

Synthesis of SAPO-41 Molecular Sieves with Different SiO₂/Al₂O₃ Ratios and their Catalytic Performance of n-Decane Hydroisomerization

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Abstract: Using di-n-propylamine (DPA) as a template, SAPO-41 molecular sieves with SiO₂/Al₂O₃ ratios (n) of 0.3, 0.5, and 0.7 were synthesized. Their structure, morphology and acidity were characterized by XRD, N₂ physical adsorption, SEM, and Py-IR. All the synthesized samples have characteristic diffraction peaks corresponding to the AFO topological structure, which means that samples are pure phase SAPO-41 molecular sieve. The samples exhibited a highly ordered prismatic morphology with regular arrangement of individual grains, wrapped in flakes, and possessed complete channel structure. With the increase of n, the specific surface area and the amount of B acid showed a downward trend after increasing. Hydroisomerization reaction results of n-decane over SAPO-41 loaded with 0.5wt% Pd (Pd/SAPO-41(n)) showed that the higher the amount of B acid, the higher the conversion of n-decane, and high specific surface area and moderate B acid are favorable for yield of isomerization products. When the conversion of n-decane catalyzed by Pd/S41(0.3)-P was 88.9%, the yield of hydroisomerization products reached 83.3%.

1. Introduction

Iso-alkanes can be obtained by hydroisomerization of *n*-alkanes. With increasing of *iso*-alkanes content, the freezing point or pour point of diesel oil or lubricating oil is significantly reduced, reduce and the fluidity is greatly improved, while maintaining a high cetane number.[1~2]. For low-carbon alkanes, the octane number of gasoline increases significantly, which meets automotive requirements for high quality fuel [3~4].

In the process of hydroisomerization of long-chain *n*-alkanes, cracking reactions are often accompanied, which reduces the selectivity of branched alkanes and yield of fuel oil [5~6]. It is important to choose a molecular sieve carrier with a suitable pore structure and acidity.

In this paper, a series of SAPO-41 molecular sieves with different silicon contents by changing SiO₂/Al₂O₃ in the initial gel used di-n-propylamine (DPA) as a template. The influences of silicon content on structure, morphology and acidity of SAPO-41 molecular sieves and the catalytic performance of n-decane hydroisomerization were discussed.

2. Experimental

Using di-n-propylamine (DPA) as a template, SAPO-41 molecular sieves with different silicon contents (SiO₂/Al₂O₃ ratio (n) are 0.3, 0.5, 0.7, named S41(n)-P) and the bifunctional catalysts of



SAPO-41 loaded 0.5wt%Pd (0.5Pd/S41(n)-P) were synthesized, referring to [7]. The process of hydroisomerization of n-decane catalyzed by 0.5Pd/S41(n)-P was carried out, referring to [8].

3. Results and discussion

3.1. Characterization of S41(n)-P

The structure, morphology, and acidity of the synthesized S41(n)-P were characterized by means of XRD, SEM, N₂ physical adsorption, and Py-IR, the results were shown in Fig.1~4 and Table 1~2.

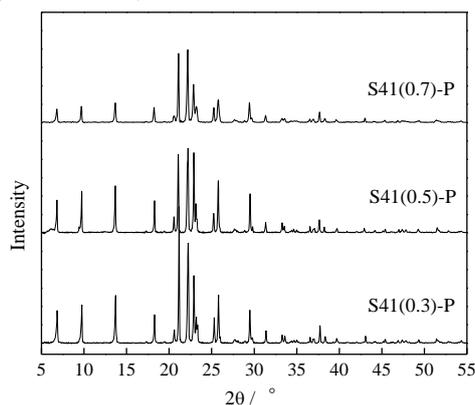


Fig. 1 XRD patterns of S41(n)-P samples

It can be seen from Fig.1 that compared with the standard spectrum of AlPO₄-41 molecular sieve, all the synthesized S41(n)-P samples have characteristic diffraction peaks corresponding to the AFO topology without the finding of diffraction peaks heterocrystals, indicating that the synthesized samples are pure SAPO-41 molecular sieve. With the increase of silicon content, the characteristic diffraction peak intensity of the sample decreases, indicating that the crystallinity of the sample decreases with the increase of silicon content. This may be due to the fact that when the silicon content in the initial gel is higher, silicon is not conducive to entering the molecular sieve framework and forming non-skeletal species.

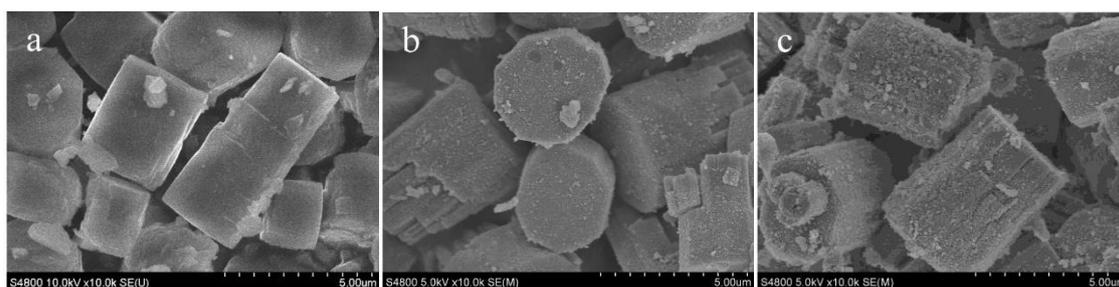


Fig. 2 SEM images of S41(n)-P samples. (a) S41(0.3)-P; (b) S41(0.5)-P; (c) S41(0.7)-P.

