loading of arenesulfonic acid groups. These results are attributed to the occupation of large organic molecules on the surface of the pores. In contrast, the SBA-15 sample functionalized with propylenesulfonic acid groups does not show significant changes in surface area and pore volume.

N<sub>2</sub> adsorption–desorption isotherms of modified SBA-15 with different concentrations of CSPTMS exhibit characteristic type IV isotherms (Fig. 2a). The steep increases in adsorption volume at  $P/P_0 = 0.7–0.8$  are due to capillary condensation of nitrogen in the mesopores. The BJH pore

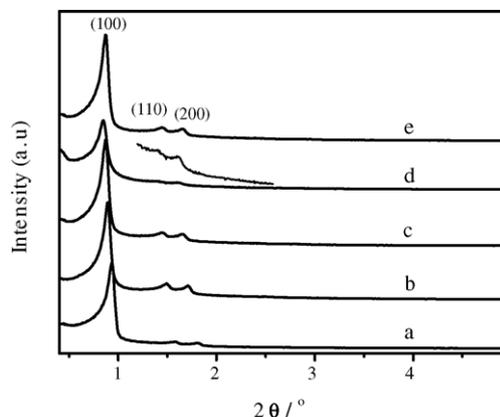


Fig. 1. X-ray powder diffraction patterns of the extracted samples: (a) pure siliceous SBA-15; (b) 5% SBA-ar-SO<sub>3</sub>H; (c) 10% SBA-ar-SO<sub>3</sub>H; (d) 15% SBA-ar-SO<sub>3</sub>H; (e) 10% SBA-pr-SO<sub>3</sub>H.

size distributions of the materials with 5–15% arenesulfonic acid groups show very narrow pore size distribution (Fig. 2b).

The results of the chemical elemental analyses reveal that sulfur contents in sulfonic acid functionalized SBA-15 mesoporous silica are proportional and close to the theoretical values calculated from the starting mixture (Table 1). This implies that most of the arenesulfonic and propylenesulfonic acid groups are effectively incorporated in the silica framework, which was also supported by TG analysis. There are also good agreements between the sulfur contents and the acid capacities determined by acid–base titration using NaCl as the exchange agent (Table 1). Such results imply that the sulfonic acid groups incorporated in the SBA-15 framework are accessible and could be used as acid catalysts.

#### 3.2. Catalysis

The liquid phase Beckmann rearrangement of cyclohexanone oxime was carried out over sulfonic acid functiona-

Table 1  
Physico-chemical properties of sulfonic acid-functionalized SBA-15 mesoporous materials and some other solid acid catalysts

Catalyst	$d_{100}$ (Å)	$D_p$ (Å) <sup>a</sup>	$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	Sulfur content (mmol H <sup>+</sup> /g SiO <sub>2</sub> )		Acid capacity (mmol H <sup>+</sup> /g SiO <sub>2</sub> ) <sup>b</sup>
					Theoretical	Empirical <sup>c</sup>	
SBA-15	95	68	767	1.03	–	–	–
5% SBA-ar-SO <sub>3</sub> H	98	71	768	1.01	0.83	0.78	0.80
10% SBA-ar-SO <sub>3</sub> H	102	65	652	0.87	1.67	1.42	1.46
15% SBA-ar-SO <sub>3</sub> H	104	62	560	0.56	2.51	1.96	2.03
10% SBA-pr-SO <sub>3</sub> H	100	61	857	1.10	1.67	1.44	1.50
H-ZSM-5	–	5.5	402	0.09	–	–	–
H-Mordenite	–	6.5	500	0.11	–	–	–
Al-MCM-41	–	27	1036	0.81	–	–	–
Al-SBA-15	–	56	877	0.91	–	–	–

<sup>a</sup> Calculated from the peak positions of the distribution curves.

<sup>b</sup> Based on acid–base titration.

<sup>c</sup> Based on S elemental analysis.

