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Catalytic Synthesis of n-Butyl Oleate by Cerium Complex Doped Y/SBA-15 Composite Molecular Sieve

DOI 10.1515/htmp-2016-0125
Received June 24, 2016; accepted November 17, 2016

Abstract: Cerium ion was successfully incorporated into Y/SBA-15 micro-mesoporous molecular sieves via the hydrothermal synthesis method to give a series of composite materials. The prepared materials were thoroughly characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray fluorescence spectroscopy (XRF), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and differential thermo gravimetric analysis (TG-DTG). The results showed that the prepared composite materials retained the highly ordered mesoporous two-dimensional hexagonal structure of SBA-15 and the octagonal structure of Y. The catalyst Ce-Y/SBA-15 was prepared and characterized, then the esterification of n-butanol and oleic acid was studied with bismuth phosphotungstate as a catalyst. Using this model reaction, the effects of Ce-HY/SBA-15, molar ratio of alcohol to oleic acid, amount of catalysts, reaction time and reaction temperature were investigated. The experimental results show that the optimal reaction conditions were: 1.8:1 molar ratio of alcohol to acid, 5 % catalyst amount (based on weight of oleic acid), 4 h reaction time and reflux conditions. Under these conditions, the yield of esterification was 90.6 %. The results suggest that the addition of Ce can effectively improve the catalytic properties of composite molecular sieves.

Keywords: micro-mesoporous composite materials, n-Butyl oleate, cerium complex doped, catalytic synthesis

Y-type zeolite molecular sieves are traditionally used as catalysts and adsorption materials. They have small dynamic pore sizes and can only be used with reactants that are smaller than about 1.2 nm. Thus, they limit the size and shape of reactants that can permeate into the catalyst's mesh framework, and influence the catalytic selectivity of the reaction. Although the pore size of the SBA-15 mesoporous molecule is uniformly sized and adjustable [1], its pore channels have long-range order and short-range disorder. In addition to that, mesoporous materials are amorphous and possess thinner pore walls which lower their thermal stability [2], hydrothermal stability and catalytic activity compared to the Y-type zeolite molecular sieve. Thus, the catalytic effect of single Y-type zeolite molecular sieve and SBA-15 mesoporous molecular sieve is not ideal [3, 4].

Micro-mesoporous composite materials contain both microporous structure and mesoporous structure, with a moderate ratio of microporous to mesoporous [5, 6]. Thus, they combine the advantages of both micro- and meso-porous materials, i. e., highly ordered structure and adjustable pore size [7, 8]. In order to improve the surface acidity of micro-mesoporous composite materials, both organic and inorganic methods have been used to modify the micro-mesoporous composite materials. For example, the SnO-SBA-15 material was prepared via incipient-wetness impregnation method and used in ester exchange reactions [9]. Additionally, Wang et al. [10] used modified composite materials in hydrocracking by taking MCM-41/Y composite molecular sieve and amorphous silica-alumina as main acid components and adding them with W-Ni active metal components.

n-Butyl oleate is an important chemical which is widely used in the preparation of reactive dyes, cationic dyes and disperse dyes. It is also used in skin care agents, hairsprays, cosmetics and leather processing agents [11].

The traditional method of preparing n-butyl oleate is the esterification of oleic acid and n-butanol in the presence of concentrated sulfuric acid as catalyst, under reflux conditions. Although this method can provide relatively high esterification rates, it has several disadvantages such as many side reactions, corrosion of the reaction equipment, and severe environmental pollution from the sulfur-containing wastewater discharge [12].

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Over the years, researchers have attempted various improvements in this reaction in terms of the catalysts used and the process, such as the use of acid cation exchange resin [13], zeolite molecular sieve [14], ionic liquid [15] and solid super acid [16] to replace sulfuric acid.

In the last decade a high number of studies about the hydrogenation cracking of heavy oil with catalysts including zeolites with a number of metals modification, like Co [17], Ni [18], Fe [19] were published.

Molecular sieves with metals modified are environmentally friendly catalysts which have the advantages of high activity and selectivity. Zi J F. [17] have previously used $Ni_2(SO_4)_3.(NH_4)_2S_2O_8$ as catalytic to synthesis n-butyl oleate. They obtained the yield of esterification by more than 90 % under the following conditions: temperature is 120 °C, time is 1.0 h, volume ratio of hydrogen and oil is 10.

