The catalytic and acidic properties of an i-Pr_2NH-templated SAPO-11 and dealuminated derivatives

Huiping Tian [a,*], Li Shi [b] and Chenglie Li [b]

[a] *Division 14, Research Institute of Petroleum Processing, 18 Xueyuan Rd., PO Box 914-14, Beijing 100083, PR China*
[b] *Petroleum Processing Research Center, East China University of Science and Technology, 130 Meilong Rd., Shanghai 200237, PR China*

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Crystalline silicoaluminophosphate (SAPO-11) samples were synthesized with i-Pr_2NH as a novel template, then dealuminated in H_4EDTA solution. These samples were characterized by catalytic skeletal isomerization of linear butylenes, IR analysis of adsorbed pyridine and ^{31}P, ^{29}Si MAS-NMR. Strong acid sites were concerned with Si domains, that were formed by either increasing the Si content of SAPO-11 via a synthesis process or dealuminating treatment of as-synthesized SAPO-11. Acid sites of medium strength were located around isolated Si together with adjacent Al and the second nearest element P. Deep dealumination led to amorphous $AlPO_4$, and reduced crystallinity degree. The maximum yield of isobutylene in catalytic skeletal isomerization of linear butylenes were achieved around 763 K. It was confirmed that these reactions were mainly performed on Brønsted acid sites of medium strength.

Keywords: SAPO-11, i-Pr_2NH template, dealuminating, skeletal isomerization, acid sites, linear butylenes

1. Introduction

It was found that SAPO-11 had the potential to convert linear olefins into branched olefins [1,2]. Since iso-olefins are facing increasing commercial requirements, such as isobutylene faces the need of MTBE (methyl tertiary butyl ether) production, studies of SAPO-11 are growing rapidly [3,4].

The formation and modification of SAPO's are possible by means of the hydrothermal method [5]. SAPO-11 has been hydrothermally synthesized with n-Pr_2NH–TPAOH (tetrapropylammonium hydroxide) or i-Pr_2NH–propanol mixtures as template [6], but the modification of SAPO-11 is to be explored.

In this paper, SAPO-11 was synthesized with i-Pr_2NH as a novel organic template, and dealuminated in H_4EDTA (ethylene diamine tetraacetic acid) solution. Dealumination and its influence on surface acidity and catalytic behavior of skeletal isomerization of linear butylenes were discussed.

2. Experimental

2.1. SAPO-11 samples

SAPO-11 was synthesized by hydrothermally crystallizing a sol–gel mixture with a composition of $SiO_2 : P_2O_5 : Al_2O_3 : H_2O : i\text{-}Pr_2NH = (0\text{–}0.5) : 1.2 : 1.0 : 55 : 1.1$ in an autoclave at 453 K for 48 h. Dealumination of SAPO-11 was achieved in a 0.01–0.08 M H_4EDTA solution at 338 K. Crystalline products of the synthesis and dealumination processes were recovered by washing and filtering, then dried at 393 K for 5 h and calcined at 773 K for 1 h.

* To whom correspondence should be addressed.

2.2. Characterization

Skeletal isomerization of linear butylenes was performed at 573–823 K in a microreactor–GC (gas chromatography) system loaded with 1.0–1.5 g SAPO-11 samples under normal pressure. The hydrocarbon feed contains linear butylenes 68.0 wt%, isobutylene 0.50 wt%, butane 31.20 wt%, C_5 and heavier 0.04 wt%, C_1–C_3 0.26 wt%. The flow rate of the hydrocarbon feed was controlled to keep a WHSV of linear butylenes of 1.0 h^{-1}. The coke content after 0.5 h reaction was determined by O_2 consumption at 873 K.

XRD (X-ray diffraction) measurement was conducted on a diffractometer D/max-gamma B using Cu Kα radiation. Chemical composition of crystalline products was determined with a Hitachi 180–80 spectrometer. ^{31}P, ^{29}Si MAS-NMR (magic angle spinning nuclear magnetic resonance) spectra were taken on a Varian VXR-200s spectrometer with a Doty Scientific CP-MAS probe.

