Comparative study of n-butane transformation over Pt/sulfated zirconia and Pt/zeolites

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Abstract

The hydroconversion of n-butane catalyzed by sulfated zirconium oxide (SZ), H-beta (HBEA) and H-mordenite (HMOR) zeolites of different Si/Al ratios with the promotion of platinum has been studied at temperature ranges of 240–340°C and at 1–27.2 atm. The results indicate that, with increased pressure and with an increased Si/Al ratio of zeolites the cracking as well as the hydrogenolysis enhance the formation of C_1–C_3 alkane products. The formation of isobutane by metal–acid bifunctional mechanism is favorable at low pressure and the bimolecular mechanism is enhanced with a higher density of acid sites over Pt/Hzeolite catalysts. The transformation of n-butane via an acid-type unimolecular mechanism is an important process on Pt/SZ, since Pt/SZ possesses less metallic function than Pt/ZrO$_2$ and Pt/HBEA as detected by the activity of benzene hydrogenation at 20.4 atm. On Pt/SZ, the conversion increases significantly with hydrogen pressure up to a total pressure of 6.8 atm and becomes constant for a total pressure of > 6.8 atm to 27.2 atm. © 1997 Elsevier Science B.V.

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1. Introduction

Skeletal isomerization of n-butane to isobutane is tied to the manufacture of alkylates and MTBE and has been of increased importance. Many studies show that transition metal or noble metal-loaded on acid carriers [1–7], H-zeolites [8–10] or sulfated zirconium oxide [11] possess high activity for the isomerization of n-butane; via (1) the bimolecular mechanism involving the metal and acid functions [6], (2) a unimolecular [11,12] or bimolecular [7] mechanism by the acid function of Lewis acid sites [2,11,13] of very strong acid strength only or with Brönsted acid sites and (3) a bimolecular mechanism on Brönsted acid sites [7,9,10,14].

In the presence of strong acid, carbenium ions are the key intermediates in hydrocarbon conversions. The C_4 carbenium ion can be formed by extraction of H^- from n-butane to a Lewis acid site

(L.A.), donation of H^+ to *n*-butane from a Brönsted acid site (B.A.) with subsequent dehydrogenation, or addition of H^+ from a Brönsted acid site to butene. Isomerization of *n*-butane to isobutane can proceed either by unimolecular mechanism via classical rearrangement of secondary butyl carbenium ion to tert-butyl carbenium ion through an energetically unfavored primary carbenium ion intermediate and successive H^- addition to tert-butyl carbenium ion; or by bimolecular mechanism via β-scission of C_8 carbenium ion intermediate, which is generated by alkylation of a butyl carbenium ion with a butene molecule as shown in the following scheme.
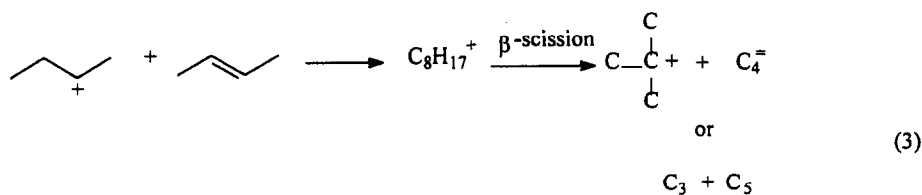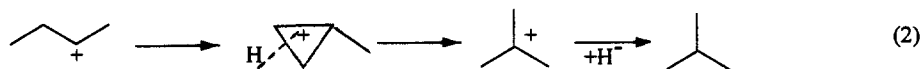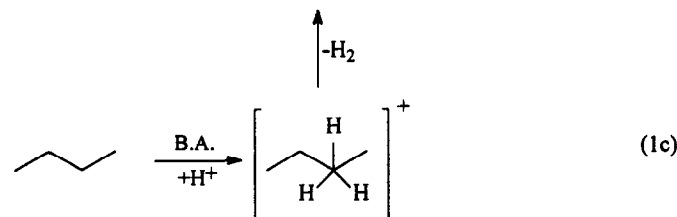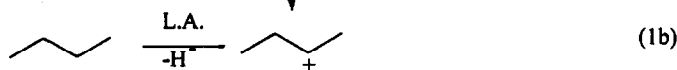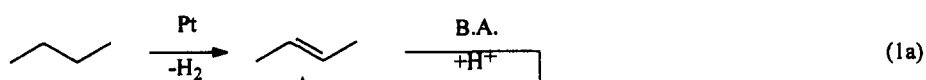
In comparison with Lewis acid sites, Brönsted acid sites of SZ were detected to be weaker than that of HZSM-5 zeolite and similar to that of HY zeolite as shown by FTIR and NMR analyses of acetonitrile adsorption [15]. Molecular hydrogen has been suggested [1] to be dissociatively adsorbed on Pt and to spillover on the Pt/SZ surface in atom form. It interacts with the surface Lewis acid sites to form H^+ protonic acid site (and H^- hydridic ion). Both strong Lewis and Brönsted acid sites were observed by IR study on pyridine adsorbed Pt/SZ in the presence of H_2 [1], with H^- ion they might

