Preparation of hierarchical SAPO-11 molecular sieve and its application for *n*-dodecane isomerization

Hao Song · Zhen Liu · Wei Xing · Zhipeng Ma ·
Zifeng Yan · Lianhong Zhao · Zhongdong Zhang ·
Xionghou Gao

Received: 9 June 2014 / Accepted: 28 July 2014 / Published online: 28 August 2014
© The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract The isomerization conversion of long chain paraffins for high quality lube oil production plays an important role in the petrochemical industry. The conventional isomerization catalyst, SAPO-11 molecular sieve, exhibits disadvantages for large molecule transfer and multi-branched isomer conversion. To overcome the difficulty of long chain paraffin isomerization, SAPO-11 with hierarchical structure was synthesized by acid modification. With comparison of citric acid modification and hydrochloride acid modification, the hierarchical SAPO-11 was obtained and characterized by nitrogen sorption, XRD, SEM, TEM, and Py-FTIR. The catalytic isomerization activity of prepared hierarchical SAPO-11 was evaluated by *n*-dodecane isomerization reaction, and the results showed that it had high isomerization conversion and multi-branched isomer selectivity.

Keywords Isomerization · *n*-Dodecane · SAPO-11 · Hierarchical structure

Introduction

Catalytic isomerization of long chain paraffins is of great significance in petro refining and petrochemical industries for the production of lube oils with low pour points and high viscosity [1–4]. The introduction of branches in the carbon skeleton of long chain paraffins while limiting the undesired cracking of the molecules, are crucial for this catalytic conversion [5–7]. For the conversion of hydrocarbons, suitable catalyst is important for its performance. Among the numerous catalytic materials explored for long chain paraffin isomerization, SAPO-11 molecular sieve as an acidic carrier for bifunctional catalysts has attracted much attention due to its outstanding isomerization activity [8].

SAPO-11, with one dimensional ten membered ring channel and AEL pore structure, showed excellent conversion of hydrocarbons into isomers [9–11]. However, the microporous structure of SAPO-11 inhibits the formation of multi-branched isomers which is much favorable for high quality lube oil production. It is generally believed that the active sites for isomerization are located near the pore mouths of the SAPO-11 [12–14]. However, due to the limitation of the micropores, hydrocarbons with long carbon chains can only interact with the active sites on the crystal surface instead of the inner side of the pores. Meanwhile, the micropores will also restrict the mass transfer of the reactants and products. Therefore, the investigation of SAPO-11 with hierarchical pore structure is of great need to satisfy the multi-branched isomers production from long chain paraffins [15–17].

H. Song · Z. Liu (✉) · W. Xing · Z. Ma · Z. Yan (✉) ·
Z. Zhang

State Key Laboratory of Heavy Oil Processing, Key Laboratory
of Catalysis, CNPC, China University of Petroleum,
No. 66 Changjiang West Road, Qingdao 266580,
People's Republic of China
e-mail: zhenliu@upc.edu.cn

Z. Yan
e-mail: zfyancat@upc.edu.cn

H. Song
e-mail: songhao0956@163.com

W. Xing
College of Science, China University of Petroleum,
No. 66 Changjiang West Road, Qingdao 266580,
People's Republic of China

L. Zhao · Z. Zhang · X. Gao
Lanzhou Petrochemical Research Center, Petro China
Petrochemical Institute, CNPC, Lanzhou 730060,
People's Republic of China

Herein, we report a facile method of preparing hierarchical SAPO-11 by acid modification, and the mesopores generated by the dealumination were systematically studied by comparing different kinds of acids. The isomerization selectivity, especially for multi-branched isomers was enhanced by hierarchical SAPO-11 during the *n*-dodecane catalytic evaluation.