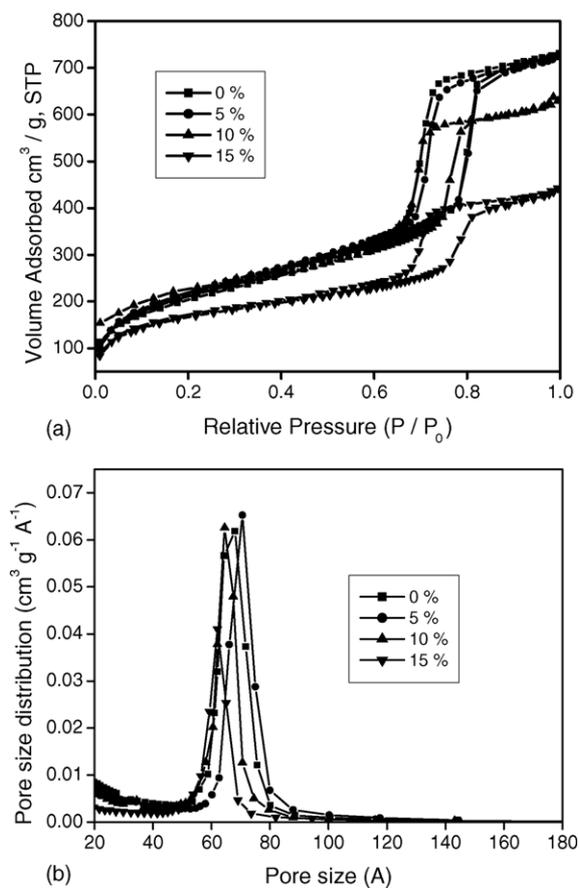


Fig. 2. N<sub>2</sub> adsorption-desorption isotherms (a) and BJH pore size distribution (b) of the SBA-15 mesoporous materials with different CSPTMS concentrations in the starting mixture.

lized SBA-15 materials as well as over several other acidic catalysts such as H-ZSM-5, H-mordenite, Al-MCM-41, and Al-SBA-15. Other than the desired product  $\epsilon$ -caprolactam, cyclohexanone and small amounts of high molecular weight products were observed. Mass balance between the reactant and products was based on the area sum, which could exceed 97%. Besides, no conversion of the substrate was observed in the absence of acid catalyst.

### 3.2.1. Comparison of catalytic activities among porous acid catalysts

The catalytic activity of 10% SBA-ar-SO<sub>3</sub>H for rearrangement of cyclohexanone oxime in chlorobenzene solvent was compared with the activities of several other porous acid catalysts. As seen in Fig. 3, both sulfonic acid-functionalized SBA-15 materials show similar high conversions (ca. 40%) of the substrate, but the selectivity to caprolactam on 10% SBA-ar-SO<sub>3</sub>H catalyst is much higher than that on 10% SBA-pr-SO<sub>3</sub>H. These phenomena may be caused by two factors. On the one hand, as an electron-withdrawing substituent, the phenyl ring adjacent to the sulfonic group can disperse the negative charge and stabilize the anion, and thus increase the acid strength of the sulfonic

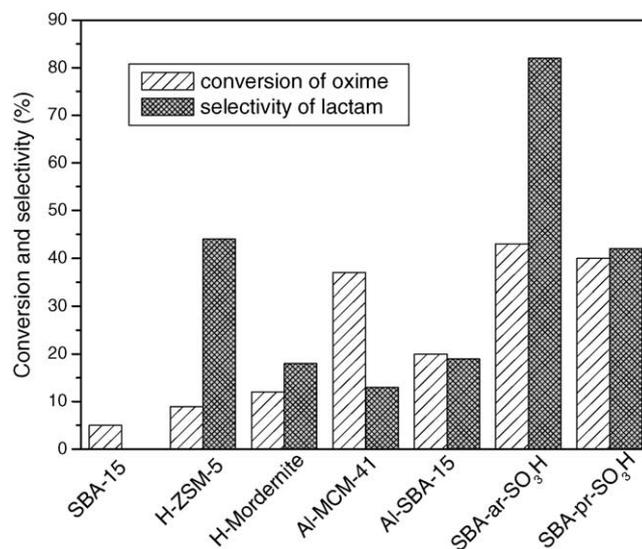


Fig. 3. Activities of oxime rearrangement reaction and lactam selectivities in chlorobenzene solvent over different porous acid catalysts. Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 10 mL chlorobenzene; 130 °C; 24 h.

group [23]. On the other hand, the phenyl group is more hydrophobic than the propylene group and thus the formation of cyclohexanone as a side product through hydrolysis of oxime is reduced [41]. Indeed, the TG analysis showed that the extracted 10% SBA-ar-SO<sub>3</sub>H contained ca. 5 wt.% of water, which was lost in the range of 30–100 °C, while the extracted 10% SBA-pr-SO<sub>3</sub>H contained up to 15 wt.% of water.