accelerate n-butane isomerization on Pt/SZ via steps (1) and (2). According to the bimolecular process of Eq. 3, the β-scission of C_8 carbenium ions can give C_3 and C_5 alkanes with C_4 moieties. In Eq. 2, the protonated cyclopropyl intermediate could rearranged into high energetic primary 2-methyl-1-propylium ion by following classical carbenium ion mechanism, but Olah et al. [16] suggested that in superacidic media this rearrangement (sec-butyl ion to t-butyl ion) was activated by a second protonation of the sec-butyl ion via bond-to-bond migration of CH_3 and H, without involvement of a primary cation and such t-butyl cation could not be easily involved in deprotonation equilibrium.

The product distribution of hydroisomerization of paraffins via bifunctional catalysis was found to be dependent on the acid site density, metal/acid ratio and acid strength of zeolite catalysts [17]. Our previous study on butane reaction over Pt/SZ [2] indicated that the selectivities of reaction pathways were significantly affected by the reaction pressure. Although industrial processes of skeletal isomerization of light alkanes always operate at high pressure, the study of butane isomerization under high pressures has seldom been reported in literature. This work is concerned with the effects of Si/Al ratio of zeolite and reaction pressure on n-butane conversion over Pt promoted zeolite (Pt/HMOR and Pt/HBEA) and sulfate-treated zirconium oxide (Pt/SZ).

If n-butane isomerization follows the bi-molecular mechanism (Eq. 3), the rate of C_8 intermediate cation formation will be increased with the hydro–dehydrogenation function of Pt. For Pt/SZ, Iglesia et al. [18] and Parera et al. [19] observed very low H_2-chemisorption at room temperature and suggested that the Pt surface of Pt/SZ could be poisoned by sulfur species formed during calcination or reduction pretreatment [20]. The role of Pt on solid acid not only has hydro-dehydrogenation function but also removes the precursor of surface coke, the latter function can be enhanced under high pressure of H_2.

Ebitani et al. [1,21] found that the catalytic role of Pt in Pt/SZ was different from the usual supported Pt. Although the lack of hydrogenation and hydrogenolysis activities, Pt/SZ could promote the generation of Brönsted acid sites from H_2. Positive H_2 kinetic orders were observed on n-heptane isomerization over Pt/SZ [18] and on n-butane isomerization over SZ and Pt/SZ [11,12] in the presence of hydrogen. This suggests that either increasing H_2 pressure can prevent catalyst deactivation or the catalyst operates by a monofunctional acid mechanism. Through kinetic analysis of n-butane transformation, Liu et al. [4] and Zarkalis et al. [22] considered the isomerization mainly via intermolecular mechanism both on Pt/SZ [4] and SZ containing Fe and Mn [22]. In terms of the Langmuir–Hinshelwood model butene is assumed to be strongly adsorbed on acid sites, the rate of bimolecular isomerization is strongly dependent on butene pressure. Under equilibrium between butane, butene and hydrogen, negative reaction orders in H_2 and positive reaction orders in butane at H_2 pressure of 1.1–6.6 atm and n-C_4H_{10} pressure of 0.04–0.11 atm were observed by Liu et al. [4]. When the equilibrium is assumed between H_2, C_4H_8 and C_4H_{10}, the pressure of C_4H_8 should remain constant with constant H_2/HC ratio over the pressure variation. In the present work, we tried to investigate the possibility of bimolecular isomerization and thus studied the n-butane transformation at total pressures of H_2 and n-C_4H_{10} in the range of 1 to 27.2 atm with constant H_2/HC ratio of 1.5. The metal hydro–dehydrogenation ability of Pt was also examined by benzene hydrogenation.

