Sulfonic acid functionalised SBA-15 as catalysts for Beckmann rearrangement and esterification reaction

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Abstract Hybrid inorganic–organic solid acid materials SBA-15–Ph–SO₃H were synthesized by the directly co-condensation method under the acid medium. The resulting materials perform well both in the liquid phase Beckmann rearrangement (The yield is 32.3%) and esterification reaction (The yield is 95.5%). And more, the catalysts show the different catalytic performance in these two reactions.

Keywords Beckmann rearrangement · Esterification reaction · SBA-15 · Arenesulfonic acids

1 Introduction

At present, the more and more harsh environmental rules incite the companies/factories to improve their technology vigorously and make the manufacture procedure more environment compatible. The conversion of cyclohexanone oximes into the corresponding lactams that is the raw material of Nylon 6 is one of the most important industrial reactions [1]. Conventionally, this process employs the fuming sulfuric acid as a catalyst [2] due to the reasons that this reaction only requires the catalytic amount of a strong acid and that the fuming sulfuric acid can prevents the secondary reactions such as hydrolysis. However, the using

of fuming sulfuric acid brings about a number of disadvantages like the large amount of low-value by-product (ammonium sulphate), the inherent corrosive nature of the acid and violent exothermic reaction. In order to overcome these inconveniences, a wide variety of solid acid was studied to instead of the fuming sulfuric acid. Based on the different vapour-phase Beckmann rearrangement systems, all sorts of the acidity, such as, the strong [3], the medium [4], the weak acid [5] and even the neural silanol [6], were reported that are responsible for this rearrangement procedure. On the contrary, only the strong Brønster acid site [7–8] shows a good performance for this conversion in the liquid-phase Beckmann rearrangement. Ethyl caprylate (EP) is widely used in the manufacturing of cosmetics or in food industry [9] and large-scale preparation of this product also need the liquid acid as catalysts. Since ethyl caprylate is related to the human consumption, the product has to be as pure as possible, and, thus, trace impurities from corrosion products are not allowed. In this paper, we synthesize the arenesulfonic functionalized SBA-15 via direct one-step synthesis method. The obtained SBA-15–Ph–SO₃H materials show a good catalytic performance on the typical strong acid catalysis reactions. Interesting, the –Ph–SO₃H groups play a different role in the liquid phase Beckmann rearrangement of cyclohexanone oxime (CHO) and esterification of caprylic acid (CA).

2 Experimental

Arenesulfonic functionalized mesoporous materials were synthesized as follows: 4 g Pluronic 123 were dissolved in 125 ml of 2 M HCl at room temperature. The solution was heated to 40 °C before adding TEOS. After 45 min of

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TEOS prehydrolysis, 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (CSPTMS) was added to the mixture. The molar composition of the resulting solution for 4 g of copolymer was $1 + x \text{ SiO}_2 : x \text{ CSPTMS} : 6.5\text{HCl} : 180\text{H}_2\text{O}$ with $x = 0.05, 0.1, 0.15$ and 0.2 , respectively. The mixture was stirred for 24 h at 40°C and then aged at 100°C for 24 h under static conditions. The solid product was recovered by filtration and air-dried at room temperature overnight. The template was first removed by extraction with ethanol under reflux for 24 h, then by calcination in air at 200°C for 24 h. The X-ray powder diffraction (XRD) data were acquired on a Bruker-axs D8 device using Cu K α radiation. The data were collected from 0.6 to 5° with a resolution of 0.02° . Nitrogen adsorption and desorption isotherms at 77 K were measured using Micromeritics ASAP 2010 system. The data were analyzed using the BJH model and the pore size distributions were calculated by the desorption branches. Sulfur and silicon composition of SBA-15-Ph-SO $_3\text{H}$ samples were determined by elemental analysis in CNRS Analysis center in Vernaison (France). The acid number of SBA-15-SO $_3\text{H}$ samples were measured by the in situ thermal desorption experiment which carried out by treatment of the samples at increase temperature in vacuum 1 h each time. The catalysis tests were carried out in a 50 ml two-necked flask equipped with a reflux condenser. The products were analyzed by gas chromatography (GC) using a Delsi-Nermag 200 instrument and a 25 m capillary column of cross linked 5% phenylmethylsilicone.

