Production of isobutene from n-butane over Pd modified SAPOs and MeAPOs

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ABSTRACT

Pd modified AlPO-11 and SAPO-5, 11, 34 were used in the direct transformation of n-butane to isobutene. The effect of acidity and porous structure on the supported Pd and the catalytic performance were discussed. For higher isobutene selectivity, some metals, such as Ti, Fe, Mg, Co and Mn, was incorporated into AlPO-11 framework and isobutene selectivity of 34.86% can be obtained over Pd/MnAPO-11. A combined catalyst system was used for a further improvement of the isobutene selectivity.

1. INTRODUCTION

Some SAPOs molecular sieves, such as SAPO-5, 11, 34, which possesses AFI, AEL and CHA topology respectively, have been proved to be very active and selective catalysts for many reactions [1,2]. SAPO-11 and metal substituted SAPO-11were reported as selective catalyst for isomerization of n-butene [3, 4].

Different processes for isobutene production including skeletal isomerization of n-butene received much attention recently with the increasing demand of isobutene in industry [5-7]. Considering the abundant supply of n-butane from natural gas and refinery streams, n-butane is the preferred raw material for isobutene production.

In the present work, the catalysts of Pd modified AlPO and SAPOs were prepared and used in dehydroisomerization of n-butane to isobutene. The effects of acidity and porous structure of the support on the catalytic performance were investigated in detail. To improve the isobutene selectivity, Ti, Mg, Fe, Co and Mn were incorpated into AlPO-11 and a combined catalyst was used for this reaction.

2. EXPERIMENTAL

2.1 Synthesis of molecular sieve

AlPO-11, SAPO-5, 11, 34, and MeAPO-11s were synthesized by hydrothermal method, following the procedure reported in the literature [8]. The products were filtrated, washed, and dried at 373 K for 3 h, then calcined at 823 K for 6 h to completely remove the template.

2.2 Catalyst preparation

Pd modified catalysts were prepared by impregnating the calcined molecular sieves with a solution of $Pd(NH_3)_4Cl_2$. The samples were then dried at 373 K for 10 h and calcined at 773 K in air for 4 h.

2.3 Characterization

Crystallinity and phase purity of the as-synthesized samples were characterized by powder X-ray diffraction. The chemical composition of the samples was determined with X-ray fluorescence technique. Surface area and porosity measurements were carried out by physical adsorption. Acidity of the samples was characterized using temperature programmed desorption (TPD) spectra of ammonia.

2.4 Catalytic testing

The catalytic tests were performed using a fixed bed reactor system at atmosphere pressure. Before reaction, the catalysts were reduced in situ with H_2 (60 cm^3/min) at 773 K for 1 h, then the atmosphere was switched from H_2 to the feed, a mixture of H_2 and n-butane (the molar ratio of H_2 /n-butane was 2). The weight hourly space velocity (WHSV) was 1.98 h^{-1} for n-butane. The reaction products were analyzed on-line by a Varian GC3800 gas chromatograph equipped with a FID detector and an Al_2O_3 capillary column.

3. RESULTS AND DISCUSSION

For the samples of SAPO-11, SAPO-34 and SAPO-5, the position and the intensity of the diffraction peaks of their XRD patterns were identical to those reported in the literature [8]. XRD patterns of AlPO-11 and metal-containing AlPO-11 showed in Fig.1 indicate that they are highly crystalline with no obvious impurity phase.

The chemical composition, BET and microporous volume of the synthesized AlPO and SAPO samples are listed in Table 1 for comparing. With modulating the composition of the starting gel, three SAPOs with nearly the same chemical composition of the crystalline products were obtained. Pore geometry difference exists between SAPO-5, 11 and 34 molecular sieves. Among the four samples,
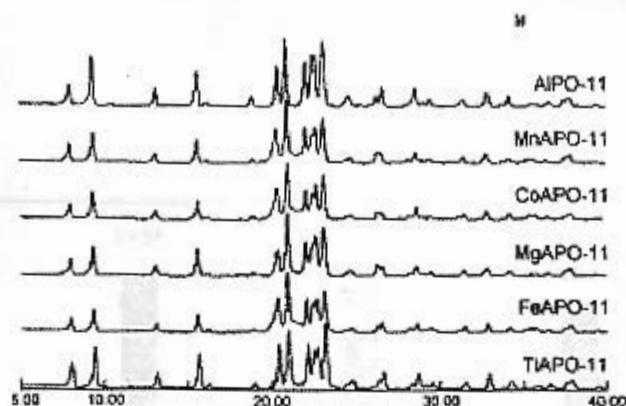
Fig.1. The XRD patterns of the synthesized AlPO-11 and McAPO-11s

SAPO-34 possessed the highest specific area and microporous volume.