IR (infrared) spectra of adsorbed pyridine on SAPO-11 were recorded on a 20SX FT spectrometer at 10^{-7} Pa. SAPO-11 samples were initially activated in vacuum at 773 K for 2 h, then reduced to room temperature, followed by contacting with pyridine vapor. After that, the temperature was stepwise increased for measurement.

3. Results and discussion

3.1. Composition and structure

The synthesis of SAPO-11 with i-Pr_2NH as a novel template was verified by XRD measurement [7]. Table 1 lists compositions of the synthesis mixtures and crystalline products. It was noted that $(x + z)$ increased with Si content of

Table 1
Molar compositions of synthesis mixtures and crystalline products.

No.	Reaction mixture composition	Framework composition $(Si_xAl_yP_z)O_2$		
	$SiO_2 : Al_2O_3 : P_2O_5 : i\text{-}Pr_2NH : H_2O$	x	y	z
1	0.4 : 1.0 : 1.0 : 1.1 : 55	0.05	0.50	0.45
2	0.5 : 1.0 : 1.0 : 1.1 : 55	0.08	0.49	0.43

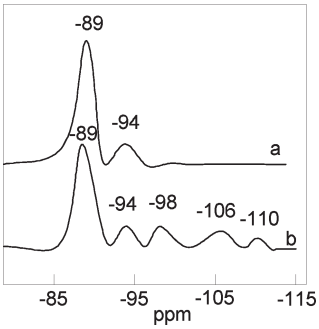

Figure 1. ^{29}Si MAS-NMR spectra of (a) SAPO-11 sample No. 1 and (b) SAPO-11 sample No. 2.

Table 2
Molar composition of sample No. 2 after dealumination.

No.	Dealumination degree	Chemical composition $(aSiO_2 \cdot bAl_2O_3 \cdot cP_2O_5)$			Framework composition $(Si_xAl_yP_z)O_2$		
		a	b	c	x	y	z
1-L1	low	1.0	4.8	4.5	0.05	0.48	0.45
1-L2	high	1.0	4.7	4.4	0.05	0.45	0.43

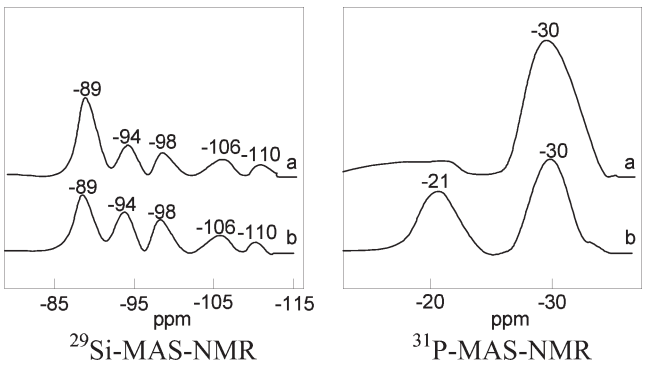

Figure 2. ^{29}Si and ^{31}P MAS-NMR spectra of SAPO-11 sample No. 1-L1 (curve (a)) and SAPO-11 sample No. 1-L2 (curve (b)) in table 2.

reaction mixtures. Since Si preferably took the same position as P in the framework [8], it was quite probable that Si domains formed in SAPO-11 sample No. 2 having Si and P content over 0.50. This was confirmed by ^{29}Si MAS-NMR analysis in figure 1. The peak at -110 ppm represented the Si(4Si) environment [9], indicating the existence of Si domains. The peak at -89 ppm was probably to be Si(4Al) environment. Peaks between -110 and -89 ppm might stand for Si having 1–3 Al atoms as adjacent neighbors.

SAPO-11 sample No. 1 was dealuminated to two Al levels, as listed in table 2. Figure 2 shows ^{31}P, ^{29}Si MAS-NMR spectra of the dealuminated SAPO-11. The chemical composition was not equivalent to the framework composition of sample No. 1-L2, which implied the formation of an amorphous phase. Since the -110 ppm peak stands for Si domains (Si(4Al)) [9], slight dealumination might lead to the formation of Si domain as in the case of sample No. 2-L1 (figure 2, curve (a)). This was evidence of easy removal of Al located between or among Si atoms in the framework. A new band peak at -20 to -23 ppm, which was assigned to amorphous $AlPO_4$ phase [10], was observed on the ^{31}P MAS-NMR spectrum of the deep-dealuminated SAPO-11 sample (No. 1-L2). This suggested that Al in a P environment was removed only in deep dealumination stage, and its removal resulted in a loss of crystallinity.