2. Experimental

The catalytic reaction was undertaken in a flow system with a fixed bed microreactor at 240–340°C and 1–27.2 atm under the conversion level of 2–25%. HMOR(37)(Si/Al = 37) was prepared from

de-alumination of HMOR(5) (Si/Al = 5, Norton) [17]. HMOR(112) (Si/Al = 112) was obtained from Tosoh Co. HBEA(77) was prepared from de-alumination of HBEA(11) (Si/Al = 10.8, P.Q. Corp.) [17]. SO_4^{2-}–ZrO_2 (2 wt% S), $Zr(OH)_4$, HMOR and HBEA were loaded with 0.5 wt% Pt by the incipient wetness technique with an aqueous H_2PtCl_6 solution and calcined in air [2]. The Pt particle size of Pt/Hzeolite was in the range 1.3 to 2.6 mm measured by TEM [17]. The catalyst was first treated in an air flow at 450°C (Pt/HMOR and Pt/HBEA) or 500°C (Pt/SZ and Pt/ZrO_2) for 1 h and then in a hydrogen stream at 450°C (Pt/Hzeolite) or 350°C (Pt/SZ and Pt/ZrO_2) for 2 h prior to reaction. n-butane (purity > 99.5%) of Ideal Gas Products was used as feed, which was analyzed by using the HP refinery gas analyzer with multiple-column switching to TCD detector (detection limit: 10^{-3} ppm), no butene was found in the feed. Benzene (purity > 99.6%) was obtained from Merck. The reaction products were analyzed on-line by GC using FID and SPB1 (0.25 × 100 m) capillary column. No catalyst deactivation was observed during runs.

3. Results and discussion

3.1. n-butane isomerization on Pt / SZ

Table 1 shows that the hydrogenation activity of Pt on Pt/SZ is much less than that on Pt/HBEA(11) and on Pt/ZrO_2 as shown by measuring the rate of hydrogenation of benzene at 20.4 atm. This indicates that the sulfur moieties poison the Pt of the SZ surface and are not easy to remove even at high pressure. The poisoning of the metallic Pt function on Pt/SZ may account for the low rate of alkane hydrogenolysis [1]. Because of this Pt/SZ may not operate as a bi-functional catalyst for n-butane isomerization.

Table 2 shows a pronounced increase of n-butane conversion and i-butane yield with increasing total pressure from 1 atm to 6.8 atm and almost constant n-C_4H_{10} conversion with increasing total pressure from 6.8 to 27.2 atm on Pt/SZ. In contrast, on Pt/Hzeolites, the conversion decreases when the pressure is increased. This leads to serious inconsistencies assuming the same intermolecular isomerization mechanism over Pt/SZ as over Pt/Hzeolites. The increase on skeletal isomerization of butane is probably due to the increase of H^+ amount over the surface of Pt/SZ with increasing H_2 pressure. For pressure > 6.8 atm, the surface concentration of H^+ seems to reach a constant value. Over bifunctional catalysts, molecular hydrogen can be regarded as an inhibitor at high partial pressure by shifting the equilibrium of butene → butane and by competitive adsorption on active sites with butane and butene. This may explain the negative effect of H_2 on Pt/Hzeolites. The variation of n-C_4H_{10} conversion with total pressure on Pt/SZ and Pt/Hzeolites indicates that the different skeletal isomerization mechanisms may exit on these catalysts and the intramolecular isomerization pathway via acid sites is important on Pt/SZ at low conversion.

Table 1
Hydrogenation of benzene at 160°C, WHSV = 5.2, H_2/HC = 10 and total pressure = 20.4 atm on Pt/SZ, Pt/ZrO_2 and Pt/HBEA(11) catalysts

Catalyst	Pt/SZ	Pt/ZrO_2	Pt/HBEA(11)
Conversion (wt%)	8.32	99.26	100
Product yield (wt%)			
Methylcyclopentane	0.78	0	7.23
Cyclohexane	7.35	99.26	92.58

Table 2
n-butane isomerization on Pt/SO$_4^{2-}$–ZrO$_2$ and Pt/Hzeolite catalysts