In recent years, new environmentally friendly green catalysts such as heteropoly acids and their salts have attracted much attention [20, 21]. Rare earth elements have unique properties which can increase the acidity of the catalyst [22–24].

In the present paper, we have studied the modification effect of Ce^{4+} on the Y/SBA-15 molecular sieve. The Ce-modified Y/SBA-15 composite material was characterized by using Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), thermo gravimetric analysis (TG-DTG), and other techniques. With n-butyl oleate synthesis as the probe reaction, the catalytic performance of the modified micro-mesoporous materials was evaluated. Moreover, the influence of the esterification reaction conditions on catalytic activities was also evaluated. The results showed that the entry of Ce into the channels of Y/SBA-15 could effectively increase the catalytically active centers and improve the catalytic properties of molecular sieves.

Experimental

Reagents

Sodium aluminate, sodium hydroxide, sodium silicate, and tetraethylorthosilicate (TEOS) were all analytical pure reagents and purchased from Sinopharm Group Co. Ltd., China. Triblock copolymer poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (Pluronic P123) was purchased from Sigma Aldrich, USA.

Hydrothermal synthesis of micro- and meso-porous composite materials [22]

Synthesis of cerium modified micro-mesoporous composite material

P123 (2 g) was dissolved in 75 mL of HCl (1.6 mol/L solution). Then, 0.023 g of ammonium fluoride and 3 g of 1,3,5-trimethylbenzene were added. The mixture was stirred for 40 h, then 5 g of TEOS and 10 g of cerium nitrate–citric acid complex were added. The mixture was continued to stir for 20 h. Then, the pH value was adjusted to 6 and the mixture was subjected to hydrothermal crystallization for 24 h. After drying in the oven, a light yellow powder was obtained.

Catalyst characterization

FT-IR (Spectrum One, Japanese Electronics Co. Ltd., Japan) was conducted to analyze the change in the components during the catalyst preparation, with a scanning range of 4,000 ~ 400 cm^{-1}. KBr (IR grade) was used to prepare the pellet (1: 200). Thus, the raw powder of the molecular sieve was ground up with KBr in the ratio of 1:200 to obtain the KBr pellet.

X-ray fluorescence spectroscopy (XRF) was performed on a JEOL XRF spectrometer (X'Pert PRO, Japanese Electronics Co. Ltd., Japan).

Scanning electron microscopy (SEM/EDS) images were recorded on a JEOL JSM-7500F SEM instrument (Japanese Electronics Co. Ltd., Japan).

Synthesis of n-butyl oleate

Certain amounts of oleic acid and n-butyl alcohol were added in a dry 100 mL round bottom flask. The mixture was shaken well before determination of the acid value. Then, the catalyst was added to the flask which was fitted with stirrer, thermometer, and reflux condenser, and heated at a certain temperature. After a certain reaction time, the heating was stopped and the reaction mixture was cooled down to room temperature. This was followed by filtration and determination of acid value, in order to determine the esterification rate.

Determination of esterification rate

The esterification yield was measured and calculated according to the following equation by employing the standard method (GB1668-81).

IR spectra analysis

Figure 1 shows the IR spectra of Y, SBA-15, Y/SBA-15 and Cerium (IV) modified Y/SBA-15 materials.

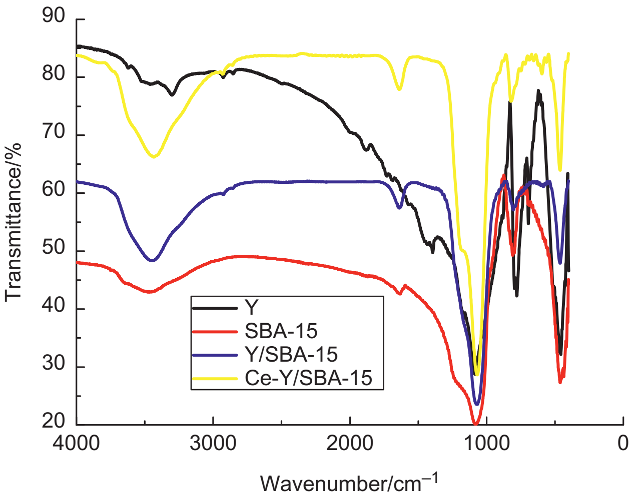


Figure 1: Infrared spectra of the four samples.

