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Dehydroisomerization of n-butane to isobutene over Pd/SAPO-11 The effect of Si content of SAPO-11, Catalyst preparation and Reaction condition

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The SAPO-11 molecular sieves with different Si content were synthesized and modified by Pd for direct transformation of n-butane to isobutene. The effects of Si content of SAPO-11, catalyst preparation and reaction condition were studied. The catalytic properties of Pd/SAPO-11 varied with Si content of the crystal products. The impregnation time of the catalyst had effect on the product distribution and catalytic activity. The catalytic properties also changed with the reaction time.

1. INTRODUCTION

Different processes for isobutene production including skeletal isomerization of n-butene received a lot of attention during recent years since the increasing demand of isobutene in industry. Direct conversion of n-butane to isobutene is a novel interesting process [1-3]. In the present work, a new series of catalysts based on the Pd modified SAPO-11 with different Si content for the direct transformation of n-butane to isobutene were prepared and studied. The effect of impregnation time of the catalyst and the effect of time on stream on the catalytic properties were also investigated in details.

2. EXPERIMENTAL

Pseudoboehmite, 85% wt orthophosphoric acid and colloidal silica were used as the aluminum, phosphorus and silicon starting materials. Di(n-propyl)amine was used as the template for AIPO-11 and SAPO-11. The synthesis followed the procedures reported in the literature [4]. The products were filtrated, washed, dried and calcined at 773 K to remove the template. The elementary analysis of the synthesized samples was determined with X-ray fluorescence spectrum. The Pd modified catalysts were prepared by impregnating the calcined molecular sieves under vacuum with Pd(NH₃)₄Cl₂ solution for a certain time. The catalysts were then calcined in air at 773 K for 2 h.

The BET and pore distribution were measured with physical adsorption at liquid nitrogen temperature. ¹H-NMR was employed to test the hydroxyl group over the

surface of the synthesized SAPO-11s. NH_3 -TPD was measured to determine the acid amount of each sample. Pulse CO chemisorption was measured to determine the metal dispersion of the prepared catalysts.

N-Butane catalytic transformations were performed in a fixed bed flow reactor at atmosphere pressure. The catalysts were reduced with hydrogen ($60 \text{ cm}^3/\text{min}$) at 773 K for one hour. The reaction parameters used were reaction temperature = 773 K, WHSV = 1.98, $\text{H}_2/\text{n-butane} = 2 \text{ mole/mole}$ and weight of catalyst = 0.5g. The catalytic reaction data was all obtained at TOS=60 min. The reaction products were analyzed by on-line gas chromatography.

3. RESULTS AND DISCUSSION

The as-synthesized solids are all highly crystalline with AEL topology, in agreement with the literature. The Si content, BET and microporous volume of the calcined samples are listed in table 1. With the increase of Si content from 0 to 5.5-wt%, the BET surface area increases, but the microporous volume of the samples changes unmarkedly.

Table1

BET and Microporous volume of the synthesized samples

Sample	Si content (wt%)	BET (m^2/g)	Microporous volume (cm^3/g)
AIPO-11	0	140.63	0.063
SAPO-11(1)	1.5	156.39	0.065
SAPO-11(2)	2.8	170.73	0.067
SAPO-11(3)	4.6	171.19	0.069
SAPO-11(4)	5.5	186.84	0.070

The transformations of n-butane over Pd/SAPO-11s with different Si content were measured. The catalytic activity and product distribution varied with Si content and extreme values of catalytic properties can be found in table 2. For the first four points of low Si content, with the increase of Si content, the conversion increased and a maximum activity was obtained around Si content 4.6 wt%. After this point, the conversion declined. Compared to the change of catalytic activity, the dehydrogenation selectivity changed in the opposite way. When Si content was 4.6 wt %, highest isobutane selectivity and lowest isobutene selectivity was obtained, but the total isomerization products (isobutane and isobutene) selectivity attained to the maximum value at the same point. These catalytic properties imply that at different silicon content, the SAPO-11 molecular sieve may have different acidity; the properties of supported palladium may also change.