	Pressure (atm)					
	27.2	20.4	13.6	6.8	1	1
Pt/SO$_4^{2-}$–ZrO$_2$ [a]						
Conversion (wt%)	5.31	5.41	5.10	4.99	2.34	4.99 [c]
Product selectivity (mol%)						
C$_1$	4.7	3.6	3.2	2.1		
C$_2$	18.2	13.2	11.4	6.9	1.5	1.2
C$_3$	6.8	5.7	5.2	4.2	4.6	3.4
i-C$_4$	70.0	77.3	79.8	86.2	93.1	94.0
C$_5$	0.3	0.3	0.4	0.6	0.3	1.4
Pt/Hβ(11) [b]						
Conversion (wt%)	4.54	5.03	4.70	5.36	6.23	
Product selectivity (mol%)						
C$_1$	14.6	14.0	7.5	6.1	1.7	
C$_2$	12.2	10.6	7.7	6.2	1.8	
C$_3$	17.5	16.6	10.2	9.2	7.6	
i-C$_4$	55.2	57.7	73.1	76.3	84.0	
C$_5$	0.6	1.2	1.5	2.2	4.7	
C$_4^{2-}$					0.3	
Pt/HM(5) [b]						
Conversion (wt%)	4.66	5.34	6.23	7.23	10.39	
Product selectivity (mol%)						
C$_1$	20.5	19.7	18.2	14.2	1.7	
C$_2$	13.1	12.4	12.1	10.4	2.0	
C$_3$	24.5	23.9	22.9	20.6	17.8	
i-C$_4$	40.4	42.1	44.3	50.6	65.6	
C$_5$	1.5	1.9	2.7	4.2	12.8	
C$_4^{2-}$					0.2	

[a] Reaction temperature = 240°C, H$_2$/HC = 1.5 and WHSV = 12 h^{-1}.
[b] Reaction temperature = 340°C, H$_2$/HC = 1.5 and WHSV = 9 h^{-1}.
[c] WHSV = 7 h^{-1}.

At the conversion level of 3–10%, isobutane is the main product derived from hydroconversion of n-butane on Pt/SZ at both 20.4 and 1 atm, that is compared with Pt/HMOR(5) and on Pt/HBEA(11) at 20.4 atm and on all Pt/HMOR and Pt/HBEA at 1 atm shown in Table 3. The isobutane selectivity over Pt/SZ at 240°C is higher than those over Pt/Hzeolite catalysts at 340°C. The selectivity of isobutane from 1 atm runs is much higher than that from 20.4 atm runs for all catalysts. Table 3 also shows that the yield of C$_1$–C$_3$ alkanes is much more than that of C$_5$H$_{12}$, especially under high reaction pressure.

3.2. Zeolitic Si / Al ratio on i-butane selectivity

Isomerization of n-butane has been suggested to proceed through bimolecular mechanism on noble metal-loaded H form zeolites [7] as on H zeolites [3]. De-alumination obviously will reduce the density of acid sites and decrease rates of C$_8$ carbenium ion formation and H transfer, with increasing life-time of carbenium ion intermediates and the likely following cracking reactions on Pt/Hzeolites. De-alumination may also shift the balance between metal and acid functions on Pt/HMOR and Pt/HBEA toward non-ideal bifunctional behavior with simultaneous hydrogenolysis. Higher yields of

Table 3
Isomerization of n-butane on 0.5 wt% Pt-promoted solid acids at 340°C, $H_2 / n\text{-}C_4 = 1.5$

Pressure (atm)	20.4						1					
Catalyst [a]	SZ [b]	HM(5)	HM(37)	HM(112)	Hβ(11)	Hβ(77)	SZ [b]	HM(5)	HM(37)	HM(112)	Hβ(11)	Hβ(77)
Conv. (wt%)	5.4	5.3	4.6	4.3	5.0	4.8	5.0	10.4	2.9	5.1	5.1	2.3
Prod. selec. [c] (%)												
C_1	1.0	6.7	14.8	17.0	4.4	15.6	—	0.4	2.5	7.4	0.5	8.7
C_2	7.3	8.4	12.7	16.2	6.6	22.4	0.6	0.1	4.7	18.6	1.0	24.7
C_3	4.8	24.3	49.3	55.3	15.5	50.8	2.6	13.8	13.8	23.2	5.9	30.0
$i\text{-}C_4$	86.3	57.2	21.5	10.1	71.8	11.2	95.0	67.9	70.5	49.2	86.8	35.6
C_5	0.6	3.3	1.8	1.4	1.8	—	1.8	16.6	8.5	1.6	5.6	0.9
$C_4^=$								0.2			0.3	

[a] Pt/SO_4^{2-}–ZrO_2 and $Pt/HM(5)$ denoted as SZ and HM(5), respectively.
[b] Reaction temp. = 240°C.
[c] Selectivities are expressed in carbon-number basis.

methane, ethane and propane with the molecular ratio of $C_3H_8/C_5H_{12} > 1$ are thus expected on Pt/HMOR and Pt/HBEA of high Si/Al ratio. When the metal activities are comparable, the initial rate of C_1–C_3 formation has been found to increase with increasing Si/Al ratio of HMOR and HBEA zeolites as shown in Table 1. Therefore, as the Si/Al ratio increases, the i-butane selectivity will decrease, this is in agreement with the conversion of n-butane on HMOR [23].

