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Skeletal Isomerization of *n*-Butane on Zeolites and Sulfated Zirconium Oxide Promoted by Platinum: Effect of Reaction Pressure

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The isomerization of *n*-butane catalyzed by sulfated zirconium oxide and H-form zeolites with the promotion of platinum has been studied by measurements of the conversion and product distribution at temperatures of 240 ~ 390°C at atmospheric pressure and at 20.4 atm. The skeletal isomerization proceeds mainly via the bimolecular disproportionation mechanism on Pt/H-zeolite at 1 atm and via the monomolecular carbocation mechanism on Pt/SO_4^{2-}–ZrO_2 at temperatures of ≦300°C at both 1 and 20.4 atm. At 20.4 atm pressure, the monomolecular cracking and isomerization of butane can also occur on Pt/H-zeolite. Hydrogen molecules may be dissociated and converted to hydride and proton ions on Pt/SO_4^{2-}–ZrO_2, promoting the desorption of surface carbenium ions and the cracking of butane molecules, which have been enhanced under high reaction pressures.

1. INTRODUCTION

Solid acid catalysts are active in the isomerization of *n*-butane to isobutane, a starting material for the high-octane gasoline additive methyl *tert*-butyl ether and gasoline alkylate. Because the yield of isobutane is limited by thermodynamic equilibrium and is favored at low reaction temperatures, several types of solid superacids with very strong acid strengths have been developed (1–3). Among them, sulfate-treated zirconium oxide SO_4^{2-}–ZrO_2, with or without promotion by platinum, possesses high activity (3–5) and has been considered to replace the Pt/chlorinated-alumina catalyst which is employed in the current commercial process (6). According to infrared spectroscopic and kinetic studies (5), protonic acid sites were suggested to be generated from the dissociation of molecular hydrogen on the platinum to hydrogen atoms which undergo spillover on the SO_4^{2-}–ZrO_2 and convert to an H^+ and an e^- or H^-. The H^+ can act as the catalytic site for acid-catalyzed reactions. Therefore, the isomerization activity was markedly enhanced in the presence of hydrogen compared to that in the absence of hydrogen. The influence of the H_2/C_4 ratio was also studied by Garin *et al.* (7). In their study, molecular hydrogen was considered to play a dual role for the conversion of *n*-butane; it was regarded as an inhibitor at high partial pressure by inhibiting the dehydrogenation or occupying active sites, but is essential for maintaining the catalytic activity due to the reduction of surface carbocations and olefins. The role of hydrogen can be clarified by examining the reaction at both high and atmospheric pressures. Despite a large number of papers devoted to the study of the conversion of *n*-butane to isobutane, the reaction at high pressure has not been stressed. In fact, due to the concern of catalyst deactivation, commercial units of skeletal isomerization of light alkanes routinely operate at high pressures. In this study, we examine the *n*-butane isomerization on sulfated zirconia promoted by supported Pt at atmospheric pressure and at 20.4 atm. Furthermore, the reaction was compared with *n*-butane transformation on H-ZSM-5, H-mordenite (HM), and H-beta zeolites promoted by Pt, designated as Pt/H-ZSM-5, Pt/HM, and Pt/Hβ. The reaction mechanism was also derived from product distributions, including the nature of active sites and their function in butane transformation.

2. EXPERIMENTAL METHODS

$Zr(OH)_4$ was prepared by hydrolysis of zirconyl chloride with aqueous ammonium hydroxide (3) and impregnated with an aqueous solution of sulfuric acid (0.35 *M*); it was dried at 115°C for 5–6 h. The dry SO_4^{2} –$Zr(OH)_4$ sample was impregnated with an aqueous solution of chloroplatinic acid by the incipient wetness method to give a platinum content of 0.5 wt%. The impregnated sample was dried at ambient temperature overnight and then at 115°C for 5–6 h and calcined in an air flow at 620°C for 3 h. Pt/H-ZSM-5, Pt/HM, and Pt/Hβ were prepared by incipient wetness impregnation of the H forms of ZSM-5 (Si/Al =

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25, PQ Corp.), mordenite (Si/Al = 10, Tosoh), and β (Si/Al = 11, PQ Corp.) zeolites with an aqueous H_2PtCl_6 solution (in order to compare with the Pt/sulfated zirconia). The samples were dried at ambient temperature and then at 55°C, calcined in an air flow for 3 h at 150°C, 3 h at 300°C, and an additional 3 h at 500°C.