In Figure 1, we can see the main characteristic peaks of the Y-type zeolite molecular sieves. The external and internal stretching vibration absorption peaks of tetrahedron SiO_4 appeared at 1,140, 1,036, 792, and 696 cm^{-1}, respectively. The bicyclic skeletal vibration absorption peak appeared at 576 cm^{-1} and the bending vibration absorption peak was at 455 cm^{-1}. The intense peak at 456 cm^{-1} was caused by the bending vibration of Si-O-Si bond in SBA-15 skeleton, while the strong absorption peaks at 807 cm^{-1} and 1,080 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of the Si-O-Si bond in SBA-15 skeleton, respectively. The appearance of a weak absorption peak at 961 cm^{-1} was caused by the symmetric stretching vibration of terminal group Si-OH. The FT-IR spectra of the composite materials show that the skeletal vibration absorption peaks of Y-type zeolite molecular sieves appeared at 565 and 693 cm^{-1}, and the specific skeletal vibration absorption peak of SBA-15 mesoporous molecular sieves appeared at 958 cm^{-1}. It was noteworthy that the characteristic absorption peaks of the composite molecular sieves were quite different from the peaks of the individual Y-type zeolite molecular sieves and SBA-15 mesoporous molecular sieves in terms of their positions, indicating that the Y/SBA-15 composite material was not achieved by simple mechanical mixing of Y and SBA-15. Besides the characteristic peaks listed above, one new absorption peak at 1,300 cm^{-1} was found in the FT-IR spectrum of Ce-Y/SBA-15. Thus, it can be inferred that new chemical bonds were formed due to the interactions between the added Ce and surface Si-OH groups of the Y/SBA-15.

XRF analysis

The synthesis of the two kinds of molecular sieves was monitored by XRF, and the results are shown in Tables 1–3.

Table 1: The XRF results of Y/SBA-15 molecular sieve.

Component	Mass fraction/%	Detection line	Element spectral line	Strength
SiO_2	95.92	0.088	Si-KA	456.523
Al_2O_3	1.56	0.037	Al-KA	72.787
Na_2O	0.73	0.031	Na-KA	2.441

Table 2: The SQF results of Ce-Y/SBA-15 molecular sieve.

Component	Mass fraction/%	Detection line	Element spectral line	Strength
SiO_2	91.36	0.096	Si-KA	399.616
CeO_2	5.84	0.032	Ce-KA	9.762
Al_2O_3	0.95	0.021	Al-KA	33.251

Table 3: Ratio of silicon and aluminum of four samples.

Samples	Ratio of silicon to aluminum
Y/SBA-15	76.2
Ce-Y/SBA-15	90.3

The silicon aluminum ratio of Ce-Y/SBA-15 was higher than that of Y/SBA-15. After doping with Ce, the acid density of the molecular sieve decreased. The acid strength of Ce-Y/SBA-15 is higher than that of Y/SBA-15, which is because the source of acidity is adjacent to the silicon aluminum. Electronegativity of silicon is large, which results in the adjacent electrons being drawn towards silicon. Especially, the electrons are pulled away from the adjacent Al-OH bond. As a result, the hydroxyl hydrogen is easily ionizable, and indicates the acid content of Al. The electronic attraction on aluminum decreased, thus decreasing the acidity. Therefore, the ratio of silicon and aluminum in Ce-Y/SBA-15 is higher than that of Y/SBA-15, and the acidity of Ce-Y/SBA-15 is higher than that of Y/SBA-15.

SEM/EDS elemental analysis

Figure 2 shows the SEM/EDS pictures of the materials, before and after the modification of Y/SBA-15 by rare-earth Ce.