Experimental section

Synthesis of meso-SAPO-11

Commercial microporous SAPO-11 molecular sieve was purchased from Nankai Catalyst Company. The meso-SAPO-11 catalysts were prepared by acid modification to generate mesopores. Typically, 3.0 g of SAPO-11 was dispersed into acid solution with certain concentration. After stirring at 40 °C for 30 min, the final products were filtered and washed with deionized water, then dried at 100 °C for 6 h and calcined at 550 °C for another 6 h to obtain the acid modified meso-SAPO-11.

Characterization methods

The crystallinity of the prepared SAPO-11 was analyzed by XRD, which was carried out on X'Pert PRO MPD (Netherlands, Cu target, $K\alpha$ radiation $\lambda = 0.1542$ nm, 35 kV, 40 mA), using molecular sieve phase analysis method, scan angle of 5°–45°. N_2 adsorption/desorption isotherms were recorded at 77 K with a Micromeritics TriStar 3000. The total surface areas of the samples were calculated by the BET method, the mesopore surface area and pore volume were calculated by the BJH method, and the pore size distributions were derived from the BJH desorption branch. The pore structure and morphology of molecular sieves were characterized by TEM, which was carried out on JEOL-2010 with an acceleration voltage of 200 kV. The particle morphology and particle size of the samples were observed by SEM, which was carried out on S-4800 (Hitachi Company, acceleration voltage of 0.5–20 kV). The surface acidity analyses were carried out on a NEXUS FTIR (Thermo Fisher Scientific Company).

Isomerization evaluation

Catalyst preparation

Bifunctional Pt/meso-SAPO-11 catalyst was prepared by incipient-wetness impregnation method. Chloroplatinic acid solution, as a source of platinum, was prepared according to 0.5 wt% Pt loading amount. Then, chloroplatinic acid solution was added into the meso-SAPO-11 in

20–40 mesh. The as-prepared meso-SAPO-11 with Pt precursor was deposited for 2 h. Finally, the products were dried at 373 K for 2 h and calcined at 753 K for another 4 h to transform into the final bifunctional Pt/meso-SAPO-11 catalyst.

Catalyst evaluation

n-Dodecane hydroisomerization was conducted on a fixed-bed micro-reactor at ambient pressure with 1.2 g catalyst loading. The catalyst was firstly activated in situ in a H_2 flow of 25 mL/min at 673 K for 4 h prior to reaction. The reaction temperature was 603 K at the WHSV feeding condition of 1.5/h with H_2/n -dodecane molar ratio of 25. Products were analyzed by an on-line Agilent 7820A GC (HP-PONA capillary column size of 50 m $\times$ 0.2 mm, FID detector).

Results and discussion

For the fabrication of hierarchical SAPO-11 molecular sieves, acid treatment method was utilized to generate mesopores in the microporous crystals. Citric acid (CA) and hydrochloric acid (HCl) have been investigated as the dealumination agents for generating mesopores in zeolite crystals [18–20]. Then, the hierarchical SAPO-11 modified by these two agents was investigated by various structural characterizations.

Modification in citric acid (CA) system

It can be seen from Table 1 that different concentrations of CA made significant effects on the pore structure of hierarchical SAPO-11. In general, the total surface area, mesoporous surface area, total volume pore and mesopore volume increased sharply with the increase of the concentration of CA. Especially, the mesoporous surface area and pore volume of product increased up dramatically when the CA concentration was 1 mol/L. It may result from the difference of dealumination extended with varied CA concentration. When the acid concentration was relatively low, the dealumination process will firstly remove the residues in the internal pores without destroying the silica-alumina framework [21], and then occurred on the surface of the crystals which only generated surface etching pores. However, at higher acid concentration, the etching of the silica-aluminate framework occurred in the inner side of the crystals, which generated more mesopores and provided higher surface area. Furthermore, the mesopores generated inside of the crystals connected between each other, which greatly improved the mesoporous specific surface area and mesopore volume.