3.3. The reaction pressure and the zeolite pore structure on product distribution

The variation of product distributions of n-butane versus the conversion on Pt/HBEA at 20.4 and 1 atm are shown in Fig. 1b and c. The C_3/C_5 molar ratio on Pt/HBEA(11) has been observed to
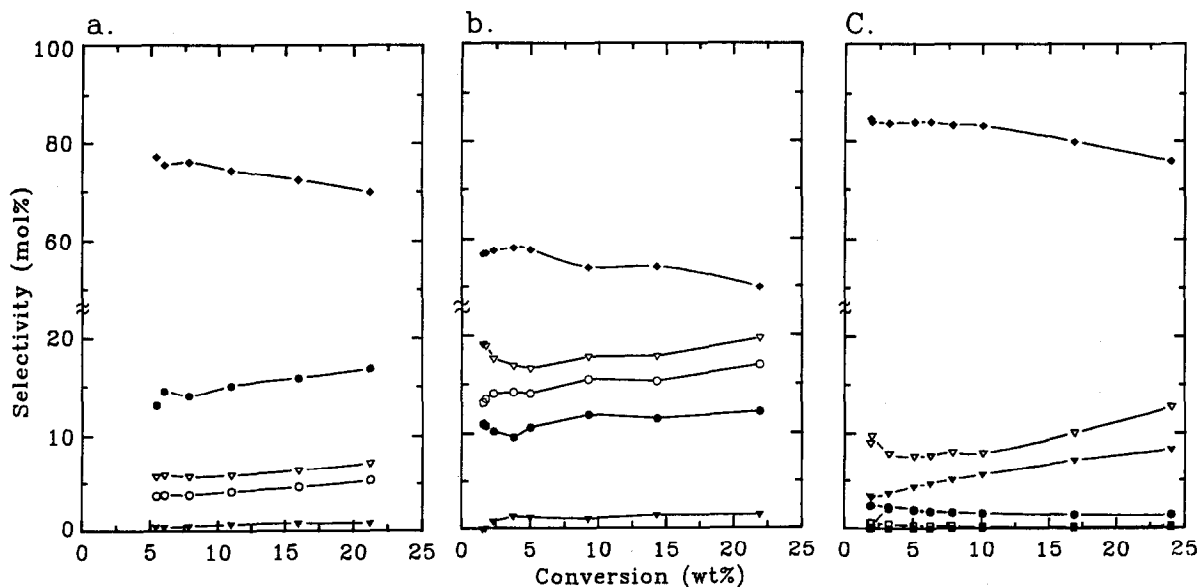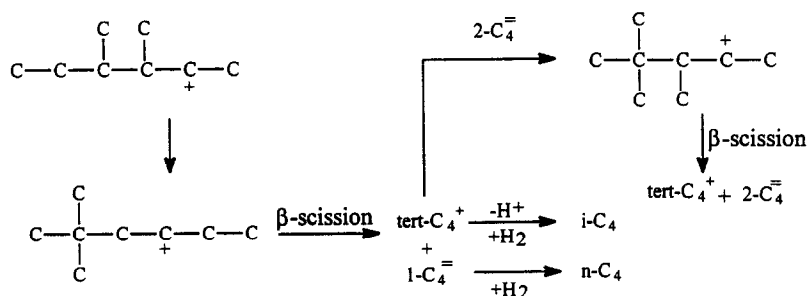

Fig. 1. Product selectivity as function of conversion of n-butane over Pt/SO_4^{2-}–ZrO_2 and $Pt/H\beta(11)$ catalyst: (O) C_1; (●) C_2; (▽) C_3; (◆) $i\text{-}C_4$; (▼) C_5; (□) C_4^{2-}; (■) C_6. (a) Catalyst, Pt/SO_4^{2-}–ZrO_2, temp. = 240°C, total pressure = 20.4 atm and H_2/HC = 1.5. (b) Catalyst, $Pt/H\beta(11)$, temp. = 340°C, total pressure = 20.4 atm and H_2/HC = 1.5. (c) Catalyst, $Pt/H\beta(11)$, temp. = 340°C, total pressure = 1 atm and H_2/HC = 1.5.