It could be seen from Figure 2 that the cerium element appeared in the X-ray spectrum peaks of the SEM/EDS images. Si, Al and C elements were observed in the Y/SBA-15 EDS data. The synthesized molecular sieve materials have the same elements as the raw materials, which are also consistent with the feeding amount. In the EDS data of Ce-Y/SBA-15, Ce element is also observed in addition to the Si, Al and C elements (intensity ratio weakened after loading). So clearly, the Ce complex was successfully doped into the molecular sieve. Cerium replaced the impregnated Al elements in the composite zeolite frame work. Inclusion of cerium changed the Si/Al molar ratios of the zeolite compound and thereby changed its structure and catalytic properties.

Ce-Y/SBA-15 catalyzed synthesis of n-butyl oleate

Catalytic effects of Ce addition

Table 4 describes the effect of the mass fraction of added catalysts on the yield of n-butyl oleate.

Table 4: Effect of different catalysts on % yield of n-butyl oleate.

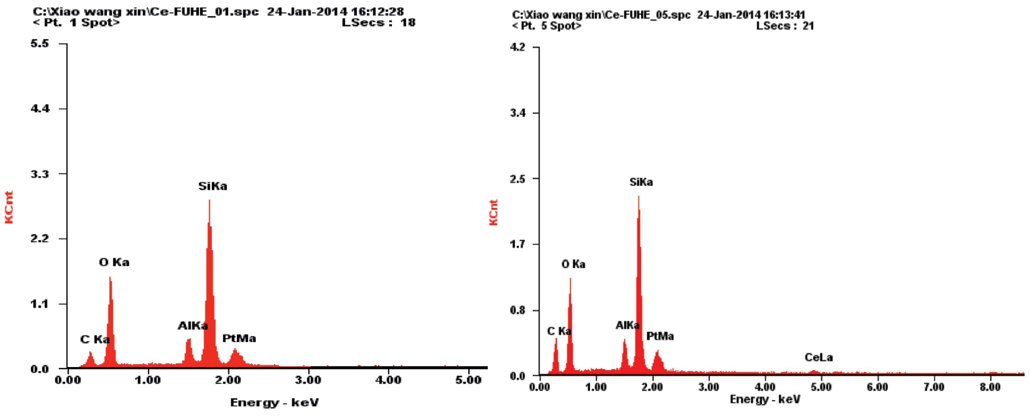
Types of catalyst	Yield
Y/SBA-15	72.16
Ce-Y/SBA-15	90.60

Catalyst reusability study

Based on previous reports, $L_9(3^3)$ orthogonal experiments were performed using Ce-Y/SBA-15 as the catalyst, to investigate the effect of the following reaction parameters: acid/alcohol molar ratio (A), catalyst weight percentage (B), and reaction time (C/h), on the esterification reaction and to optimize the n-butyl oleate preparation conditions. The orthogonal experiments were conducted according to the designed table and the results are shown in Table 5.

Table 5: Results of orthogonal experiments.

The serial number	Factors			*E*/%
	A	*B*	*C*	
1	1.4:1	3 %	2	56.8
2	1.6:1	5 %	2	68.3
3	1.8:1	7 %	2	90.5
4	1.6:1	3 %	4	80.2
5	1.8:1	5 %	4	90.6
6	1.4:1	7 %	4	72.1
7	1.6:1	3 %	6	80.7
8	1.4:1	5 %	6	67.9
9	1.8:1	7 %	6	83.2
k_1	65.31	73.55	70.98	
k_2	76.31	76.46	84.33	
k_3	89.04	81.49	76.32	
R	11.45	6.08	6..48	



(a)Y/SBA-15 (b)Ce-Y/SBA-15

Figure 2: SEM/EDS pictures, before and after the modification of micro-mesoporous molecular sieve by rare-earth Ce.

As shown in Table 5, the *R* values indicate that the order of influence of the different parameters, from large to small, is A>C>B:acid/alcohol molar ratio > reaction time > catalyst weight percentage, respectively. The highest esterification yield of 90.6 % was obtained when the reaction time was 4 h, the acid/alcohol molar ratio was 1.8:1, and the catalyst loading was 5 wt%. The influence of acid/alcohol molar ratio was most significant. This is likely because the molecular sieves drastically lowered the activation energy barrier of the reaction and therefore accelerated the reaction.