The SEM images of S41(n)-P shown in Figure 2 represent the typical morphology of SAPO-41 molecular sieves, which all show a regular arrangement of single crystal, a sheet-like wrapping, and a highly ordered prismatic structure. With the increase of silicon contents in the initial gel, the morphology of the S41(n)-P sample did not change significantly, but irregular small crystal aggregates appeared on the sample surface, which may be part of the non-skeletal species mentioned above.

It can be seen from the N₂ adsorption-desorption isotherms of S41(n)-P samples shown in Fig.3 that the isotherms of all samples have the characteristics of type I isotherms presented by microporous molecular sieves.

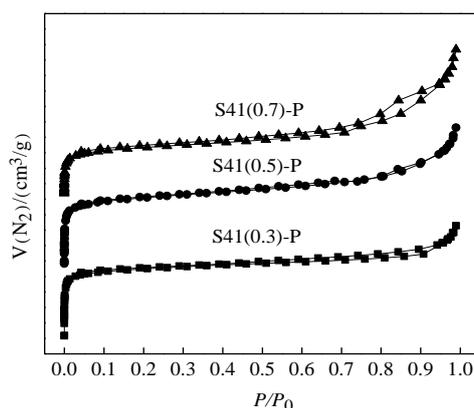


Fig. 3 N₂ adsorption-desorption isotherms of S41(n)-P samples

The S41(0.7)-P sample showed obvious hysteresis loops at the relative partial pressure $P/P_0 = 0.5\sim 0.9$, which may be due to the existence of structural defects in the sample or the formation of intergranular pores with small crystals.

It can be known from Table 1 that as the silicon content increases, the microporous specific surface area and micropore volume of the sample increase, indicating that the channel structure of S41(n)-P is more complete. When the silicon content further increases, the microporous specific surface area and microporous volume of the sample decrease, which may be due to the clogging of the pores due to the formation of some non-skeletal species.

Table 1 N₂ adsorption data of S41(n)-P samples

Samples	Surface area(m ² /g)			Pore volume (cm ³ /g)		
	BET ^a	Micropore ^b	External	Total ^c	Micropore ^b	Mesopore
S41(0.3)-P	215	190	25	0.129	0.074	0.055
S41(0.5)-P	236	196	40	0.165	0.077	0.088
S41(0.7)-P	167	131	36	0.166	0.052	0.114

^aBET method, ^bt-plot method, ^cVolume adsorbed at $P/P_0 = 0.99$.

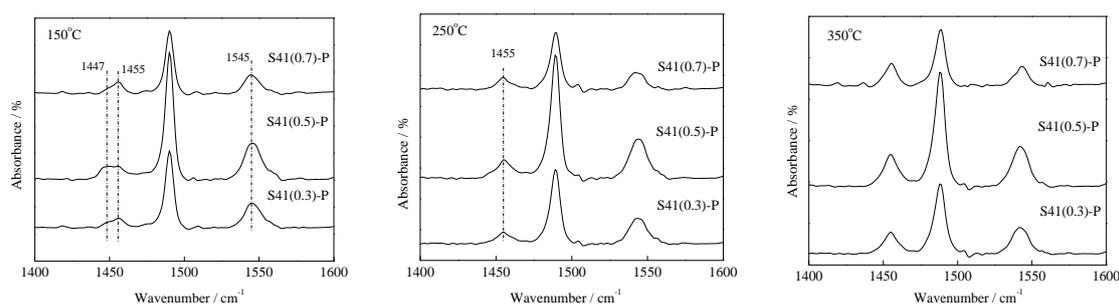


Fig. 4 Py-IR spectra of S41(n)-P samples

It can be seen from Fig.4 that when the pyridine desorption temperature is 150°C, two absorption peaks appear in the vibration region of 1440~1462 cm⁻¹. The peak at 1447 cm⁻¹ is due to the interaction between pyridine and Si-OH, and the peak 1455 cm⁻¹ is attributed to the variable-angle vibration of the CH bond of the pyridine molecule adsorbed on the L acid site, that is, the interaction between pyridine and the L acid site. As the desorption temperature of pyridine increases, the absorption peak at 1447 cm⁻¹ decreases. This is due to the decrease in the adsorption of pyridine molecules and Si-OH at high temperature, which results in the desorption from the surface of Si-OH. The acid sites for desorbing

pyridine at relatively low temperatures belong to weaker acid sites, while the acid sites for desorbing pyridine at higher temperatures belong to stronger acid sites. In S41(n)-P, the L acidic site is derived from a framework defect site or a non-framework species in the molecular sieve, and the B acidic site is derived from Si substituted P or Al and P to generate a bridge hydroxyl group in Si-OH-Al. The acid amount of the sample was calculated from the peak area of the pyridine infrared spectrum, and the results are shown in Table 2.