3.2. Acidity

IR spectra of adsorbed pyridine were applied to detect the number of acidic sites of SAPO-11 samples. The band at 1550 cm^{-1} was attributed to cation chain stretching of pyridine ions and exhibited Brønsted acidity, and the 1455 cm^{-1} band was assigned to carbon chain stretching of coordinatively bonded pyridine complexes, indicating the presence of Lewis acidity [11–13]. Figure 3 shows the change of 1455 and 1550 cm^{-1} band intensities of SAPO-11 at different temperatures. Pyridine desorbed from Brønsted sites more facile than from Lewis sites with temperature increase, especially above 673 K. This indicated that Brønsted acidity mainly remained in the intermediate range below 673 K, and its strength is lower than that of Lewis acidity. After slight dealumination (No. 1-L1), the amount of Lewis acidity below 673 K decreased, while the acidity at 773 K kept stable. After deep dealumination (No. 1-L2), Lewis acidity decreased in the whole temperature range. Dealumination brought a different effect on Brønsted acidity than on Lewis acidity. The amount of Brønsted acidity below 673 K reduced with dealumination, while the amount of Brønsted acidity at 773 K increased with dealumination. This meant that Brønsted acidity was uniformly distributed in the whole temperature range upon dealumination. Taking into account the structure and composition changes, it was believed that the formation of Si domain enhanced the amount of Brønsted acidity at 773 K and restrained the intermediate Brønsted acidity below 673 K.

When sample No. 1-L1 was pretreated with steam, the amount of pyridine on Brønsted sites and Lewis sites varied a great deal (figure 3). The amount of Brønsted acidity increased below 673 K, unchanged at 773 K. The amount of Lewis acidity decreased, probably due to the conversion of Lewis sites to Brønsted sites by H_2O chemisorption.

3.3. Catalysis

The product distribution of catalytic skeletal isomerization of linear butylenes is exemplified in table 3. The following reactions were inferred to be included in the process:

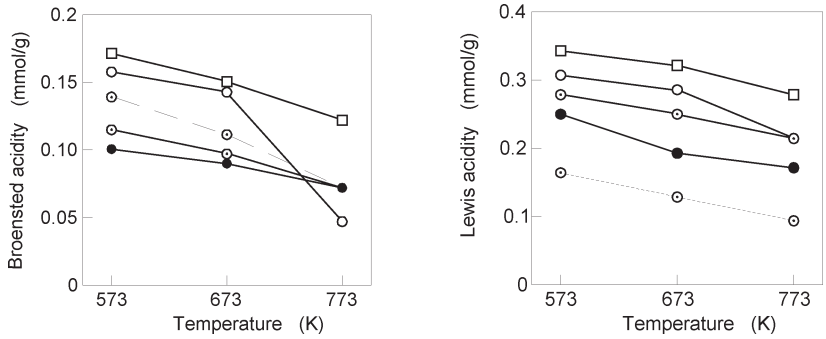

Figure 3. Temperature dependence of the amount of pyridine on Brønsted sites (left) and Lewis sites (right) of SAPO-11 samples (○) No. 1, (□) No. 2, (⊙) No. 1-L1, and (●) No. 1-L2 in tables 1 and 2. Dashed line stands for the experiment in which sample No. 1-L1 has been pretreated in steam at 773 K for 0.5 h.