Conclusions and future work

1) The results showed that the frameworks of the prepared Ce-Y/SBA-15 composite materials were intact, and the micro-mesoscopic structures remained highly ordered.
2) Catalytic performances of the obtained Y/SBA-15 and Ce-Y/SBA-15 materials were evaluated in the catalyzed synthesis of n-butyl oleate, and their esterification rates were 76.2 % and 90.6 %, respectively. The results suggest that the addition of Ce^{4+} can effectively improve the catalytic properties of composite molecular sieves.
3) The experimental results show that the optimum conditions are: acid/alcohol molar ratio of 1.8:1, catalyst loading amount of 5 %(based on weight of oleic acid), reaction time of 4 h and reflux conditions. Under these optimal conditions, the yield of esterification was 90.6 %.

Funding: Project supported by National Natural Science Foundation of China (51274060), the Innovation and entrepreneurship training program for College Students of Liaoning Shihua University (2016008) and the talent scientific research fund of LSHU (2016).

References

[1] G.P. Li, S.M. Zhang and B.M. Zhang, Chin. J. Inorg., 21 (2013) 75–80.
[2] Z.F. Tao, Q. Zhao, Y. Ma and L.H. Li, J. Chin. Ceram. Soc., 40 (2012) 1466–1472.
[3] Y.M. Song, N. Ren, Y. Tang and B. Pan, Chin. Catal., 33 (2010) 192–198.
[4] H.L. Zhang, C.J. Tang, C.Z. Sun and W.D. Shi, Microporous Mesoporous Mater., 151 (2012) 44–55.
[5] F.J. Shiring, R. Wenkaladri and T.J.G. Goodwin, Can. J. Chem. Eng., 61 (2009) 218–222.
[6] L.P. Liu, G. Xiong, X.S. Wang and Z.X. Yang, Microporous Mesoporous Mater., 123 (2009) 221–227.
[7] Y.M. Song, N. Ren and Y. Tang, Chin. J. Catal., 33 (2012) 192–198.
[8] F.X. Chen, H.K. Luo and Y.F. Han, Catal. Today, 131 (2008) 76–81.
[9] Z.Y. Feng, X.W. Huang and H.J. Liu, J. Rare Earths, 30 (2012) 903–910.
[10] C.X. Lin, S.Z. Qiao, C.Z. Yu and M.Q. Sheng, Mesoporous Mater., 117 (2009) 213–219.
[11] J.L. Lai, G. Liu and J. Wang, J. Liaoning Shihua Univ., 33 (2013) 16–18.
[12] S. Blagov, S. Paradaa, O. Bailer and M.B. Thill, Chem. Eng. Sci., 61 (2006) 753–765.
[13] B. Toukoniitty, J.P. Mikkola and K. Eränen, Catal. Today, 100 (2005) 431–435.
[14] B.R. Jermy and A. Pandurang, Appl. Catal. A, 288 (2005) 25–33.
[15] B.R. Jermy and A. Pandurangan, J. Mol. Catal. A: Chem., 237 (2005) 146–154.
[16] F.T. Sejidov, Y. Mansoori and N. Goodarzi, J. Mol. Catal. A: Chem., 40 (2005) 186–190.
[17] J.F. Zi, Ind. Catal., 26 (2013) 56–58.
[18] G.X. Luo, J. Wang, C.S. Liu and W. Cui, J. Petrochem. Univ., 23 (2010) 44–47.
[19] L. Li, Q. Luo and L. Kou, J. Northwest Univ. Nationalities, 25 (2015) 16–19.
[20] S. Yang, L. Chen, J. Sun and Q. Chen, Rare Metals, 22 (2003) 75–77.
[21] I.V. Kozhevnikov, Chem. Rev., 98 (1998) 171–198.
[22] S.H. Yin, S.W. Li, B. Zhang, J.H. Peng and L.B. Zhang, Chem. Eng. Res. Des., 104 (2015) 92–97.
[23] S.H. Yin, S.W. Li, F. Xie, L.B. Zhang and J.H. Peng, RSC adv., 5 (2015) 64550–64556.
[24] S.H. Yin, L.B. Zhang, J.H. Peng and S.W. Li, Chem. Eng. Process. Process Intensif., 91C (2015) 1–6.