Table 1 Pore structure properties of commercial and hierarchical SAPO-11 with different concentration of CA

C_{CA} (mol/L)	A_{BET} (m^2/g)	A_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{meso} (cm^3/g)	Crystallinity (%)
0*	64	50	0.146	0.139	100
0.10	74	51	0.154	0.143	95.68
0.25	80	57	0.164	0.154	91.07
0.50	106	86	0.288	0.280	90.49
0.75	102	91	0.257	0.253	79.47
1.00	269	241	0.472	0.484	53.10

* The commercial microporous SAPO-11

According to the results in Fig. 1, when the concentration of CA increased, the volume of hysteresis loop gradually raised up. Especially, the volume of the hysteresis loop remarkably increased when the concentration of CA reached 1.0 mol/L, with the hysteresis loop of H3 type. The mesopore may be generated by the inter crystal stacking of small particles formed by deep corrosion. For the pore size distribution of the hierarchical SAPO-11, it can be seen that the higher

Fig. 1 N₂ sorption isotherms (a) and pore size distribution (b) of hierarchical SAPO-11 under different concentration of CA

concentration of the citric acid, the more of mesopores would be generated. Even though the mesopores were not obvious at the concentration of CA below 1.0 mol/L, there was still the slight improvement of pores with higher concentration. While at 1.0 mol/L, the mesopores generated was quite obvious and the pore size was centered at about 10 nm. That may be caused by the slow corrosion of surface framework at low concentration of CA, in which dealumination process only partly happened on the surface without obvious and concentrated mesopores generated. However, when the concentration was high enough, CA can effectively permeate into the microporous SAPO-11 crystals, and the dealumination of the framework inside of the crystal caused the large crystal splitting into small particles with stacking mesopores.

Figure 2 shows that with the increase of concentration of CA, the intensities of characteristic peaks of AEL structure gradually decreased. At the CA concentration below 1.0 mol/L, the relative crystallinity of the prepared hierarchical SAPO-11 decreased slightly. However, when the concentration of CA reached 1.0 mol/L, the intensities of characteristic peaks sharply dropped off, indicating the severe damage of SAPO-11 crystals.

Taking both of the mesoporosity and crystallinity into consideration, the final product should possess relatively high mesopore and relatively high crystallinity. The citric acid concentration of 0.5 mol/L was selected as the optimal concentration for CA modification to prepare hierarchical SAPO-11.

Modification in hydrochloride acid (HCl) system

It can be seen that the total surface area, mesoporous specific surface area, total pore volume and mesopore

Fig. 2 XRD patterns of commercial and hierarchical SAPO-11 under different concentration of CA

Table 2 Pore structure properties of commercial and hierarchical SAPO-11 under different concentration of HCl

C_{HCl} (mol/L)	A_{BET} (m^2/g)	A_{meso} (m^2/g)	V_{total} (m^3/g)	V_{meso} (m^3/g)	Crystallinity (%)
0*	64	50	0.146	0.139	100
0.10	59	45	0.126	0.119	99.54
0.25	71	58	0.157	0.152	94.96
0.50	102	86	0.232	0.226	82.99
0.75	176	180	0.426	0.433	58.82
1.00	252	270	0.476	0.486	39.32

* The commercial microporous SAPO-11

volume of samples in Table 2 increased remarkably with the concentration of HCl raised up. It indicated that the concentration of treating agent was a key factor for the textural properties of the modified hierarchical SAPO-11. To be noticed that at higher HCl concentration than 0.5 mol/L, the mesoporous specific surface area and pore volume nearly doubled. This may be caused by the severe dealumination at the high concentration of HCl, generating much of mesopores inside of the crystals and getting connected between the pores, thereby dramatically increased the mesopore volume.

N_2 adsorption/desorption isotherms of the HCl modified hierarchical SAPO-11 at different concentrations were given in Fig. 3. It can be identified from the isotherms that the samples are of mesopores with the varied volumes. With higher HCl concentration, the adsorption isotherm with P/P_0 about 0.6–1.0 tends to be even steep, which indicates that more mesopores were generated at high concentration. At the concentration higher than 0.5 mol/L, the H3-type hysteresis loop was broadened, indicating that the obvious mesopores were generated by crystals stacking and gapping.

