Mn-containing AlPO-11 and SAPO-11 catalysts for simultaneous isomerization and dehydrogenation of *n*-butane

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MnAPO-11 and MnAPSO-11 were synthesized hydrothermally, and supported Mn-AlPO-11 and Mn-SAPO-11 were also prepared for comparison. Characterization results showed that there were differences in acidity and reducibility caused by the different incorporation methods of manganese. The manganese species in the samples also weakened the metallic properties of the palladium particles when the latter was added into the catalysts. Catalytic testing results for dehydroisomerization of *n*-butane indicated that incorporation of manganese increased the selectivity toward isomerization products. The highest isobutene selectivity (34.86%) could be obtained over a Pd/MnAPO-11 catalyst. When a combined catalyst system containing Pd/SAPO-11 and MnAPSO-11 was used in a single bed of two layers, the isobutene selectivity could be greatly improved, as compared to the single catalyst alone.

KEY WORDS: MnAPO-11; MnAPSO-11; acidity; metallic property; dehydroisomerization; *n*-butane; isobutene.

1. Introduction

With the increasing demand of isobutene in industry, different processes for isobutene production received much attention recently. *n*-Butane is considered as the preferred raw material for isobutene production because of its abundant supply from natural gas and refinery streams. Compared with the two-step production of isobutene from *n*-butane comprising isomerization and dehydrogenation units, direct transformation of *n*-butane to isobutene is a novel process. Pt/ZSM-5, Zn/KZSM-5 and Pt/MnAPSO-11 have been used as catalysts for this one-step process [1–4].

Metal-substituted AlPO-11 and SAPO-11 molecular sieves have been proved to be very selective catalysts for skeletal isomerization of *n*-butene [5–7]. In our previous study, MeAPO-11s and MeAPSO-11s (Me = Fe, Co, Mg, Ti, Mn) were synthesized and used as the catalysts for dehydroisomerization of *n*-butane to isobutene, and MnAPO-11 and MnAPSO-11 exhibited high isobutene selectivity [8]. In the present work, a series of molecular sieves of Mn-containing AlPO-11 and SAPO-11, as well as Pd-containing analogues, were prepared and used in the dehydroisomerization of *n*-butane. The effects of the incorporation of manganese on the catalytic properties were investigated in detail. For improving the selectivity toward isobutene, combined catalyst systems containing Pd/SAPO-11 and MnAPO-11 or Pd/SAPO-11 and MnAPSO-11 were also used in this reaction.

2. Experimental

2.1. Molecular sieve sample preparation

AlPO-11, SAPO-11, MnAPO-11 and MnAPSO-11 were prepared with the hydrothermal method. Pseudoboehmite, orthophosphoric acid (85 wt%), colloidal silica and $Mn(CH_3COO)_2 \cdot 4H_2O$ were used as the sources of aluminum, phosphorus, silicon and manganese, respectively. Di(*n*-propyl)amine was used as the template. The synthesis of AlPO-11 and SAPO-11 followed the procedure reported in the literature [9]. The chemical composition of the starting gel was $Al_2O_3 \cdot P_2O_5 \cdot 1.1 DPA \cdot 40 H_2O$ for AlPO-11 and $Al_2O_3 \cdot P_2O_5 \cdot 0.4 SiO_2 \cdot 1.1 DPA \cdot 55 H_2O$ for SAPO-11. Samples of MnAPO-11 and MnAPSO-11 were also synthesized according to the procedure described in the literature [10]. The chemical composition of the starting gel was $Al_2O_3 \cdot P_2O_5 \cdot 1.1 DPA \cdot 0.04 MnO \cdot 40 H_2O$ for MnAPO-11 and $Al_2O_3 \cdot P_2O_5 \cdot 0.4 SiO_2 \cdot 1.1 DPA \cdot 0.04 MnO \cdot 55 H_2O$ for MnAPSO-11. The gels were sealed in stainless steel autoclaves lined with polytetrafluoroethylene (PTFE) and heated at 473 K for 96 h. The products were filtered, washed, dried at 373 K for 3 h and then calcined at 823 K for 6 h to completely remove the template.