The reaction results of Pd modified SAPO-5, SAPO-11 and SAPO-34 in Fig. 2 showed the effect of pore geometry on the catalytic properties. For Pd/SAPO-11, n-butane was mainly transferred to isobutene and other butenes. A small quantity (<20%) of cracking and hydrogenolysis products was also obtained. But for Pd/SAPO-34 and Pd/SAPO-5, an abrupt change in product distribution and catalytic activity was observed. Though the dehydrogenation product was also obtained, the simultaneous skeletal isomerization is virtually suppressed over the two samples. The pores of the catalyst are thought to accommodate the intermediate of isomerization and the metal particle with dehydrogenation function, so pore geometry of the molecular sieve may play an important role for the catalytic performance. Among the catalysts, SAPO-34 has the largest micropore volume and area, but its 8-member ring pore opening may sterically inhibit the isomerization of n-butane or n-butene; for Pd/SAPO-5, with the 12-ring pore-opening molecular sieve, no sterical inhibition for isomerization exists in this catalyst, the low isomerization selectivity may come from its weak acidity.

Table 1

Molar compositions, specific area and microporous volume of the crystalline products

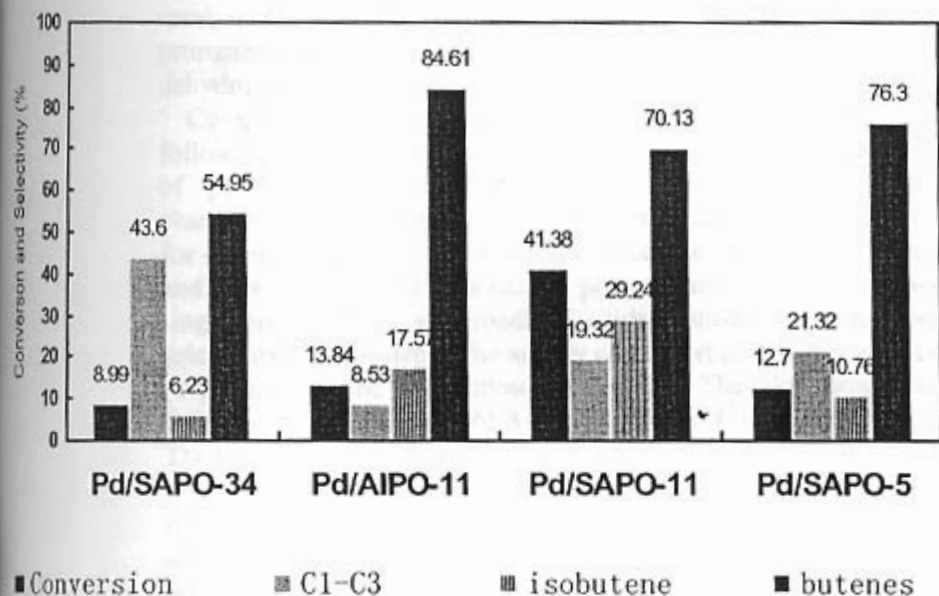| Product	Mole composition	Specific area (m^2/g)	Microporous volume (cm^3/g)
SAPO-34	$Al_{0.50}P_{0.44}Si_{0.06}O_2$	554	0.273
AlPO-11	$Al_{0.50}P_{0.50}O_2$	120	0.063
SAPO-11	$Al_{0.50}P_{0.44}Si_{0.06}O_2$	137	0.067
SAPO-5	$Al_{0.50}P_{0.44}Si_{0.06}O_2$	158	0.063

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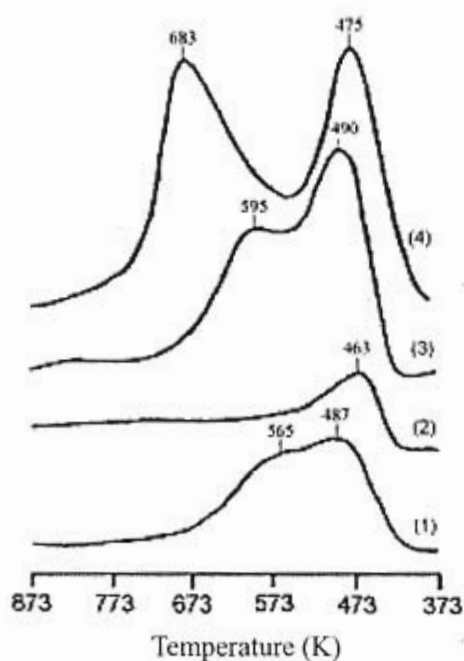Fig. 2 The catalytic performance of Pd/AlPO-11 and Pd/SAPOs.