As shown in Fig. 3, the pore size distribution of the hierarchical SAPO-11 modified by HCl at different concentrations, the increase of concentration generated more mesopores with relatively narrow pore size distribution. At the HCl concentration of 1.0 mol/L, the mesopores were centralized at about 10 nm which were generated by the enhanced-dealumination at high concentration.

According to the XRD patterns as shown in Fig. 4, the relative crystallinity of the hierarchical SAPO-11 was relatively high when the concentration of HCl ranged from 0.1 to 0.5 mol/L, and the characteristic diffraction peaks of AEL structure could be obviously detected. At concentration higher than 0.5 mol/L, the intensities of the characteristic peaks, especially for the peak with 2θ around 21.21° , decreased dramatically, which was caused by the severe dealumination of [002] facet in the framework in SAPO-11 [22]. The enhanced-dealumination at high acid concentration not only generated abundant mesopores, but

Fig. 3 N_2 sorption isotherms (a) and pore size distribution (b) of hierarchical SAPO-11 under different concentrations of HCl

also partly destroyed the crystal framework, and even etched most part of the SAPO-11 forming amorphous species. It suggested that the higher concentration of HCl could generate more mesopores, however, it adversely damaged the framework of molecular sieve.

Take both mesoporosity and crystallinity into consideration, the prepared hierarchical SAPO-11 needs to possess as much of mesoporous structures and keep relatively high crystallinity. The HCl concentration of 0.5 mol/L was selected as the optimal condition for the preparation of hierarchical SAPO-11.

Characterization of hierarchical SAPO-11

By the investigation of hierarchical SAPO-11 prepared in both CA and HCl systems, the optimal modifying conditions were obtained. The morphologies and surface acidities of the optimized catalysts were characterized by SEM, TEM and in situ Py-FTIR. The pore structures and acidity

differences were analyzed in relation with the acid modification process with different acids.

As shown in Fig. 5, the SEM and TEM images of microporous SAPO-11 and hierarchical SAPO-11 modified by CA and HCl, the large particle aggregates of microporous SAPO-11 crystals were dissolved into small pieces after the modification of acids. The surface of the crystal was not smooth as before acid etching, instead, mesopores were generated inside of the crystals. Specifically, the dealumination of CA occurred in both surface and inside of the crystal, which generated mesopores about 10 nm by etched small particles stacking. However, for HCl modification, the dealumination process mainly occurred on the crystal surface, the initial rod-like crystal structure was obtained by etching the surface framework and generating mesopores with generally wide distribution.

As shown in Fig. 6, the hierarchical SAPO-11 modified by both CA and HCl had improved surface acidities. Specifically, more Lewis acid sites were generated by HCl

modification. However, relatively more Brønsted acid sites were generated by CA modification. The difference of the surface acidity distribution may have different isomerization performance for both of them, since it is generally believed that the Brønsted acid sites are responsible for the catalytic isomerization conversion.

Isomerization evaluation of hierarchical SAPO-11

As characterized of the hierarchical SAPO-11 modified by CA and HCl, the pore structures and surface acidities were different, and this difference may have an effect on their application in long-chain paraffin isomerization. Here, the isomerization performances of these two catalysts were displayed in Tables 3 and 4.