The samples of supported Mn-AlPO-11 and Mn-SAPO-11 for comparison were prepared by impregnating the samples of AlPO-11 and SAPO-11 with a solution of $Mn(NO_3)_2$. The samples were dried at 373 K for 3 h and then calcined at 823 K for 6 h, the same as the procedure for the samples of MnAPO-11 and MnAPSO-11.

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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. The metal loading was 0.1 wt% of palladium for all Pd-containing catalysts.

2.3. Characterization of samples

XRD patterns of the samples were obtained by using a RIGAKU D/max-rb powder diffractometer with Cu $K\alpha$ radiation. The chemical composition of the samples was determined with a Bruker SRS-3400 XRF spectrometer.

Acidity of the samples was characterized on the basis of temperature-programmed desorption (TPD) profiles of ammonia obtained with a Micrometric 2910 chemisorption equipment. A 200-mg sample was preheated at 873 K under pure helium (20 mL/min) for 1 h. The sample was then cooled down to 373 K in a flow of helium. After this, it was exposed to NH_3 that was injected into the helium stream (40 mL/min) until the adsorption reached saturation. The desorption process was monitored with a thermal conductivity detector at a temperature ramp from 373 to 873 K.

Pulse CO chemisorption experiments were also performed with the Micrometric 2910 chemisorption equipment to determine the metal dispersions of the catalysts. Prior to CO chemisorption, the catalysts were prereduced *in situ* with H_2 at 773 K for 1 h. Then the samples were flushed under helium for 1 h at 773 K and finally cooled down to ambient temperature in the helium stream, where it was held for 0.5 h. CO chemisorption was measured at 323 K. The diluted CO gas (5% CO and 95% He) was injected automatically till the adsorption reached saturation. The volume of adsorbed CO was measured and used to calculate the metallic dispersion on the basis of the assumption that the stoichiometric ratio of CO : Pd was 1 : 1.

2.4. Catalytic testing

Dehydroisomerization experiments of *n*-butane were performed at atmosphere pressure using a fixed-bed reactor system. The catalyst (particle size 0.4–0.9 mm, 0.5 g) was loaded in a stainless reactor of 5 mm i.d. Before the reaction, the catalyst was reduced *in situ* with H_2 (60 mL/min) at 773 K for 1 h, and then the flowing gas was switched from H_2 to the feedgas, which was a mixture of H_2 and *n*-butane (the molar ratio of H_2/*n*-butane was 2). The reaction condition was as follows: weight hourly space velocity (WHSV), 1.98 h^{-1} based on *n*-butane and temperature of 773 K. The reaction products were analyzed on-line by a Varian star 3800 gas chromatograph equipped with an FID and a capillary Plot/Al_2O_3 (50 m × 0.53 mm × 10 μm) column.

A dehydroisomerization–isomerization reaction over a dual-layered catalyst bed was conducted using the same reactor, but with a bed of two consecutive catalysts, i.e., dehydroisomerization catalyst (Pd/SAPO-11) and isomerization catalyst (MnAPO-11 or MnAPSO-11), as one integrated fixed bed. The upper part of the bed was loaded with 0.3 g of Pd/SAPO-11 and the lower part with 0.2 g of MnAPO-11 or MnAPSO-11. The catalysts were pretreated with a H_2 stream (60 mL/min) at 823 K for 1 h. Then the feedgas of H_2 and *n*-butane (the molar ratio of H_2/*n*-butane was 2) was introduced, and the tests were performed at 823 K.

3. Results and discussion

The as-synthesized solids were all highly crystalline with AEL topology, in agreement with the literature [9,10]. After calcination, the chemical compositions and the manganese contents of the four samples were determined by XRF. Supported samples of Mn-AlPO-11 and Mn-SAPO-11 were also prepared and characterized for comparison. The chemical composition is listed in table 1.