The Pt/SO_4^{2-}–ZrO_2 catalyst was examined by powder X-ray diffraction in a Rigaku DMAXII X-ray diffractometer using Cu*Kα* radiation. XPS spectra were recorded on a VG Scientific Escalab 200X system with Al*Kα* X rays. The sulfur content (2.0 wt%) of the 0.5 Pt/SO_4^{2-}–ZrO_2 sample was analyzed using a Tacussel Coulomax 78 elemental analyzer.

The catalytic reactions were carried out in a flow system with a fixed-bed microreactor. The catalyst was first treated in an air flow at 400 (Pt/ZSM-5, Pt/HM, and Pt/Hβ) or 500°C (Pt/SO_4^{2-}–ZrO_2) and then in a hydrogen stream at 350°C (Pt/SO_4^{2-}–ZrO_2) or 450°C (Pt/H-zeolite) for 2 h prior to reaction. *n*-Butane was introduced into the gas flow of hydrogen in gaseous form for runs at atmospheric pressure and in liquid form for runs at high pressure. The reaction products were analyzed by on-line gas chromatography using a FID and a SPB1 0.25 mm × 100 m capillary column or a GP 80/100 Carbopack C/0.19% picric acid $\frac{1}{8}$ in. × 2 m packed column. The product selectivities are expressed on a carbon-number basis.

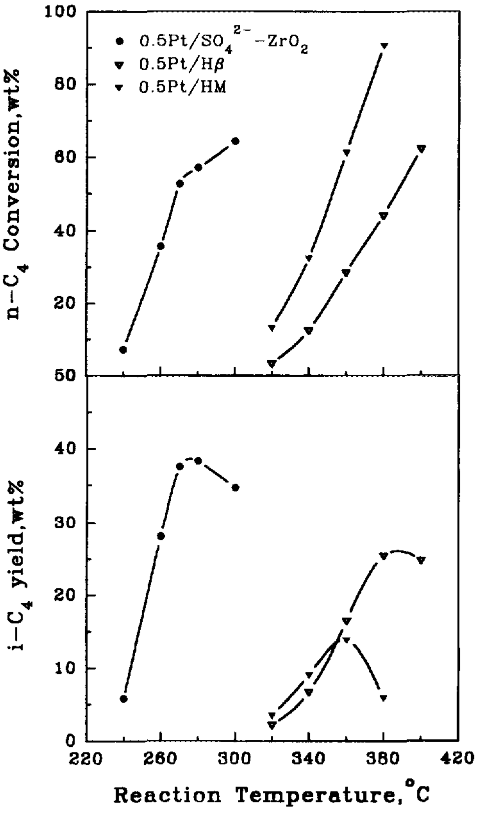


FIG. 1. Catalytic activities and yields of *i*-C_4 as a function of reaction temperature over 0.5Pt/SO_4^{2-}–ZrO_2, 0.5Pt/Hβ and 0.5Pt/HM catalysts (WHSV = 2 h^{-1}; pressure, 20.4 atm; and H_2/*n*C_4H_{10} = 0.9).