As shown in Tables 3 and 4, both of the catalysts have 90 % conversion of dodecane at the reaction temperatures above 280 °C. However, CA-modified hierarchical SAPO-11 has lower cracking products but higher isomer selectivity compared with the HCl-modified SAPO-11 at the same temperature. At 280 °C, the isomer yields are highest for both catalysts, up to 74.45 % for CA-modified SAPO-11 and 70.04 % for HCl-modified SAPO-11, respectively. However, referring to the composition of the isomer products, the optimal reaction condition is different. Especially, the multi-branched selectivity of the CA-modified SAPO-11 can reach 42.89 % at 300 °C. Comparing with the catalytic performance of commercial microporous SAPO-11 with multi-branched selectivity of 40.81 % and cracking selectivity of 31.11 %, the introduction of mesopores by CA modification will enhance the isomerization process of *n*-dodecane. It may be resulted from the mesopore generated inside of the SAPO-11 molecular sieves with CA modification. Not only the large amount of micropore structure was effectively retained, but also more of the active sites were exposed. Therefore, the enhanced isomerization occurred in the

Fig. 4 XRD pattern of commercial and hierarchical SAPO-11 under different concentration of HCl

Fig. 5 SEM and TEM images of commercial and hierarchical SAPO-11 modified by CA and HCl

Fig. 6 Py-FTIR spectroscopy of commercial and hierarchical SAPO-11 by acid treatment

Table 3 Isomerization evaluation of meso-SAPO-11 prepared by CA modification

Temperature	Conversion (%)	Selectivity (%)			Isomer yield (%)
		Cracking	Mono-branched	Multi-branched	
330	99.65	82.98	3.45	13.57	16.96
300	97.71	30.14	26.97	42.89	68.26
280	90.59	17.82	52.77	29.41	74.45
260	68.93	20.41	64.76	14.83	54.87

Table 4 Isomerization evaluation of meso-SAPO-11 prepared by HCl modification

Temperature	Conversion (%)	Selectivity (%)			Isomer yield (%)
		Cracking	Mono-branched	Multi-branched	
330	99.79	93.59	1.89	4.52	6.39
300	98.70	47.35	14.50	38.15	51.97
280	94.14	25.60	40.93	33.47	70.04
260	65.22	17.69	68.01	14.30	53.68

hierarchical SAPO-11 catalysts. The mesopores in HCl-modified SAPO-11 were rich in surface dents derived from the surface etching, which rendered the long chain paraffin a low isomerization activity. Besides, according from the Py-FTIR result, the Lewis acidity of HCl-modified SAPO-11 increased after modification, which may result in the higher cracking selectivity comparing with the microporous SAPO-11.

Conclusion

SAPO-11 with hierarchical pore structure was synthesized by acid modification, using citric acid and hydrochloride acid. After modification, the mesopores were generated in the microporous SAPO-11 molecular sieves. The concentration of acid solution played an important role for mesopores generation, and the synthesis conditions were optimized as the concentration of both acid of 0.5 mol/L. The commercial and hierarchical SAPO-11 samples were also evaluated by *n*-dodecane isomerization reactions, and the results showed that the CA-modified SAPO-11 exhibited multi-branched isomer selectivity of 42.89 %, which is higher than the commercial microporous SAPO-11.

Acknowledgments This work was supported by Science and Technology Development Project of CNPC (No. 11-13-01-05); National Science Foundation China (U1362202 and 21206196), Innovation Foundation of CNPC (2013D-5006-0404), and funds for distinguished youngs of Shandong Province (BS2012NJ013).