NH_3-TPD profiles of the prepared samples are shown in figure 1. For the Mn-containing samples prepared by the impregnation method, the Mn-AlPO-11 shows exactly the same profile as that of the AlPO-11, indicating that no change in acidity happened when manganese was supported on AlPO-11. This implies that the Mn-AlPO-11 was nonacidic, just like AlPO-11. On the other hand, when manganese was supported on SAPO-11, the desorption peak representing weak acidity and mid-strong acidity decreased, as compared to that

Table 1
The composition of the prepared samples

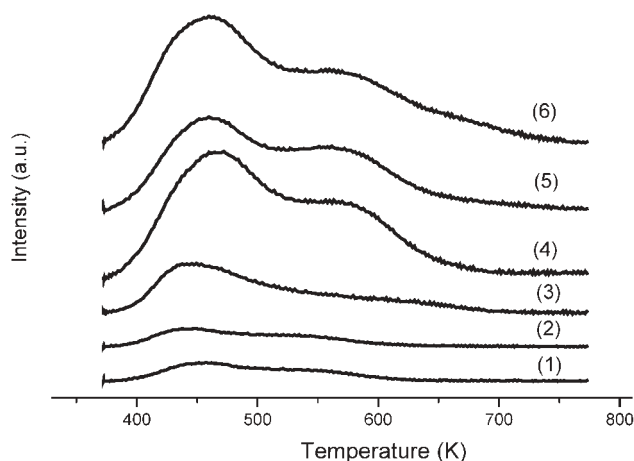| Sample	Molar composition of the molecular sieve	Mn content (wt%)
AlPO-11	$Al_{0.500}P_{0.500}O_2$	0
Mn-AlPO-11	$Al_{0.500}P_{0.500}O_2$ and impregnated MnO_x	1.50
MnAPO-11	$Al_{0.494}P_{0.491}Mn_{0.015}O_2$	1.34
SAPO-11	$Al_{0.502}P_{0.438}Si_{0.060}O_2$	0
Mn-SAPO-11	$Al_{0.502}P_{0.438}Si_{0.060}O_2$ and impregnated MnO_x	1.50
MnAPSO-11	$Al_{0.495}P_{0.431}Si_{0.062}Mn_{0.012}O_2$	1.08

Figure 1. NH_3-TPD profiles of the samples: (1) AlPO-11, (2) Mn-AlPO-11, (3) MnAPO-11, (4) SAPO-11, (5) Mn-SAPO-11, (6) MnAPSO-11.

Figure 2. The TPR patterns of Mn-containing AlPO-11 and SAPO-11: (1) Mn-AlPO-11, (2) Mn-SAPO-11, (3) MnAPO-11, (4) MnAPSO-11.

of the SAPO-11. The integration result of the peak area, as shown in table 2, also indicates a decrease in acidity for this Mn-supported sample. For the samples of MnAPO-11 and MnAPSO-11, in which the manganese was incorporated via hydrothermal synthesis, except for the NH_3 desorption at relatively low temperature (<650 K), they show the existence of weak or media-strong acidic sites; interestingly, the NH_3-desorption peaks still exist at relatively high temperatures (>650 K), indicating the generation of more strong acidic sites. The amount of acidity obtained from NH_3-desorption profiles shows that the hydrothermally synthesized MnAPO-11 and MnAPSO-11 possess more acidic sites than the AlPO-11 and the SAPO-11 samples. An acidity sequence can be obtained roughly from the profiles as follows: MnAPSO-11 > SAPO-11 > Mn-SAPO-11 > MnAPO-11 > AlPO-11 and Mn/AlPO-11, which is in agreement with the acidity order of isomorphous substituted molecular sieves given by Akolekar [11].