3 Results and discussion

The results of N_2 adsorption-desorption isotherms measurements for the different SBA-15 samples prepared with various concentrations of CSPTMS in the initial mixture (Fig. 1) suggest that all the samples are the mesoporous materials.

Among them, the isotherm of sample b and c are the typical type IV isotherm, like that of pure SBA-15 (sample a). However, the isotherms of sample d and e that have the CSPTMS/(CSPTMS + TEOS) ratio above 0.1 in the initial mixture are obviously different from the type IV isotherm. Indeed, there are two hysteresis loops as a result of a double pore diameter distribution appear in these isotherms. There is another smaller pore about $39\text{ \AA}$ besides the $60\text{ \AA}$ one which present solely in the pure silica SBA-15 material, obviously exist in these two samples. And for sample e, this pore ($39\text{ \AA}$) became the major one (The volume of this pore is 74% of the total pore volume). In order to know the reason and the stability for this two pores system, we calcined the sample e under a drastic condition (600°C). The resulting sample (Fig. 1f) shows the two

Fig. 1 N_2 adsorption/desorption isotherm (left) and pore size distributions (right) of SBA-15-SO $_3\text{H}$ samples. a: Pure-SBA-15; b: CSPTMS/ SiO_2 + CSPTMS = 0.05; c: CSPTMS/ SiO_2 + CSPTMS = 0.1; d: CSPTMS/ SiO_2 + CSPTMS = 0.15; e: CSPTMS/ SiO_2 + CSPTMS = 0.2; f: Sample e calcined at 600°C

pores system is still exist while the part of the big pore ($60\text{ \AA}$) become the major pore again (The volume of this pore is 77% of the total pore volume, while, it is only 26% for sample e). This result is corresponded well to the results of XRD. The XRD pattern of sample e (Fig. 2) is improved greatly and corresponds to the typical hexagonal texture structure after calcinations at 600°C (Fig. 2f).

Based on above results, we think the two pores system mainly forms at the self-assembling process while the introduction of arenesulfuric group into the channel of SBA-15 also can cause partly the two pores system. Both the reason that the two pores system loses the order of the hexagonal pore structure and the reason that the introduction

Fig. 2 XRD patterns of of SBA-15-SO₃H samples. a: Pure-SBA-15; b: CSPTMS/SiO₂ + CSPTMS = 0.05; c: CSPTMS/SiO₂ + CSPTMS = 0.1; d: CSPTMS/SiO₂ + CSPTMS = 0.15; e: CSPTMS/SiO₂ + CSPTMS = 0.2; f: Sample e calcined at 600 °C

of arenesulfuric group into the channel of SBA-15 can lead to a substantial loss in scattering contrast between the channel and the wall [10] are responded to the poor XRD pattern of these functionalized materials. Simultaneously, the two pore systems also suggest that the arenesulfuric

group probably concentration in some part of the channel in contrast to distribute orderly in the channel. That's why the big pore (60 Å) can be recovered obviously after calcinations of 600 °C. The sulfur amount and acid number increase linearly with the amount of CSPTMS in initial mixture (Table 1) also suggests that the arenesulfonic groups had been incorporated into the channel of SBA-15 successfully.

Just as shown in Scheme 1, since the part of 2-(4-chlorosulfonylphenyl) ethyl (–CH₂CH₂–Ph–SO₂Cl) contains the more hydrophobic organic groups of ethyl and benzene ring (with π electron) that has powerful dispersion force with the Pluronic 123, so, this part will prefer to enter the organic phase (P123) during the self-assemble procedure. It means the arenesulfonic groups will be only inside of mesoporous walls but no other choice, such as, be into or on the surface of mesoporous walls.