3. RESULTS AND DISCUSSION

Platinum-Treated Zeolites

The *n*-butane conversions and isobutane yields at various temperatures on Pt/SO_4^{2-}–ZrO_2, Pt/HM, and Pt/Hβ are shown in Fig. 1. The HM and Hβ zeolite catalysts promoted by Pt were totally inactive at temperatures lower than 320°C under 20.4 atm for *n*-butane conversions. The higher catalytic activities on Pt/SO_4^{2-}–ZrO_2 than on Pt/Hβ and Pt/HM may be related to the presence of its strong Brønsted acid sites and Lewis acid sites which can activate *n*-butane by H^- abstraction to proceed by a carbenium ion mechanism. Major products in *n*-butane conversions were isobutane, pentane, propane, and ethane (Table 1) with the highest isobutane yield on Pt/H-zeolite at about 25 wt% at 380°C (Fig. 1) under 20.4 atm. In Table 1, the propane/pentane molar ratio is shown as a function of the total conversion of *n*-butane on Pt/Hβ at 1 atm while the production of propane and pentane is slightly higher than that of isobutane on Pt/H-ZSM-5 at 310°C and 1 atm. These indicate that pentane, isobutane, and propane are primary products. Thus, the primary reactions at low conversion on Pt/H-zeolite at 1 atm are explained by a bimolecular disproportionation mechanism. As the temperature increased to 390°C, the medium-pore zeolite of H-ZSM-5, with stronger acidity than the large-pore β zeolite, favors the cracking of C_4 via a pentacoordinated carbonium ion, which is generated through protonation of butane catalyzed by Brønsted acid sites, with subsequent C–C bond rupture or dehydrogenation. The resulting carbenium ions, i.e., $C_3H_7^+$, can proceed by hydride-transfer with *n*-butane. This results in propane being observed as the major product at high conversion on Pt/H-ZSM-5 (Table 1) similar to that on H-ZSM-5 (8, 9). With the hydrogenation activity of Pt crystallites on Pt/H-zeolite, the yield of olefins, i.e., butene, is very small, even at 1 atm.

Table 1 also shows that ethane as well as propane has been formed in a comparable fraction of products with a propane/pentane molar ratio of much greater than 1, even in low conversion runs on zeolites with or without Pt promotion at 20.4 atm. On H-form zeolites, the formation of *i*-butane from *n*-butane was reported to follow the bimolecular disproportionation (10–13); the bimolecular disproportionation seemed to be followed by successive cracking to yield more propane than pentane under high pressure. With the promotion of Pt, the yields of methane, ethane, and propane were observed to be enhanced. If the bimolecular disproportionation mechanism was the only route for *n*-butane activation of Pt/H-zeolite, the yields for these inert products, especially methane and ethane, should not

TABLE 1

Isomerization of *n*-Butane on Zeolites with and without Pt Promotion

	Pressure: 20.4 atm						1 atm						
Catalyst:	Pt/HM		HM	Pt/Hβ		Hβ	Pt/Hβ					Pt/H-ZSM-5	
Temperature (°C):	340	360	360	340	360	340	340	340	340	360	360	310	390
WHSV (h^{-1}):	2	2	2	2	2	2	1	2	4	2	2^{a}	2	2
Conversion (wt%)	32.5	61.3	52.1	12.5	28.6	16.7	33.9	24.7	15.5	36.4	18.5	8.7	71.2
Product (wt%)													
C_1							0.06	0.03	0.02	0.06	0.04	—	0.2
C_2	10.9^{b}	17.9^{b}	1.1^{b}	2.4^{b}	5.4^{b}	1.0^{b}	0.28	0.14	0.07	0.42	0.11	0.1	4.4
C_3	13.2	28.7	22.1	3.3	6.7	2.0	6.7	3.8	2.1	10.2	1.3	3.1	51.4
i-C_4	9.1	13.9	21.2	6.7	16.5	12.8	21.6	16.8	10.8	19.8	15.2	2.8	9.0
n-C_4	67.5	38.7	47.9	87.5	71.4	83.3	66.1	75.3	84.5	63.6	81.5	91.3	28.8
i-C_5	0.1	0.5	5.1	—	—	0.6	3.2	2.3	1.4	3.3	0.9	1.1	3.0
n-C_5	—	0.2^{c}	2.5^{c}	—	—	0.3^{c}	1.8	1.4	1.0	2.1	0.6	1.2	2.1
C_6	—	—	—	—	—	—	0.3	0.2	0.1	0.4	—	0.3	0.9
C_4^{2}	—	—	—	—	—	—	0.02	0.03	0.05	0.09	0.04	0.01	0.2
i-C_4 selectivity (%)	28.0	22.7	40.7	53.6	57.8	76.6	63.8	68.1	69.2	54.4	82.2	32.9	12.8
$(C_3/C_5)^{d}$	129.6	40.3	2.9	—	—	2.2	1.3	1.0	0.9	1.9	0.9	1.3	9.9

[a] H_2/HC = 2.7 instead of H_2/HC = 0.9 for other cases.

[b] $C_1 + C_2$.

[c] *n*-$C_5 + C_6$.

[d] Molar ratio.

be this large. This indicates that another pathway, including the monomolecular cracking of butane via the carbonium-ion mechanism and bimolecular hydride-transfer between *n*-butane and carbenium ion, should be involved.