As mentioned above, two different methods were used for manganese incorporation in this study. When the Mn-containing samples were prepared by impreg-nating AlPO-11 or SAPO-11 with an aqueous $Mn(NO_3)_2$ solution and calcined, it was quite sure that the metal oxides were supported on the molecular sieve materials. However, when the Mn-containing samples were prepared via the hydrothermal synthesis method,
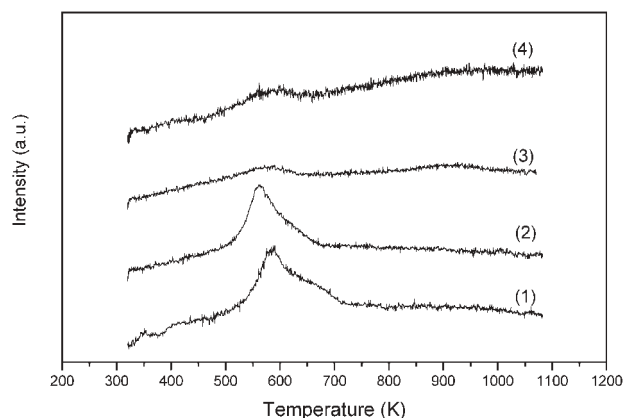
then the question is whether the manganese was incorporated into the framework of the molecular sieve or whether it was just dispersed over the surface. This question needs to be confirmed by means of certain characterization methods. It is easy to speculate that different methods employed for the incorporation of the manganese component will generate manganese species in different chemical environments, and the reduction properties of the Mn-containing samples can give out information for differentiating the manganese environ-ment of the samples. It is well known that H_2-TPR is an ideal technique for such investigations. Accordingly, the H_2-TPR profiles of the Mn-containing samples in this study are shown in figure 2. For the impregnated samples of Mn-AlPO-11 and Mn-SAPO-11, a clear reduction peak can be observed in the temperature range of 500–700 K, indicating that some manganese species can be reduced at this temperature range. However, for the hydrothermally synthesized samples of MnAPO-11 and MnAPSO-11, only a very weak reduction peak can be found at the temperature range of 500–650 K, while a weaker reduction peak exists at the high temperature range of 900–1000 K, which does not exist for the impregnated samples.

The determined chemical composition in table 1 showed that the manganese content of the impregnated samples of Mn-AlPO-11 and Mn-SAPO-11 was 1.5 wt%, which was higher than that of the synthesized samples. However, this difference in manganese content is not remarkable enough to explain the difference of the reduction peaks between these two kinds of catalysts. The reduction behavior of the metal species that is attached to the supports can reveal the extent of interaction between the metal species and the environ-ment. In a study of supported MnO_x over Al_2O_3 [12], reduction peaks at high temperatures were regarded as a manifestation of the strong interaction between the support and the manganese species. Thus, in the present study, since the impregnated samples of Mn-AlPO-11 and Mn-SAPO-11 can be easily reduced at relatively low

Table 2
Extent of NH_3 desorption of the samples

Sample	Extent of NH_3 desorption (mmol/g)
AlPO-11	0.063
Mn-AlPO-11	0.062
MnAPO-11	0.184
SAPO-11	0.526
Mn-SAPO-11	0.418
MnAPSO-11	0.534

temperatures, this indicates that weak interaction existed between the molecular sieve supports and the manganese species, envisaging that these manganese species are very likely dispersed over the outer surface of the molecular sieves. On the other hand, as the reduction of the synthesized samples of MnAPO-11 and MnAP-SO-11 was quite difficult, this implies that it was difficult to change the coordination states or the valence of the manganese species. This can be visualized to be due to the fact that the manganese atoms in these two samples were incorporated into the framework, yielding isomorphous substitution products.