Table 2

The influence of the Si content in SAPO-11 on the catalytic properties of Pd/SAPO-11s.

Catalyst	Catalytic properties				
	Conversion (%)	Selectivity (%)			
		iC ₄ ⁼	Total C ₄ ⁼	iC ₄ ⁰	C1-C3 ^a
Pd/AlPO-11	13.8	17.57	84.61	6.58	8.53
Pd/SAPO-11(1)	16.6	33.73	80.82	11.55	7.22
Pd/SAPO-11(2)	22.01	28.44	67.15	16.49	11.81
Pd/SAPO-11(3)	24.46	25.63	61.12	24.86	12.81
Pd/SAPO-11(4)	22.97	31.61	77.71	9.23	8.29

^aC₁-C₃ selectivity: the selectivity of (CH₄+C₂H₆+C₂H₄+C₃H₈+C₃H₆)

Figure 1 shows the ¹H NMR spectra of the synthesized SAPO-11 with different Si content. For AlPO-11, very weak resonance peaks can be found, indicating the character of the nearly neutral framework. With the incorporation of silicon into the framework, the line at 3.45ppm due to surface bridge hydroxyl group Si(OH)Al appears and with the increase of Si content, the strength increases and shows the maximum value at 4.6 wt % silicon content. It is well known that one Si substitution for one Al will generate one Si(4Al) species and one corresponding bridge hydroxyl group. The result of ¹H NMR shows this trends at low Si content -- the increase of Si incorporation will generate more bridge hydroxyl groups; But for the SAPO-11 with high Si content, Si substitution may also happen in another way -- two Si substitution for one Al and one P. This kind of Si incorporation may generate more neutral Si (0Al) species and the bronsted acid amount associated with Si(4Al) species decreases. The catalytic property difference of Pd/SAPO-11 with different Si content should be mainly attributed to the acidity difference of SAPO-11 as the catalyst support.

The catalysts Pd/SAPO-11 with different Pd impregnation time (0, 6, 12, 24h) were tested in n-butane's transformation. The result is showed in table 3. It can be found that with the impregnation time increase, the catalytic activity and isomerization selectivity increased, but the dehydrogenation selectivity decreased. The CO pulse adsorption was employed to test the Pd properties of this series of catalysts. With impregnation time increasing from 0 to 24 h, the metal dispersion increased from 32.67% to 52.53%; the catalytic properties associated with bifunctional catalyzing such as isomerization and cracking became more violent, but dehydrogenation selectivity decreased. This indicates that increasing the impregnation time will strengthen the interaction between the acid support and supported metals and weaken the metallic properties of the Pd particles.

Table 3

The catalytic properties and metal dispersion of Pd/SAPO-11 with different impregnation time

Catalyst	Pd/SAPO-11 □ 0.1% Pd □			
	0	6	12	24
Impregnation time (h)	0	6	12	24
Conversion (%)	12.94	21.89	24.46	25.64
Selectivity (%)				
i-C ₄ ⁰	8.11	20.24	24.86	42.20
i-C ₄ ⁺	33.62	28.14	25.63	17.71
i-C ₄ ⁰ + i-C ₄ ⁺	41.73	48.38	50.49	59.91
^a Total C ₄ ⁺	79.60	66.96	61.12	45.83
^b C ₁ -C ₃	12.21	12.11	12.10	10.10
^c C ₅ ⁺	0.08	0.69	1.92	1.87
Metal Dispersion (%)	32.67	43.19	47.43	52.53

^aTotal C₄⁺: n-C₄H₁₀ + i-C₄H₁₀ + t-C₄H₁₀ + c-C₄H₁₀

^bC₁-C₃: CH₄ + C₂H₆ + C₂H₄ + C₃H₈ + C₃H₆

^cC₅⁺: C₅ and products larger than C₅

The changes of the catalytic properties, acidity and metallic properties of Pd/SAPO-11 with time on stream were tested. The NH₃-TPD and CO pulse adsorption results in table 4 show that when time on stream increased, the acid sites amount of the catalyst decreased at the beginning, then reached to a stable value and the Pd dispersion decreased at the same time. The catalytic properties listed in figure 3 are consistent with the characterization results of the catalyst. The acidity, isomerization selectivity and cracking selectivity decreased with reaction time but the dehydrogenation selectivity associated the metallic function increased.