We first tested the catalytic properties of the new materials in the liquid phase Beckmann rearrangement of cyclohexanone oxime to produce ϵ -caprolactam (CL). Learning from the results of Table 2, we found: (1) for the pure SBA-15 sample, there is nearly no conversion of oxim.

(2) for the sulfonic acid functionalised SBA-15, the acid number of the catalyst has a good line relationship with the selectivity of CL while the conversion of CHO also increase slightly with the enhance of acid number, but it begin to decrease for sample e (Fig. 3). The first result suggests that the cyclohexanone oxime cannot be absorbed

Table 1 The results of elemental analysis for different SBA-15–SO₃H materials

Material	S (wt%)	Si (wt%)	Acid number(mmol/g)
CSPTMS/SiO ₂ + CSPTMS = 0.05	2.28	34.26	0.61
CSPTMS/SiO ₂ + CSPTMS = 0.1	3.66	30.68	1.14
CSPTMS/SiO ₂ + CSPTMS = 0.15	4.37	29.74	1.37
CSPTMS/SiO ₂ + CSPTMS = 0.2	5.31	27.65	1.66

Scheme 1

Table 2 Catalytic activities of different SBA-15–SO₃H materials (1)

Material	Acid number (mmol/g)	Conv. of CHO (%)	Selec. of CL (%)	Yield (%)	TON ^a
No	0	0	–	0	–
Pure-SBA-15	0	1.7	0	0	–
CSPTMS/SiO ₂ + CSPTMS = 0.05	0.61	47.0	20.7	9.7	1.47
CSPTMS/SiO ₂ + CSPTMS = 0.1	1.14	52.3	41.6	21.8	1.69
CSPTMS/SiO ₂ + CSPTMS = 0.15	1.37	53.0	51.5	27.3	1.76
CSPTMS/SiO ₂ + CSPTMS = 0.2	1.66	49.6	66.5	33.0	1.76

Reaction conditions: catalyst: 0.1 g; solvent: 20 ml (toluene); cyclohexanone oxime (CHO): 0.1 g; 130 °C; 24 h

^a TON: ε-caprolactam(mol)/Acid(mol)

Fig. 3 The relationship between the catalytic activity and the acid number of catalysts**Table 3** Catalytic activity of different SBA-15–SO₃H materials (2)

Materials	Acid number (mmol/g)	Conv. of CA (%)	Selec. of EP (%)	Yield (%)	TON ^a
No	–	3.1	100	3.1	–
Pure-SBA-15	0	3.8	100	3.8	–
CSPTMS/SiO ₂ + CSPTMS = 0.05	0.61	95.5	100	95.5	109.6
CSPTMS/SiO ₂ + CSPTMS = 0.1	1.14	92.1	100	92.1	56.6
CSPTMS/SiO ₂ + CSPTMS = 0.15	1.37	87.9	100	87.9	44.9
CSPTMS/SiO ₂ + CSPTMS = 0.2	1.66	80.1	100	80.1	33.8

Reaction conditions: catalyst: 0.1 g; solvent: 25 ml (ethanol); *n*-caprylic acid (CA): 7 mmol; 80 °C; 5 h

^a TON: Ethyl caprylate (mol)/Acid(mol)

Another application of the new materials was studied in the esterification of Ethyl caprylate (EP). On the contrary to the above experiment results, the sample with less arenesulfonic groups but better channel structure showed the highest conversation meanwhile the selectivity of EP are similar for all samples. And more, only the catalytic amount of strong acid is necessary for this reaction (Table 3). In this case, we think the procedure of this reaction is more simple and it is not necessary provide a special environment for the forming of the product.

The more the channel is advantage to the diffusion of substrate and products the faster the reaction can be proceed.

4 Conclusions

In conclusion, the arenesulfonic groups had been incorporated into the channel of SBA-15 successfully and probably concentration in some part of the channel. Based on the different reaction mechanism, the chemical amount strong acid and the catalytic amount strong acids are necessary for the liquid phase beckmann rearrangement and esterification reaction respectively. We believe these new type solid acid

materials will have wide application in the chemical industry.

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