Disproportionation was proposed to proceed via a C_8 intermediate generated by the alkylation of butyl carbenium ion with butene. Since the production of olefins was disfavored under high pressure, secondary hydride transfers between butane and carbenium ions might compete with alkylation of butyl carbenium to butene. For Pt/Hβ, the skeletal isomerization of *n*-butane is the dominant process, probably due to the more open structure of Hβ.

Platinum- and Sulfate-Ion-Treated Zirconium Oxide

The Pt/SO_4^{2-}-ZrO_2 catalyst presents higher activity and selectivity than Pt-promoted zeolite catalysts for the production of isobutane, the former being active even at a reaction temperature of 240°C. The stabilization and enhancement in activity at high pressure are obvious, and the catalytic activity can be maintained at 40 wt% conversion and 80% isobutane selectivity at 260°C for at least 10 h. A similar yield of isobutane could also be reached initially at 300°C under atmospheric pressure on the catalyst of the same batch. It is interesting to compare the product distributions of high-pressure runs with those of 1-atm-pressure runs on Pt/SO_4^{2-}-ZrO_2 and high-pressure runs on Pt/HM and Pt/Hβ. In high-pressure runs, however, the selectivities for propane, ethane, and methane are higher, and low for pentane. Another important fact noted is that the molar ratio *i*-C_4H_{10}/*n*-C_4H_{10} is close to the thermodynamic equilibrium value at 300°C and 20.4 atm on Pt/SO_4^{2-}-ZrO_2.

Skeletal isomerization of *n*-butane proceeded both via the monomolecular reaction route, involving the formation of C_4 carbocations, and via the bimolecular reaction route, involving the formation of C_8 carbenium ions (9–12). The C_8 intermediates are usually proposed to be generated by the alkylation of butyl carbenium ions with butene molecules. Concerning the thermodynamic equilibrium between butane and butene, the concentration of butene should be very low at pressures under 20.4 atm and at reaction temperatures lower than 300°C (14). Although the skeletal isomerization of alkanes can proceed either by an acid-catalytzed reaction or by a metal–acid bifunctional reaction, there is no indication that the Pt of Pt/SO_4^{2-}-ZrO_2 acts as a metal functional catalyst to give gas phase butene to help the formation of C_8 carbonium ions. However, Pt/SO_4^{2-}-ZrO_2 did produce a significant amount of propane and pentane with isobutane at 300°C and atmospheric pressure, as shown in Table 2. Sayari and Dicko (15) reported that in the presence of sulfate ions, platinum could be formed in the metallic state even by air calcination at 600°C. Although the C–H bond rupture was considered to be more rapid on platinum sites than on acidic sites,

TABLE 2

Isomerization of n-Butane on $0.5Pt/SO_4^{2-}-ZrO_2$ Catalyst[a]

Reaction pressure:	20.4 atm			1 atm
Reaction temperature:	240°C	260°C	300°C	300°C
Conversion (wt%)	7.3	35.8	64.3	38.3
	Product distribution (wt%)			
C_1	0.1	0.8	3.5	0.1
C_2	0.9	3.9	10.7	0.4
C_3	0.4	2.8	13.8	4.7
i-C_4	5.8	28.1	34.7	29.1
n-C_4	92.7	64.2	35.7	61.7
i-C_5	—	0.2	1.2	2.7
n-C_5 + C_6	—	—	0.5	1.4
	Selectivity (mol%)			
C_1	1.2	2.0	5.0	0.2
C_2	12.2	10.6	16.3	1.0
C_3	6.0	7.8	21.5	12.5
i-C_4	80.6	79.2	54.7	78.3
i-C_5	0	0.4	1.8	7.0
n-C_5 + C_6	0	0	0.7	1.1
i-C_4/n-C_4	0.06	0.44	0.97	0.47
(i-C_4/n-C_4)[b]	1.1	1.1	0.97	0.97

[a] WHSV = 2 h^{-1}, $H_2/n\text{-}C_4H_{10}$ = 0.9.