Table 2 Acid distribution of S41(n)-P samples

Samples	Brönsted acid ($\mu\text{mol/g}$)		
	150°C	250°C	350°C
S41(0.3)-P	30.23	29.03	21.30
S41(0.5)-P	44.62	41.34	28.94
S41(0.7)-P	20.71	17.01	11.64

It can be seen from Table 2 that as the silicon content increases, the amount of B acid on the sample increases. This is because more silicon enters the molecular sieve framework and generates more negative charges, and more hydrogen protons are needed to balance the framework charge, which leads to more B acid sites generated on the molecular sieve. With the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the initial gel, Si follows the SM3 mechanism, that is, the proportion of two Si replacing one P and one Al into the molecular sieve framework increases, forming more border area, more strong B acid sites are generated. However, when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the initial gel was increased to 0.7, the amount of B acid in the sample decreased. This may be due to the excessive amount of silicon in the initial gel, which prevents it from entering the molecular sieve framework, forming some non-framework silicon species in the molecular sieve product.

3.2. 0.5Pd/S41(n)-P catalytic hydroisomerization

Fig. 5 shows the results of n-decane conversion and isomerization selectivity at different reaction temperatures in the n-decane hydroisomerization reaction under the action of the bifunctional catalyst 0.5Pd/S41(n)-P.

It can be seen from Fig.5 that as the reaction temperature increases, the conversion of n-decane on each catalyst increases. In the high temperature region, the increase in the conversion of n-decane tends to be gentle, which may be due to the influence of the diffusion rate at high conversion. The order of the reactivity of each catalyst is 0.5Pd/S41(0.5)-P > 0.5Pd/S41(0.3)-P > 0.5Pd/S41(0.7)-P, which is consistent with the order of its B acid amount. When the conversion of n-decane is greater than 55%, the selectivity order of isomerization on the catalyst is 0.5Pd/S41(0.3)-P > 0.5Pd/S41(0.5)-P > 0.5Pd/S41(0.7)-P. 0.5Pd/S41(0.5)-P has a large amount of strong B acid, which leads to an intensified cracking reaction. Due to the presence of some non-skeletal species on 0.5Pd/S41(0.7)-P, the pore channels are blocked, and the microporous channels are smaller, which limits the diffusion of reaction intermediates and products, and increases the probability of cracking reactions.

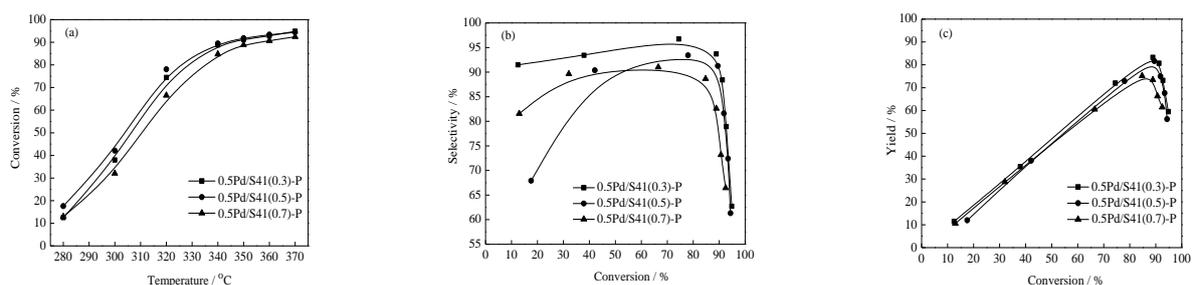


Fig. 5 Catalytic performance of 0.5Pd/S41(n)-P in n-decane hydroisomerization

(a) Conversion of n-decane; (b) Selectivity for i-decane; (c) Yield of iso-decane.

0.5Pd/S41(0.3)-P with suitable acid strength and pore volume can effectively inhibit the cracking reaction under certain active conditions, and therefore shows the highest selectivity of hydroisomerization products. It can be seen from Fig.5(c) that the yield of the isomerization product on 0.5Pd/SAPO-41 first increases and then decreases with the increase of the n-decane conversion, which is consistent with the conversion mechanism of n-alkanes on bifunctional catalysts. The carbocations obtained from the dehydrogenation of n-decane at the metal site undergo isomerization or cracking reaction at the acid site. When the reaction temperature is higher, the conversion of n-decane is increased, but the cracking reaction is intensified, resulting in a decrease in the yield of the isomerization product.

Among three catalysts, the highest hydroisomerization yield on 0.5Pd/S41(0.3)-P reached 83.3% at the n-decane conversion of 88.9%.

4. Conclusions

The pure phase SAPO-41 molecular sieves with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were synthesized using DPA as a template. With the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the specific surface area and the amount of B acid showed a downward trend after increasing. The conversion of n-decane rises with the increase of B acid amount, but high specific surface area and moderate B acid are favorable for the yield of hydroisomerization products. Pd/S41(0.3)-P is the best catalyst and the yield of isomerization products reached 83.3% at a conversion of n-decane of 88.9%.

5. References

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