Al-MCM-41 and Al-SBA-15 gave 37 and 20% conversions of cyclohexanone oxime; however, the selectivities to  $\epsilon$ -caprolactam were only 13 and 19%, respectively. According to the report by Melero et al. [23], the acid strength of these mesoporous materials increases in the order of Al-MCM-41 (Si/Al = 30) < 10% SBA-pr-SO<sub>3</sub>H < 10% SBA-ar-SO<sub>3</sub>H, which is in good agreement with the catalytic activities and lactam selectivities observed in Fig. 3. On the other hand, microporous H-ZSM-5 and H-mordenite gave very low conversions of cyclohexanone oxime and low selectivities to  $\epsilon$ -caprolactam, though they possess large amounts of acid sites and high acid strengths. The catalytic reaction probably proceeded mainly on the exterior surface due to the diffusion limitation of the liquid in the micropores. Similar results on the micropore zeolites, however, were also observed in the heterogeneous gas-phase Beckmann rearrangement [36–40]. It is clear that the relatively large mesopores on SBA-15 facilitate the diffusion of the reactant and product molecules in liquid phase Beckmann rearrangement reaction. Moreover, the catalytic activity strongly depends on the amounts of acid sites accessible by the reactant and the strength of the acid sites. The strong acid strength would enhance the selectivity of  $\epsilon$ -caprolactam.

Table 2  
Effect of solvent on catalytic performance of the extracted SBA-15 with 10 mol% CSPTMS in the synthesis mixture

Solvent	Dielectric constant <sup>a</sup>	Conversion of oxime (%)	Selectivity to lactam (%)
<i>o</i> -Xylene	2.57	28.9	47.9
Anisole	4.33	31.2	56.1
Chlorobenzene	5.62	46.1	73.5
Pentanol	20.3	14.2	0
Nitropropane	23.2	46.2	43.5
<i>N,N</i> -Dimethylformamide	37.3	–	–
Dimethyl sulfoxide	46.7	51.7	23.6

Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 20 mL solvent; 130 °C; 24 h.

<sup>a</sup> Values at 20 °C.

### 3.2.2. Effects of different solvents on rearrangements of cyclohexanone oxime

The catalytic performance of 10% SBA-ar-SO<sub>3</sub>H in oxime rearrangement reaction in various solvents is shown in Table 2. The solvent was found to have great influence on the oxime conversion and lactam selectivity. The oxime conversion in aprotic solvents generally increases with the dielectric constant or the polarity of the solvent, but chlorobenzene with medium polar strength displays the highest selectivity to lactam. These results can be explained by considering that the polar solvent molecule can stabilize the reaction intermediates such as *N*-protonated oxime. In contrast, *N,N*-dimethylformamide, which possesses weak basicity, probably poisons the active acid sites on the catalyst and therefore hinders the catalytic reaction. In protic solvent pentanol, 14.2% of oxime was transformed to parent hexanone and no lactam was formed, similar to the liquid phase rearrangement reaction of oxime on H-beta zeolite [8].

It is well known that the polarity of solvent has great effect on the oxime conversion and product selectivity in liquid phase Beckmann rearrangement. According to Nguyen et al. [33,34], oxime rearrangement is initiated by the attack of the proton from a Brønsted acid site to the nitrogen atom of oxime, followed by the proton transfer from nitrogen to oxygen atom. Then, the alkyl migration occurs simultaneously with the elimination of the protonated hydroxyl group. The proton transfer from nitrogen to oxygen is a 1,2-H-shift reaction with high activation energy. This process of forming O-protonated oxime is considered the rate-determining step in Beckmann rearrangement. In the presence of polar solvent, the stabilizing interaction between the solvent molecule and the migrating hydrogen in the transition structure would lower the energy barrier of 1,2-H-shift. It was suggested that a solvent having larger proton affinity would induce a more positive catalytic effect in Beckmann rearrangement [35]. Our catalytic results in aprotic solvents are consistent with this proposal. However, in protic solvents the large amount of adsorbed water facilitates the hydrolysis of oxime to form ketone instead of rearrangement to form lactam.