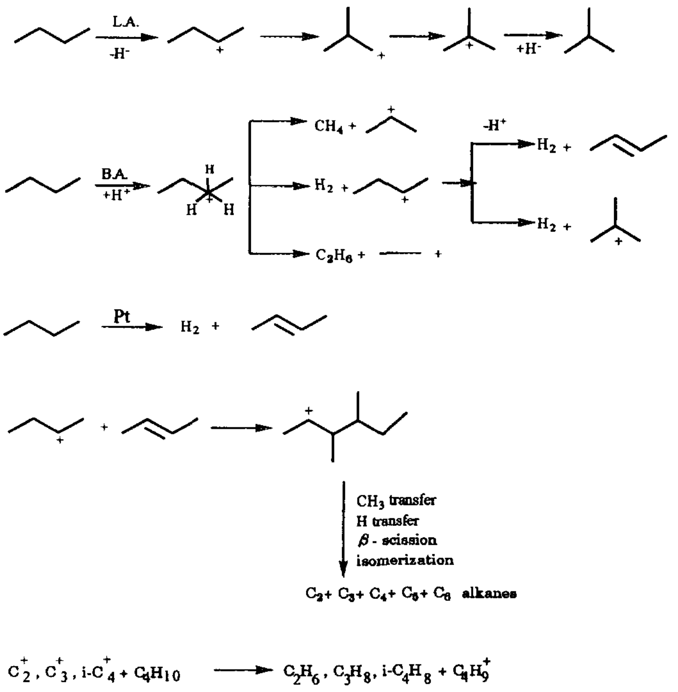
[b] Thermodynamic equilibrium ratio.

butene might also be generated via hydrogen dissociation of n-butane on strong protonic acid sites at higher reaction temperatures.

Reducing reaction pressure and increasing reaction temperature may enhance the possibilities of C_8 intermediate generation and a disproportionation process. By comparing the product selectivities listed in Tables 1 and 2, it can be concluded that the monomolecular reaction route seems to be the dominant reaction for isobutane formation on $Pt/SO_4^{2-}-ZrO_2$. With the presence of Pt, dihydrogen can be dissociated and converted to a hydridic ion (H^-) and a protonic ion (H^+) on $SO_4^{2-}-ZrO_2$. Proton ions act as Brønsted acid sites to promote the formation of pentacoordinated C_4 carbonium ions and the successive decomposition to C_1, C_2, and C_3 fragments, while hydride ions can combine with carbenium ion intermediates to give weakly adsorbed alkanes such as isobutane and decrease the surface lifetime and β-scission possibility of carbenium ions. This was confirmed on heptane isomerization catalyzed by $Pt/SO_4^{2-}-ZrO_2$ (15). Clearly, the Brønsted acid sites on $Pt/SO_4^{2-}-ZrO_2$ are more active than those on H-form zeolites. At high pressure, the $Pt/SO_4^{2-}-ZrO_2$ was found to be more active than at 1 atm; this was not found for Pt/H-zeolite and apparently occurred through a combination of Lewis acidity and Brønsted acidity, involving the enhancement of n-butane conversion and the cracking of butane, as reflected by higher yields of propane, ethane, and methane as shown in Table 2. As for the generation of acidity due to SO_4^{2-} species on ZrO_2, XPS was used to examine the state of sulfur in catalysts of as-prepared and reduced forms and mainly S^{6+} was detected. It is suggested that the acidity and activity of the $Pt/SO_4^{2-}-ZrO_2$ catalyst remain unchanged after hydrogen treatment.

Conclusion

The reaction scheme shown below can be proposed to account for the n-butane conversion



where L.A. and B.A. are Lewis and Brønsted acid sites, respectively. On $Pt/SO_4^{2-}-ZrO_2$, the high reaction pressure enhances i-butane formation by increasing H^+ and H^- formation and carbenium ion desorption; this can be seen since the molar ratio of i-C_4H_{10} to n-C_4H_{10} was found to be close to the thermodynamic value at 300°C. Through the help of strong Brønsted acid sites on $Pt/SO_4^{2-}-ZrO_2$, C_4H_{10} was cracked by a monomolecular mechanism, producing CH_4, C_2H_6, and C_3H_8. This was also observed on Pt/H-zeolite and H-zeolite at high pressure. At atmospheric pressure, a small amount of C_5H_{12} was produced, probably through the secondary alkylation reaction of C_2 and C_3 with disproportionation of butane.

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