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Applications of solid catalysts in reactions of fine chemicals (3/3)

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SBA-15

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SBA-15 mesoporous silica functionalised with propylene- and arene-sulfonic acid groups were prepared by co-condensation method, and the arene-sulfonic acid functionalised mesoporous silica was found to be more efficient than the one with propylene-sulfonic acid as the catalyst for the liquid phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

INTRODUCTION

The importance of the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, which is a valuable starting material for the manufacture of nylon fibers, has been widely documented in the literature.[1, 2] Current commercial processes for this reaction, however, require the use of oleum or sulfuric acid as a reaction medium.[3] That caused problems in product separation, corrosion hazard of the reactor and the substantial 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 decade, various solid catalysts have been applied to the Beckmann rearrangement of cyclohexanone oxime,[4] 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. 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.[5] However, their uses are often restricted by the small pore diameters of less than 1nm. For reactions performed in the liquid phase, the reaction substrates and products need to diffuse rapidly toward and

away from the catalytic active sites. The discovery of mesoporous molecular sieves of M41S family attracted much attention of many research groups because these 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.[6] 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.[7] 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 having larger pore dimensions, acidity of mesoporous materials like Al-MCM-41 and Al-SBA-15, is much weaker than that of microporous zeolites.[8] In order to overcome this drawback, ordered sulfonic-acid modified mesoporous silica has been prepared ether via post-grafting technique or through one-pot synthesis.[9-14] The purpose of this study is to reveal the catalytic performance of the propylene- and arene-sulfonic acid- functionalised SBA-15 in liquid phase Beckmann rearrangement of cyclohexanone oxime to caprolactam.

EXPERIMENTAL
Catalyst Preparation
Propylene- and arene-sulfonic acid-functionalised SBA-15 materials were prepared by one-pot synthesis according to the procedures described in the literature.[10] For the arene-sulfonic acid-functionalised SBA-15, 4 g of Pluronic 123 (Aldrich) was dissolved in 125 g of 1.9 M HCl solution at room temperature. After adding tetraethyl orthosilicate (TEOS, Aldrich), the resultant solution was equilibrated at 40°C for 45 min. before CSPTMS (2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane, Gelest) and H_2O_2 were introduced into the solution. The molar composition of the gel versus 4 g of P123 was 0.0369 TEOS : 0.0041 CSPTMS : 0.0123 H_2O_2 : 0.24 HCl : 6.67 H_2O, where CSPTMS : TEOS = 1 : 9. The mixture was stirred at 40 ^{o}C for 20 h and then transferred

into 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-synthesised material by refluxing in ethanol for 24 h. Finally, the material was filtered, washed several times with water and ethanol and dried at 50°C. The sample is abbreviated as SBA-arene-SO$_3$H. Similarly, propylene-sulfonic acid-functionalised SBA-15 (abbreviated as SBA-propyleneSO$_3$H) was synthesized via the co-condensation of MPTMS (mercaptopropyltrimethoxysilane) and TEOS (MPTMS : TEOS = 1 : 9).

RESULTS AND DISCUSSION
Characterization of Catalysts
As shown in Fig. 1, the small-angle X-ray powder diffraction (XRD) patterns of the three mesoporous samples, pure siliceous SBA-15 and those functionalised with propylene- and arene-sulfonic acids, all exhibit one very intense peak and two weak peaks indexed to (100), (110) and (200) reflections, indicating that the materials contained well-ordered hexagonal arrays of one-dimensional channel structure.[9] Besides, the lattice expands as the sulfonic acid groups were introduced in the framework by co-precipitataion, in agreement with the results reported in the literature.[10] Thermogravimetric analysis (TGA, Du Pont 951) in air and elemental analysis (EA, Heraeus) showed that the surfactants in the as-synthesized samples were almost removed by extraction. The N_2 adsorption-desorption isotherms showed characteristic of type IV of the IUPAC classification. The analysis of the isotherms of the sulfonic acid functionalised samples demonstrated no obvious change in BET surface area for SBA-propyleneSO$_3$H but slight decrease for SBA-areneSO$_3$H, in comparison to that of pure siliceous SBA-15 (Table 1). The mean pore size and pore volume were smaller for the sulfonic acid functionalised samples. Between the two functionalised samples, the values for SBA-propyleneSO$_3$H were smaller than those for SBA-areneSO$_3$H, 38 Å and 0.81