In Dumesic's work, tin was used to help the platinum dispersion over KL zeolite; in the presence of tin, the catalysts exhibited high dehydrogenation activity and selectivity [13,14]. In the present study, Pd-modified molecular sieves were employed as the dehydroisomerization catalysts. Chemical adsorption of CO were conducted to understand the effect of manganese incorporation on the supported palladium catalysts, and the results are summarized in table 3. The molecular sieve sample of MnAPO-11, Mn-AlPO-11, MnSAPO-11 and Mn-SAPO-11 only chemisorbed a very small amount of CO, which was negligible compared with the CO chemisorbed by the Pd-modified catalysts. For the Pd-modified samples, CO uptake followed the following sequence: Pd/AlPO-11 > Pd/Mn-AlPO-11 > Pd/MnAPO-11 for the AlPO-11 series, and Pd/SAPO-11 > Pd/Mn-SAPO-11 > Pd/MnAPSO-11 for the SAPO-11 series. These results show that the presence of manganese decreased the amount of CO held by the palladium particles. This can be explained by the fact that the manganese species in the proximity of the supported palladium may shield a certain fraction of the accessible palladium particles [2], especially for the

Table 3
CO chemisorption results of the samples

Catalyst	CO uptake (mL/g_{cat} STP)	CO/Pd
Mn-AlPO-11	Negligible	–
MnAPO-11	Negligible	–
Mn-SAPO-11	Negligible	–
MnAPSO-11	Negligible	–
Pd/AlPO-11	0.132	0.63
Pd/Mn-AlPO-11	0.115	0.55
Pd/MnAPO-11	0.092	0.43
Pd/SAPO-11	0.138	0.65
Pd/Mn-SAPO-11	0.098	0.46
Pd/MnAPSO-11	0.066	0.31

well-dispersed manganese samples of Pd/MnAPO-11 and Pd/MnAPSO-11. The supported manganese species in the samples of Mn-AlPO-11 and Mn-SAPO-11 also caused a decrease of the CO chemisorption to a certain extent.

The transformation of *n*-butane to isobutene was then studied over the Pd-promoted molecular sieves, and the results on Pd/AlPO-11, Pd/Mn-AlPO-11 and Pd/MnAPO-11 are compared in figure 3, while those for Pd/SAPO-11, Pd/Mn-SAPO-11 and Pd/MnAPSO-11 are compared in figure 4. From these results, it can be seen that there exists a difference between the catalysts with or without manganese incorporation, as well as a difference caused by the methods of manganese incorporation.

The results in figure 3 show that manganese incorporation improved the catalytic activities of Pd-modified AlPO-11 molecular sieves, and relatively high *n*-butane conversion could be obtained over the samples containing manganese. For the catalysts of Pd/SAPO-11 with or
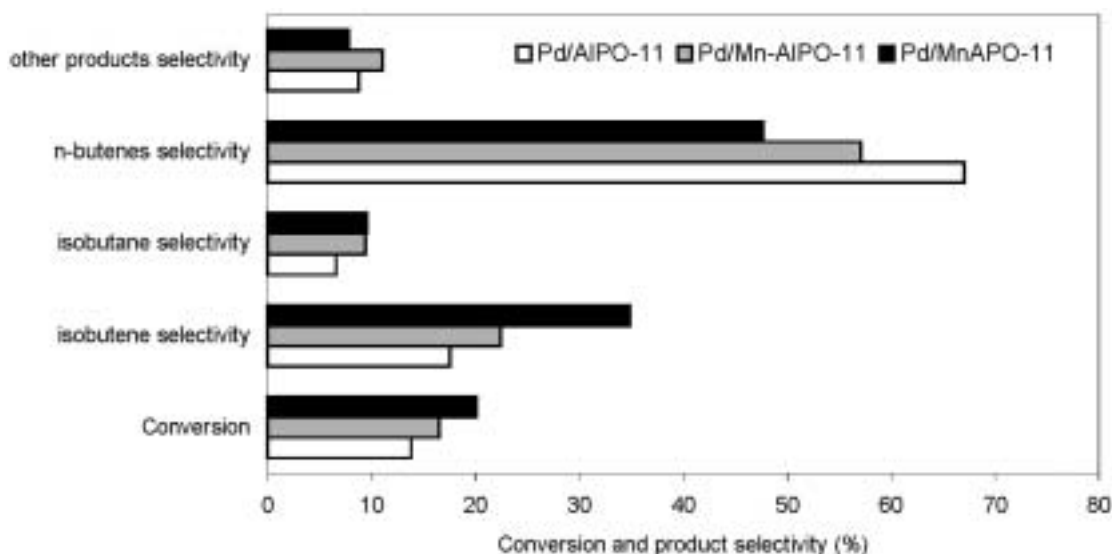