### 3.2.3. Effect of reaction temperature on catalytic performance

The effect of the reaction temperature on oxime conversion and lactam selectivity was examined in chlorobenzene solvent over 10% SBA-ar-SO<sub>3</sub>H; the results are illustrated in Fig. 4. It was found that the oxime conversion increases gradually with the reaction temperature from 23.2% at 110 °C to 46.1% at 130 °C. The yield of the desired product lactam also increases with reaction temperature, while the yield of parent hexanone slightly decreases with the temperature. Since the lactam selectivity is maintained around 70–76% and does not significantly vary with temperature, these results indicate that elevated temperature might favor the formation of high molecular weight by-products.

### 3.2.4. Effect of arenesulfonic acid loading

The catalytic performance of the arenesulfonic acid-modified SBA-15 with different acid loadings were studied in chlorobenzene solvent at 130 °C. As shown in Table 3, pure siliceous SBA-15 shows very low activity, and oxime was only converted to parent cyclohexanone through hydrolysis reaction. Over the sulfonic acid-functionalized

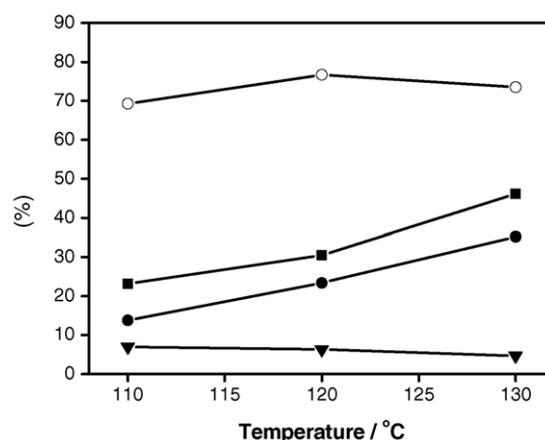


Fig. 4. Effect of reaction temperature on the reaction performance. (■) Conversion of oxime; (●) lactam yield; (▼) cyclohexanone yield; (○) selectivity of lactam. Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 20 mL chlorobenzene; 24 h.

Table 3  
Effect of CSPTMS loading in the synthesis mixture on the catalytic performance of the extracted SBA-15

Catalyst	Conversion of oxime (%)	Cyclohexanone yield (%)	Lactam yield (%)	Selectivity to lactam (%)	TON <sup>a</sup>
SBA-15	6.0	6.0	0	0	–
5% SBA-ar-SO <sub>3</sub> H	30.5	4.9	21.4	70.2	3.21
10% SBA-ar-SO <sub>3</sub> H	46.1	4.7	33.9	73.5	3.09
15% SBA-ar-SO <sub>3</sub> H	51.9	5.4	42.2	81.3	2.98

Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 20 ml chlorobenzene; 130 °C; 24 h.

<sup>a</sup> TON: expressed as  $\epsilon$ -caprolactam (mol)/SO<sub>3</sub>H (mol).

SBA-15, the oxime conversion and lactam selectivity increase with the acid loading. Moreover, the yield of lactam is directly proportional to the amount of sulfonic acid groups on SBA-15 (Fig. 5). These results confirm that the Beckmann rearrangement of oxime to lactam is catalyzed by the SO<sub>3</sub>H sites. In contrast, it is noticeable that the yield of side-product cyclohexanone seems to be independent of the acid loading, and the value observed over arenesulfonic acid-modified SBA-15 is slightly less than that over pure siliceous SBA-15. These results suggest that the formation of parent hexanone is probably catalyzed by the Si–OH silanol groups. In other words, the formation of lactam and that of parent hexanone were catalyzed by different active sites. The catalytic activity of each sulfonic acid site in lactam formation is expressed by turnover number (TON) and these values are also given in Table 3. It can be seen that the TONs over all the arenesulfonic acid-functionalized SBA-15 samples with different loadings are similar, revealing that the arenesulfonic acid groups were highly homogeneously dispersed on the surface of SBA-15 framework and were accessible to the oxime molecules.

### 3.2.5. Dependence of reaction period

The catalytic performance of 10% SBA-ar-SO<sub>3</sub>H catalyst as a function of reaction period was examined