cm^3/g in comparison to 52 Å and 1.20 cm^3/g. That is attributed to the relatively large size of the benzene ring in comparison to the propylene group. Nevertheless, the pore diameter still remained very narrow distributed with major fractions in 5.5- 7.0 nm. The acid capacity of the sulfonic acid modified samples was determined by acid-base titration.[9, 15] The exchange values were both around 1.5 mmol of H$^+$ per g of SiO$_2$, and that was in consistence with the results from TG analysis and sulfur elemental analysis.
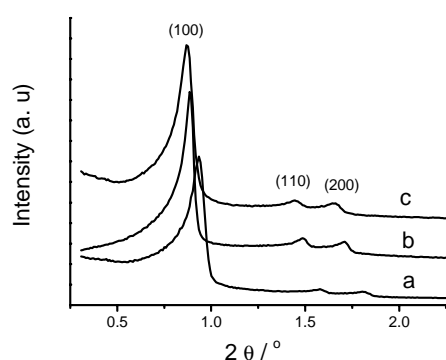

Fig. 1.
X-ray powder diffraction patterns of the extracted samples: (a) pure siliceous SBA-15, and those prepared with (b) 10 mol% propylenesulfonic acid, and (c) 10 mol% arenesulfonic acid.

Catalytic Studies

The Beckmann rearrangement of cyclohexanone oxime was carried out in chlorobenzene solvent at 132°C for 24 h under nitrogen. In order to remove adsorbed moisture in the catalyst, 0.2 g of the solid catalyst was pre-refluxed with toluene for 2 h, then *in-situ* dried in N$_2$ flow at 150°C overnight, then cooled to ca. 130°C before 2 mmol cyclohexone oxime solution in 10 mL chlorobenzene solvent was poured into the reactor. For comparison, several other acidic catalytic materials such as H-ZSM-5, H-mordernite, Al-MCM-41, and Al-SBA-15 were examined under similar conditions. The products were analyzed using a Chrompak CP 9000 gas chromatograph and identified with a HP 6890 GC-MS. It was found that other than the desired product, ε-caprolactam, cyclohexanone and small amount of high

molecular weight products were also observed. The reaction results were shown in Table 1. No conversion of cyclohexanone oxime was observed in the absence of catalyst. Pure siliceous SBA-15 only showed negligible activity, and caprolactam could hardly be detected in the products. H-ZSM-5 and H-mordernite showed very low conversion of cyclohexanone oxime and low selectivity to ε-caprolactam, though they possessed large amounts of acid sites and high acid strength in their small pores. The catalytic reaction might be performed only on the exterior surfaces due to the diffusion limitation of the liquid in the small pores. Al-MCM-41 and Al-SBA-15 showed 37 % and 20 % conversions of cyclohexanone oxime, however, the selectivities to ε-caprolactam were only 13 % and 19 %, respectively. In comparison, both sulfonic acid functionalised SBA-15 showed similar high conversions of substrate, but the selectivity to caprolactam on SBA-areneSO$_3$H catalyst was much higher than that on SBA-propyleneSO$_3$H. This phenomenon may be caused by two factors. On 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.[10] On the other hand, the phenyl group is large enough to make the active sites on the surface more hydrophobic than the propylene group, and thus facilitate the diffusion of the organic reactants and products in the liquid phase.[13] Thermogravimetric analysis showed that the extracted SBA-areneSO$_3$H contained ca. 5 wt% of water, which lost in the range of 30-100°C, while the extracted SBA-propyleneSO$_3$H had up to 15 wt% of water. As shown in Table 1, the liquid phase Beckamnn rearrangement reaction of cyclohexanone oxime to ε-caprolactam strongly depends on the amounts of acid sites and the acid strength on the catalyst surface. The strong acid strength would enhance the selectivity of ε-caprolactam.

Leaching of sulfonic acid groups in the catalytic reaction was examined with SBA-areneSO$_3$H catalyst. Acid-base titration

revealed that the acid amount was slightly reduced from 1.5 to 1.4 mmol of H^+ /g SiO_2 after the catalytic reaction at 132^oC. However, elemental analysis of the used SBA-15 catalyst indicated slight increase in carbon and nitrogen contents after the reaction, in agreement with the result of thermogravimetric analysis, where a new weight loss (5~6%) was observed at ca. 330^oC, 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.[14]

Table 1.