Figure 3. Catalytic properties of the Pd/AlPO-11, Pd/Mn-AlPO-11 and Pd/MnAPO-11. Conditions: WHSV = $1.98\,h^{-1}$, H_2/n-butane = 2, $T = 773\,K$. Data obtained at $60\,min$ TOS (time onstream).
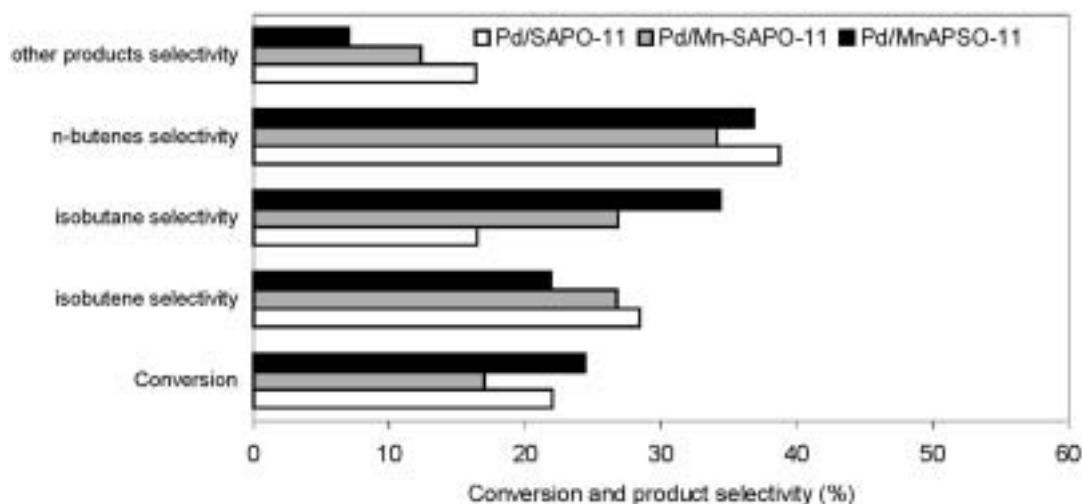
Figure 4. Catalytic properties of the Pd/SAPO-11, Pd/Mn-SAPO-11 and Pd/MnAPSO-11. Conditions: WHSV = 1.98 h^{-1}, H$_2$/*n*-butane = 2, *T* = 773 K. Data obtained at 60 min TOS.

without manganese incorporation (in figure 4), the sequence of conversion is: Pd/Mn-SAPO-11 < Pd/SAPO-11 < Pd/MnAPSO-11, which is consistent with the sequence of acidity from the NH$_3$-TPD measurements.

It was observed that incorporation of manganese to the molecular sieve supports influenced the product distribution, especially for the samples in which manganese was incorporated by the hydrothermal synthesis method. Relatively high selectivity toward isomerization products (isobutane and isobutene) and low selectivity to dehydrogenation products (*n*-butenes and isobutene) were found over these Mn-substituted samples.

The three catalysts of Pd-modified AlPOs (Pd/AlPO-11, Pd/Mn-AlPO-11 and Pd/MnAPO-11) all showed dehydrogenation selectivity of higher than 80%, but those with manganese incorporation yielded more isobutene in the product. The isobutene selectivity was 34.80% for the Pd/MnAPO-11, 22.44% for the Pd/Mn-AlPO-11 and 17.57% for the Pd/AlPO-11.