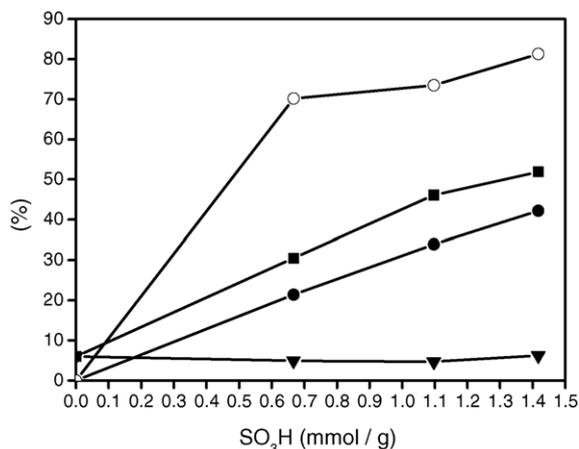


Fig. 5. Dependence of catalytic activity on the SO<sub>3</sub>H loadings in arenesulfonic acid-modified SBA-15. (■) Conversion of oxime; (●) lactam yield; (▼) cyclohexanone yield; (○) selectivity of lactam. Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 20 ml chlorobenzene; 130 °C; 24 h.

in chlorobenzene at 130 °C; the results are illustrated in Fig. 6. In the first 3 h, the oxime conversion and lactam yield increase dramatically to 32.5 and 22.5%, respectively. Then, the reaction rate slows down. The oxime conversion and lactam yield increase almost in parallel as the reaction proceeds up to 50 h. Over the whole course of the catalytic reaction, the selectivity of lactam only increases slightly. On the other hand, the conversion of oxime to parent hexanone rapidly reaches a maximum in about 1 h. It decreases slightly as the reaction continues up to 50 h, indicating that the catalytic active sites for oxime hydrolysis reaction deactivate rapidly at the beginning of the reaction. These results again indicate that the active sites for the formation of lactam and cyclohexanone are probably different. The almost constant rate of lactam yield after ca. 3 h implies that the reaction is independent of the oxime concentration in this period. These results also show that the catalytic active sites for Beckmann rearrangement do not deactivate during the reaction period. On the other hand, the lack of a maximum in lactam selectivity during the reaction time course implies that the conversion of oxime to lactam and the formation of small amount of high molecular weight by-products may proceed in parallel pathways on the same SO<sub>3</sub>H sites. The possible pathways of the reactions

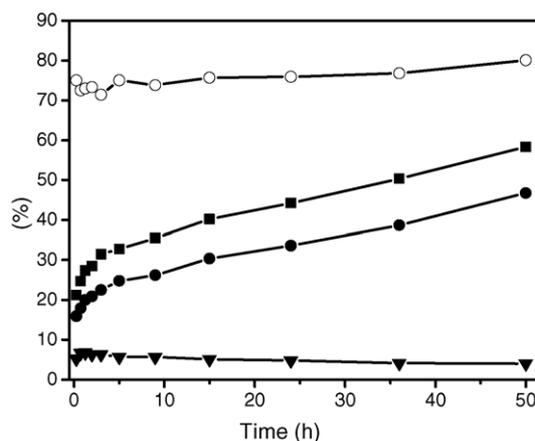
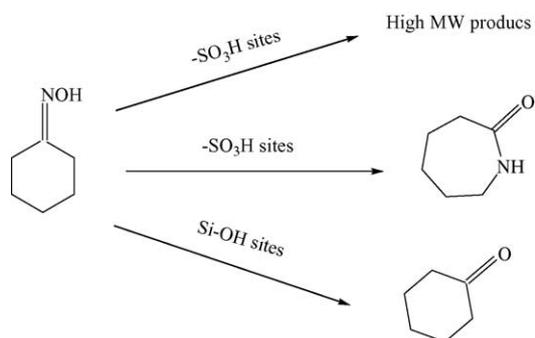


Fig. 6. Catalytic activity of arenesulfonic acid-functionalized SBA-15 as a function of reaction period: (■) conversion of oxime; (●) lactam yield; (▼) cyclohexanone yield; (○) selectivity of lactam. Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime; 20 mL chlorobenzene; 130 °C.



Scheme 1. Reaction pathways of oxime rearrangement on arenesulfonic acid-functionalized SBA-15 catalyst.

occurring on the surface of sulfonic acid-functionalized SBA-15 are proposed in Scheme 1.

The intra-particle diffusion can be excluded from being the rate-determining step, based on the results of Figs. 5 and 6. For a reaction controlled by diffusion inside the nanopores, the rate of the reaction should be  $(n + 1)/2$  order to the reactant concentration and independent of the concentration of catalytic active sites, where  $n$  is the true reaction order of the chemical reaction and should be an integer value or 0 [42]. As a result, the apparent order would be  $1/2$ , 1,  $3/2$ , etc. However, Fig. 5 shows that the oxime conversion and lactam yield are almost linearly proportional to the concentration of the catalytic active sites. Moreover, Fig. 6 shows that the oxime conversion and lactam yield increased almost linearly with time in 3–50 h. In other words, the rate of lactam formation was almost constant in this period. A constant rate implies that the order of the reaction is zero order to the reactant concentration. That occurs only when the rate-determining step is the surface chemical reaction, and the rate is constant because the surface active sites are saturated with adsorbed reactant molecules. These results further support the general recognition that the relatively large pores of mesoporous materials would facilitate the diffusion of molecules, even in liquid phase.