Liquid phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam over various solid catalysts

Entry	Catalyst	S_{BET} (m^2/g)	D_p (Å)	Conv.[a] (%)	Select.[b] (%)
1	blank	-	-	0	-
2	SBA-15	786	52	< 5	-
3	H-ZSM-5[c]	402	5.5	9	44
4	H-Mordernite[d]	500	6.5	12	18
5	Al-MCM-41[e]	036	26	37	13
6	Al-SBA-15[f]	877	56	20	19
7	SBA-15-arene-SO_3H[g]	652	38	43	82
8	SBA-15-propyl ene-SO_3H[g]	857	45	40	42

[a] Conversion of cyclohexanone oxime. [b] Selectivity of ε-caprolactam. [c] Si/ Al = 115.
[d] Si/ Al = 10. [e] Si/ Al = 32. [f] Si/ Al = 60.
[g]acid capacity = 1.5mmol H^+ /g SiO_2

In conclusion, arenesulfonic acid-functionalised SBA-15 is a new and very effective acid catalyst for the liquid phase Beckmann rearrangement of cyclohexanone oxime. It shows high selectivity to ε-caprolactam and no leaching of acid sites during the reaction.

REFERENCES

1. F. Cavani and F. Trifiro, *Appl. Catal. A,* 1992, **6**, 245.

2 *European Chemical News*, 18 (25-31 October 1999)

3 H. Ichihashi and H. Sato, *Appl. Catal. A*, 2001, **221**, 359.

4 Y. Izumi and T. Fujita, *J. Mol. Catal.,* 1996, **106**, 43. H. Sato, H. Yoshioka and Y. Izumi, *J. Mol. Catal.,* 1999, **149**, 25. Y. Chung and H. Rhee, *J. Mol. Catal.,* 2001, **175**, 249. R. Maheswari, K, Shanthi, T. Sivakumar and S. Narayanan, *Appl. Catal. A*, 2003, **248**, 291. R. Bechara, A. D'Huysser, M. Fournier, L. Forni, G. Fornasari, F. Trifiro and A. Vaccari, *Catal. Lett.*, 2002, **82**, 59.

5 M. E. Davis, *Micropor. Mesopor. Mater.,* 1998, **21**, 173. R. A. Sheldon, J. A. Elings, S. K. Lee, H. E. B. Lempers and R. S. Downing, *J. Mol. Catal. A*, 1998, **134**, 129. A. Corma and H. Garcia, *Catal. Today*, 1997, **38**, 257. W. F. Hölderich, M. Hesse and F. Näumann, *Angew. Chem., Int. Ed. Engl.,* 1988, **27**, 226.

6 J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins and J.L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834. P.T. Tanev and T.J. Pinnavaia, *Science*, 1995, **267**, 865. X.S. Zhao, G.Q. Lu and G.J. Miller, *Ind. Eng. Chem. Res.*, 1996, **35**, 2075.

7 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Frederichson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.

8 A. Corma, V. Fornes, M.T. Navarro and J. Perez-Pariente, *J. Catal.*, 1994, **148**, 569.

9 D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.* 2000, **12**, 2448.

10 J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, *J. Mater. Chem.,* 2002, **12**, 1664.

11 Q. Yang , M. P. Kapoor and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 9694. J. G. C. Shen, R. G. Herman and K. Klier, *J. Phys. Chem., B*, 2002, **106**, 9975. K. W. Wilson, A. F. Lee, D. J. Macquarrie and J. H. Clark, *Appl. Catal. A,* 2002, **228**, 127.

12 E. Cano-Serrano, J. M. Campos-Martin and J. L. G. Fierro, *Chem. Commun.*, 2003, 246. V. M. V. Rhijn, D. E. De Vos, V. F. Sels, W. D. Bossaert and P. A. Jacobs, *Chem. Commun.*, 1998, 317.

13 S. Hamoudi and S. Kaliaguine, *Micropor. Mesopor. Mater.,* 2003, **59**, 195.

14 D. Das, J. F. Lee and S. F. Cheng, *Chem. Commun.*, 2001, 2178.

15 J. G. C. Shen, T. H. Kalantar, R. G. Herman, J. E. Toberts and K. Klier, *Chem. Mater.*, 2001, **13**, 4479.