Table 4

The acidity and metallic properties of the Pd/SAPO-11 at different reaction time

Reaction Time (h)	Acidity Amount (mmol/g)	Metallic Properties	
		CO Adsorption Amount (ml/g STP)	Palladium Dispersion (%)
0	0.610	0.100	47.43
0.5	0.559	0.076	36.17
1.5	0.535	0.066	31.21
6	0.526	0.055	25.83

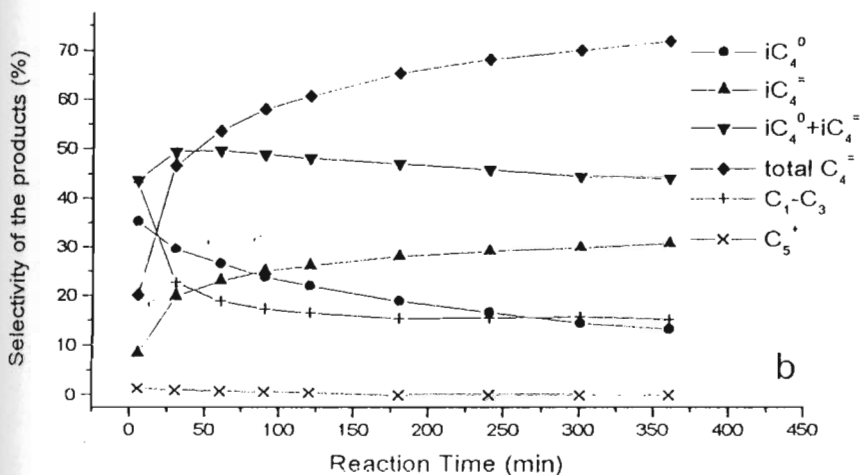
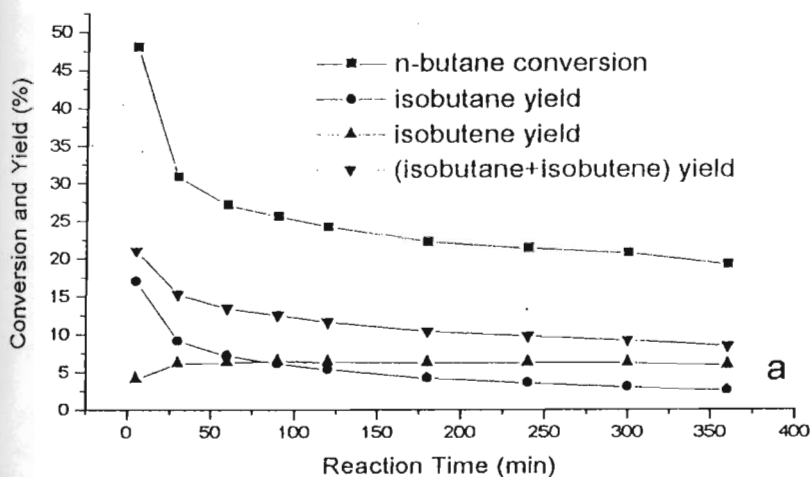


Figure 2 The yield and selectivity of the products at different reaction time

CONCLUSION

The structure of Si species in SAPO-11 changed with Si content and an extreme difference for bronsted acid amount can be found. This can be used to explain the extreme difference of the catalytic properties. Increasing the impregnation time of the catalyst will promote bifunctional catalyzing reaction such as isomerization and cracking, but weaken the function of supported Pd particles. The acid function and metallic function

of the catalyst changed with time on stream in the opposite way, and the catalytic property changes indicate the same trends. All the effect talked above, the effect of the Si content of SAPO-11, preparation condition and reaction time, show the interaction of acid support and supported metal particles of the catalysts.

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