### 3.2.6. Effect of oxime concentration

The effect of oxime concentration was examined in chlorobenzene on 10% SBA-ar-SO<sub>3</sub>H catalyst; the results are shown in Fig. 7. The oxime conversion decreased from 50.5 to 42.8% when the oxime concentration in chlorobenzene increased from 0.02 to 0.20 mol/L, while the lactam selectivity increased from 64.8 to 82.2%. In addition, the hexanone yield decreased slightly from 6.5 to 3.7%. These results show that, although polar solvent would induce a positive catalytic effect in Beckmann rearrangement, an excess amount of solvent was not beneficial to selective conversion of oxime to lactam.

### 3.2.7. Leaching of arenesulfonic acid groups

Leaching of arenesulfonic acid groups in the catalytic reaction was examined with 10% SBA-ar-SO<sub>3</sub>H catalyst.

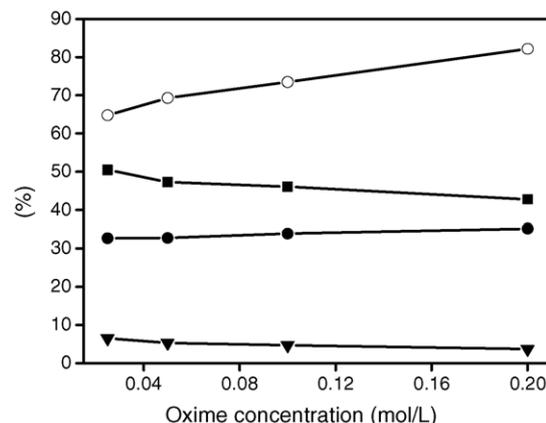


Fig. 7. Effect of the oxime concentration on the catalytic activity. (■) Conversion of oxime; (●) lactam yield; (▼) cyclohexanone yield; (○) selectivity of lactam. Reaction conditions: 0.2 g catalyst; 2 mmol cyclohexanone oxime;  $x$  mL chlorobenzene; 130 °C; 24 h.

Acid–base titration revealed that the acid amount was slightly reduced from 1.46 to 1.40 mmol of H<sup>+</sup>/g SiO<sub>2</sub> after the catalytic reaction at 130 °C for 24 h. However, elemental analysis of the used SBA-ar-SO<sub>3</sub>H catalyst showed slight increases in carbon and nitrogen contents after the reaction, which is in agreement with the result of TG analysis, where a new weight loss (5–6%) was observed at ca. 330 °C and was assigned to the adsorbed organic species in the reaction. As a result, the leaching of sulfonic acid groups during the catalytic reaction is considered negligible and the slight decrease in acid amount is attributed to the increase in weight basis from adsorption of organic species during the reaction [29].

## 4. Conclusions

Arenesulfonic acid-functionalized SBA-15 with up to 15% acid loadings was synthesized by co-condensation of TEOS and CSPTMS using P123 as the pore-directing agent. The materials were found efficient in catalyzing the Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam in the liquid phase. The oxime conversion and lactam selectivity increase with the amount of arene-SO<sub>3</sub>H groups. The polarity of solvent affected the performance of the catalyst tremendously, and chlorobenzene gave the highest lactam selectivity. The liquid phase reaction of oxime rearrangement to form lactam and hydrolysis to form parent hexanone are suggested to proceed on different active sites of SO<sub>3</sub>H and Si–OH, respectively. In comparison with other porous acid catalysts such as SBA-pr-SO<sub>3</sub>H, H-ZSM-5, H-mordenite, Al-MCM-41 and Al-SBA-15, the mesoporous SBA-ar-SO<sub>3</sub>H showed higher catalytic activity and lactam selectivity. The strong acid strength of the SBA-ar-SO<sub>3</sub>H catalysts is in favor of Beckmann rearrangement of cyclohexanone oxime to form  $\epsilon$ -caprolactam.

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