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Wang Z, Tian Z, Teng F, Wen G, Xu Y, Xu Z, Lin L (2005) Hydro isomerization of long-chain alkane over Pt/SAPO-11 catalysts synthesized from nonaqueous media. *Catal Lett* 103:109–116
- Akhmedov V, Al-Khowaiter S (2007) Recent advances and future aspects in the selective isomerization of high *n*-alkanes. *Catal Rev* 49:33–149
- Ono Y (2003) A survey of the mechanism in catalytic isomerization of alkanes. *Catal Today* 81:3–16
- Miller S (1994) Studies on wax isomerization for lubes and fuels. *Stud Surf Sci Catal* 84:2319–2326
- Guo L, Bao X, Fan Y, Shi G, Liu H, Bai D (2012) Impact of cationic surfactant chain length during SAPO-11 molecular sieve synthesis on structure acidity and *n*-octane isomerization to dimethyl hexanes. *J Catal* 294:161–170
- Deldari H (2005) Suitable catalysts for hydroisomerization of long-chain normal paraffins. *Appl Catal A Gen* 293:1–10
- Taylor R, Petty R (1994) Selective hydroisomerization of long chain normal paraffins. *Appl Catal A Gen* 119:121–138
- Geng C, Zhang F, Gao Z, Zhao L, Zhou J (2004) Hydroisomerization of *n*-tetradecane over Pt/SAPO-11 catalyst. *Catal Today* 93–95:485–491
- Wilson S, Lok B, Messina C (1982) Alumino phosphate molecular sieves: a new class of microporous crystalline inorganic solids. *J Am Chem Soc* 104:1146–1147
- Lok BM, Messina C, Patton R (1984) Silicoaluminophosphate molecular sieves: another new class of microporous crystalline inorganic solids. *J Am Chem Soc* 106:6092–6093
- Xu B, Han X, Qian L, Wang H, Yan Z (2006) Application of CoAPO-11 molecular sieve for 1-hexene isomerization and its deactivation in the reaction. *Chin J Catal* 26:842–846

12. Marterns J, Parton R, Uytterhoeven L, Jacobs P (1991) Selective conversion of decane into branched isomers: a comparison of platinum/ZSM-22, Platinum/ZSM-5 and Platinum/USY zeolite catalysts. *Appl Catal* 76:95–116
13. Marterns J, Vanbutsele G, Jacobs P, Denayer J, Ocakoglu R, Baron G, Munoz Arroyo J, Thybaut J, Marin G (2001) Evidences for pore mouth and key-lock catalysis in hydroisomerization of long *n*-alkanes over 10-ring tubular pore bifunctional zeolites. *Catal Today* 65:111–116
14. Campelo J, Lafont F, Marinas J (1995) Hydroisomerization and hydrocracking of *n*-heptane on Pt/SAPO-5 and Pt/SAPO-11 catalysts. *J Catal* 156:11–18
15. Yang X, Lu T, Chen C, Zhou L, Wang F, Su Y, Xu J (2011) Synthesis of hierarchical AlPO-*n* molecular sieves templated by saccharides. *Micropor Mesopor Mater* 144:176–182
16. Ryoo R, Srivastava R, Choi M (2006) Organosilane surfactant-directed synthesis of mesoporous aluminophosphates constructed with crystalline microporous frameworks. *Chem Commun* 42:4380–4382
17. Fan Y, Xiao H, Shi G, Liu H, Bao X (2012) Alkylphosphonic acid- and small template synthesis of hierarchical silicoaluminophosphate molecular sieves with high isomerization selectivity to di-branched paraffins. *J Catal* 285:251–259
18. Liu X, Yan Z (2000) Modification of USY zeolites with citric acid. *Acta Chim Sinica* 58:1009–1014
19. Wang L, Qu W, Wang B, Xu Y, Yang X, Xu Z, Tian Z, Lin L (2006) Hydroconversion of F-T waxes on SAPO-11 molecular sieves modified by acid leaching. *Acta Pet Sinica B10*:142–145 (Petroleum Processing Section)
20. Liu Z, Song H, Feng Z, Yan Z (2013) Hierarchical meso-microporous SAPO-11 synthesis from acid assistant dealumination effect of acid strength. *Appl Mech Mater* 313–314:219–222
21. Yan Z, Ma D, Zhuang J, Liu X, Liu X, Han X, Bao X, Chang F, Xu L, Liu Z (2003) On the acid-dealumination of USY zeolite: a solid state NMR investigation. *J Mol Catal A Chem* 194:153–167
22. Cao G, Shah M, Brody J (2003) Synthesis of silicoaluminophosphates. US Patent 6927187, ExxonMobil Chemical Patent Inc