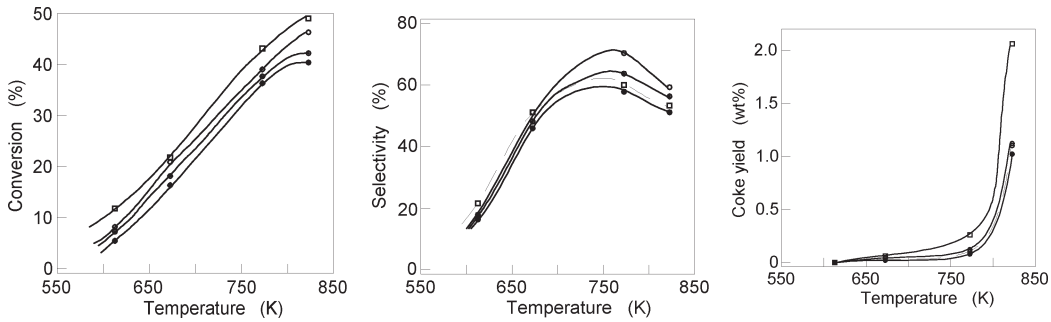

Figure 4. Temperature dependence of conversion, selectivity and coke yield in activity evaluation over SAPO-11 samples (○) No. 1, (□) No. 2, (⊙) No. 1-L1, and (●) No. 1-L2 in tables 1 and 2.

Table 3
Product distribution of linear butylenes isomerization over SAPO-11 sample No. 1-L1 (wt%).

Product	Reaction temperature (K)			
	613	673	773	823
C_3 and lighter hydrocarbons	0.26	0.42	0.84	1.97
butane	35.19	37.31	39.34	40.23
isobutylene	1.41	6.45	16.74	16.64
linear butylenes	63.10	55.70	42.64	39.17
C_5 and heavier hydrocarbons	0.04	0.10	0.30	0.84
coke	0	0.02	0.14	1.15

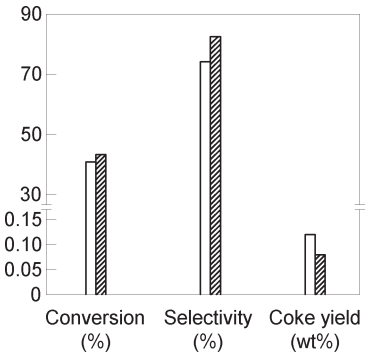

Figure 5. Influence of trace amount of water on catalytic behavior of SAPO-11 No. 1 in table 1 at 763 K.

isomerization of linear butylenes, hydrogenation of olefins, oligomerization of olefins, and cracking of hydrocarbons. Furthermore, all of these reactions but isomerization were accelerated by increasing temperature. This was explained by means of thermodynamic equilibrium [14].

Figure 4 shows temperature dependence of coke yield, linear butylene conversion and isobutylene selectivity. Linear butylene conversion was defined as (decrease of linear butylenes after reaction)/linear butylenes in feed, and isobutylene selectivity was defined as (increase of isobutylene after reaction)/(decrease of linear butylenes after reaction). Isobutylene selectivity varied in a volcano fashion with temperature, and the maximum selectivity was achieved at 673 K. Coking became serious at 673 K and higher temperatures due to the selectivity drop, while the conversion linearly increased. Sample No. 1 had a preferred isobutylene selectivity, and sample No. 2 that was rich in Si showed high linear butylene conversion. Dealumination inhibited both linear butylene conversion and isobutylene selectivity. Compared with sample No. 1, increase of Si content (sample No. 2) or slight dealumination (sample No. 1-L1) caused a rise in coke yield. These results suggested the dominative effect of strong acidic sites that existed in the vicinity of Si domains on coking. As known in the foregoing acidity section, well-spread Si favored intermediate acidity and improved isobutylene selectivity, while deep dealumination destroyed the zeolite structure (amorphous $AlPO_4$ was then formed) and led to a poor product distribution.

To confirm the positive effect of intermediate acidity on the titled reactions, a trace amount of H_2O vapor was introduced into the reaction system from a saturator. This

enhanced catalytic activity a great deal, as shown in figure 5 due to the increase of intermediate acidity by H_2O chemisorption.

4. Conclusion

Si domains were formed in SAPO-11 when the synthesis mixture contained excessive Si. During dealumination, Al adjacent to Si in SAPO-11 was firstly removed which led to formation of Si domains, and amorphous $AlPO_4$ was then resulted.

SAPO-11 possessed intermediate acidity and met the needs of skeletal isomerization of linear butylenes. Si domains induced strong acidic sites, and amorphous $AlPO_4$ destroyed the acidity distribution. These unbenefited the effective conversion of linear butylenes into isobutylene. A trace amount of H_2O in the reaction system might improve the acidity of SAPO-11 and favor isobutylene formation.

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