As for the catalysts using SAPOs as the supports, less dehydrogenation products could be obtained. The acidic sites generated by silicon in the framework may weaken the metallic function of the supported palladium particles, so that more isomerization products will be yielded over these catalysts. By comparing the catalytic performances of Pd/SAPO-11 with Pd/MnAPSO-11 and Pd/Mn-SAPO-11, the sequence of selectivity for dehydrogenation products (*n*-butenes and isobutene) is: Pd/SAPO-11 (67.15%) > Pd/Mn-SAPO-11 (60.83%) > Pd/MnAPSO-11 (58.67%). However, the sequence of selectivity for isomerization products (isobutane and isobutene) shows an opposite trend, which increases from 44.93% for Pd/SAPO-11 to 53.57% for Pd/Mn-SAPO-11 and further to 56.17% for Pd/MnAPSO-11.

The results of catalytic evaluation demonstrate the apparent effect of manganese incorporation on the catalytic properties. Pd/MnAPSO-11, which was incorporated with manganese and prepared by the hydrothermal synthesis method, showed the highest isomerization selectivity. Also, the highest selectivity toward the target product isobutene can be obtained over the Pd/MnAPO-11 catalyst.

The dehydrogenation reactivity of the catalysts was found to be associated with the properties of the palladium particles. Compared with Pd/AlPO-11 and Pd/SAPO-11, the decrease in dehydrogenation selectivity of the Pd/Mn-AlPO-11 and Pd/Mn-SAPO-11 catalysts may be attributed to the impregnated manganese species, which is thought to weaken the metallic properties of the supported palladium [15]. As for the catalysts of Pd/MnAPO-11 and Pd/MnAPSO-11, the relatively low dehydrogenation selectivity may result from two aspects: one is the weakening of the metallic properties of palladium by the manganese species and the other is the incorporation of manganese causing an increase in acidity. For catalysts with weakened metallic palladium particles, the isomerization reactivity becomes more prominent. Thus, the highest isomerization selectivity was obtained over Pd/MnAPSO-11, while at the same time it showed the lowest dehydrogenation selectivity.

The highest dehydroisomerization selectivity (34.86%) at a corresponding isobutene yield of 7.02% was obtained over the catalyst of Pd/MnAPO-11. 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 MnAPO-11 or MnAPSO-11 in the lower part were used in one fixed catalyst bed. The catalytic performance of *n*-butane transformation at

Table 4
Catalytic performances of catalysts in a two-layered bed at 823 K

Catalyst	Conversion (%)	Isobutene yield (%)	Selectivity (%)			
			$iC_4^=$	Total $C_4^=$ [a]	iC_4^0	Other products[b]
Pd/SAPO-11	36.36	9.40	25.87	80.18	3.31	16.51
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
Pd/SAPO-11 (upper) + MnAPSO-11 (lower)	29.33	10.31	35.16	76.84	6.62	16.54

Note: Condition: WHSV = 1.98 h^{-1}, H_2/n-butane = 2, T = 823 K, TOS = 60 min.
[a] Total $C_4^=$: n-C_4H_8 + i-C_4H_8 + t-C_4H_8 + c-C_4H_8.
[b] 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.

823 K over these dual-layered catalysts are shown in table 4. Compared with the catalytic performance of Pd/ SAPO-11, relatively high selectivity toward isobutene could be obtained over the combined catalysts bed, and the isobutene yield could be approximately at the same level as that of the single catalyst of Pd/SAPO-11.

4. Conclusions

Hydrothermally synthesized MnAPO-11 and MnAP-SO-11 are respectively more acidic than AlPO-11 and SAPO-11, while manganese incorporation via the impregnation has no effect on the acidity. TPR measurements showed that the manganese species in MnAPO-11 and MnAPSO-11 are difficult to be reduced. The increased acidity and the difficulty in reduction of the manganese species indicated that the manganese component has substituted into the molecular sieve framework during the hydrothermal synthesis process. The manganese incorporation for both the methods has effects on the metal palladium in the catalyst, resulting in a weakening of the metallic properties of palladium to some extent. The Pd/ MnAPSO-11 catalyst showed the highest isomerization selectivity, while the Pd/MnAPO-11 showed the highest isobutene selectivity. A combined system of two different catalysts can improve the isobutene selectivity to 35%, while about 10% yield of isobutene can be obtained.

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