Fig. 3 NH₃-TPD patterns of AlPO-11 and SAPOs
(1) SAPO-5 (2) AlPO-11 (3) SAPO-11 (4) SAPO-34

For Pd/AIPO-11 and Pd/SAPO-11, the molecular sieve as the support possessing the same AEL topology, the difference of the catalytic performance should be attributed to the acidity. AIPO-11 showed the weakest acidity (see Fig. 3), which results from the absence of acidic sites over the neutral framework, so over the catalyst of Pd/AIPO-11, the dehydrogenation catalyzed by noble metal is prominent; while over the Pd/SAPO-11, with the medium-acidic support, the dehydrogenation and isomerization can happen simultaneously.

Comparing the NH_3-desorption peaks in the Fig 3, the acid strength roughly followed the order that: SAPO-34>SAPO-11>SAPO-5; while we know the order of pore opening is: SAPO-34<SAPO-11, AIPO-11<SAPO-5. From the characterization results and catalytic performance, poor activity and selectivity for isobutene were obtained over the catalysts of Pd/SAPO-5 with weak acidity and over Pd/SAPO-34 with narrow pore opening. Pd/SAPO-11 with 10-member ring pore opening and medium acidity showed the highest activity and selectivity for isobutene. The acidity of support also has an effect on the metallic properties of the bifunctional catalysts. The dehydrogenation selectivity followed the order of Pd/AIPO-11>Pd/SAPO-5>Pd/SAPO-11>Pd/SAPO-34. The butenes selectivity order is opposite to the order of acidity.

Metal incorpored AIPO-11 have been proved to be selective catalysts for n-butene isomerization [3,4]. In this study, MeAPO-11 also showed special catalytic properties in n-butane's dehydroisomerization. More isobutene selectivity can be obtained over the sample of Pd/MeAPO-11, especially for Pd/MnAPO-11, the isobutene selectivity attained to 34.86% (see table 2).

To improve the isobutene selectivity, two consecutive catalysts, a dehydroisomerization catalyst of Pd/SAPO-11 in the upper part and a complementary skeletal isomerization catalyst of SAPO-11or MnAPO-11 in the lower part were used in one fixed catalyst bed. The catalytic performance of n-butane transformation at 823 K over these dual-layered catalysts are showed is shown in Table 3. Compared with the catalytic performance of Pd/SAPO-11, a relatively high selectivity towards isobutene could be obtained over the combined catalysts bed.

Table 2

The catalystic properties of Pd/AIPO-11 和 Pd/MeAPO-11 at 773 K

Catalyst	Conversion (%)	Selectivity (%)				
		$iC_4^=$	Total $C_4^=$	iC_4^0	C_1-C_3[b]	C_5^{+c}
Pd/TiAPO-11	15.87	30.38	83.11	7.49	8.56	0.84
Pd/FeAPO-11	15.33	30.70	83.20	7.69	8.69	0.42
Pd/MgAPO-11	16.27	32.64	82.91	7.19	9.59	0.31
Pd/CoAPO-11	18.89	33.61	81.54	10.65	7.81	0
Pd/MnAPO-11	20.14	34.86	82.52	9.63	7.85	0

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Table 3
Catalytic performances of catalysts in a two-layered bed at 823 K

Catalyst	Conversion (%)	Isobutene yield (%)	Selectivity(%)			
			$iC_4^=$	Total $C_4^=$	iC_4^0	Other [a]
Pd/SAPO-11(upper) +SAPO-11(lower)	28.62	9.27	32.40	76.62	6.73	16.65
Pd/SAPO-11(upper) +MnAPO-11(lower)	27.10	9.65	35.63	77.14	7.32	15.54

[a] Other products: C_1-C_3(CH_4+C_2H_6+C_2H_4+C_3H_8+C_3H_6), C_5 and products higher than C_5.

3. CONCLUSION

SAPO-5, 11, 34 and metal-containing AlPO-11 were synthesized. Characterization results showed that the acid strength order is: SAPO-34>SAPO-11>SAPO-5>AlPO-11. The Pd modified catalysts based on these molecular sieves were used for the dehydroisomerization of n-butane to isobutene. Poor activity and selectivity to isobutene were obtained over the catalyst based on the SAPO-5 or AlPO-11 with weak acidity and SAPO-34 with narrow pore opening. The Pd modified SAPO-11 with 10-member ring pore opening showed highest activity and selectivity to isobutene among the four catalysts. A medium strong acidity and suitable pore geometry may be needed in this transformation of n-butane to isobutene in one step. Metal incorporation into AlPO-11 generated good isomerization properties, and 34.86% isobutene selectivity was obtained over Pd/MnAPO-11. With combined catalysts Pd/SAPO-11 and MnAPO-11, the isobutene selectivity can be further improved.

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