keep almost constant with n-butane conversion $> 5\%$ during runs conducted under atmospheric pressure, the C_3 (and C_5) selectivity increases with the conversion while the isobutane selectivity decreases. This suggests that C_3, C_5 and i-C_4 are generated from the isooctyl-carbenium ion intermediate at atmospheric pressure and at 340°C. Since Pt/HBEA(11) shows high selectivity for i-C_4 at low conversion, one may suggest that 2,3-dimethylhexyl carbenium ion generated from dimerization between 2-butene and sec-butyl ion on bifunctional catalyst rearranges rapidly into 2,2-dimethylhexyl carbenium ion which, in turn, converted into tert-butyl ion and 1-butene through cracking.

$$
\begin{array}{c}
\overset{\text{C}\quad\text{C}}{\underset{+}{\text{C—C—C—C—C—C}}} \\[2pt]
\Big\downarrow \\[2pt]
\overset{\text{C}}{\underset{\text{C}}{\text{C—C—C—C—C}}}\ \xrightarrow{\ \beta\text{-scission}\ }\ \text{tert-C}_4^+ \xrightarrow[+\text{H}_2]{-\text{H}^+} i\text{-C}_4
\end{array}
$$

$$\text{2-C}_4^= \longrightarrow \overset{\text{C}}{\underset{\text{C}\ \text{C}}{\text{C—C—C—C—C}}}^+ \xrightarrow{\beta\text{-scission}} \text{tert-C}_4^+ + 2\text{-C}_4^=$$

$$\text{1-C}_4^= \xrightarrow{+\text{H}_2} n\text{-C}_4$$

When the contact time was increased or when the WHSV value was lowered, the following carbenium ions were formed and they subsequently converted into C_3, C_4 and C_5 species.

$$
\overset{\text{C}\quad\text{C}}{\underset{+}{\text{C—C—C—C—C—C}}}\ \xrightarrow{\ \beta\text{-scission}\ }\ C_3^= + \text{sec-}C_5^+
$$

$$
\overset{\text{C}\qquad\text{C}}{\underset{\text{C}\qquad +}{\text{C—C—C—C—C}}}\ \xrightarrow{\ \beta\text{-scission}\ }\ \text{tert-}C_4^+ + i\text{-}C_4^=
$$
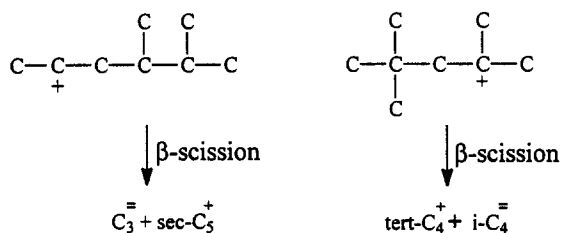
The slightly bulky intermediates of tertiary 2,2,4-trimethylpentyl, secondary 2,2,3-trimethylpentyl and 2,2-dimethylhexyl carbenium ions seem to be not much more easily formed than 2,3-dimethylhexyl carbenium ions in the intraframework void space of mordenite zeolites of one-dimensional 12-membered channel system, but the former three may be easily generated in BEA zeolites of three-dimensional channel system. A similar pore structure effect was observed on the hydroconversion of C_5–C_7 paraffins [17]. As for the diffusion of gaseous molecules or the migration of surface species, zeolite BEA usually has less steric hindrance than zeolite MOR of similar channel openings. With the strong acidity and one dimensional micropore structure and long residence time of intermediate carbenium ion in mordenite, the selectivity to i-C_4 is expected to be lower and the selectivity of C_3 and C_5 to be higher. Since C_3 and C_5 increase simultaneously with conversion as shown in Fig. 1c, one may predict that the possibility of secondary cracking is low on Pt/HBEA(11) at 340°C and 1 atm. Fig. 1c depicts a quasi lack of C_1 and C_2, an indication that monomolecular protolytic cracking is not important on Pt/HBEA(11) under 1 atm. By contrast, at high pressure, the selectivities of C_1, C_2 and C_3 are enhanced. The C_1, C_2 and C_3 selectivities are almost constant with the conversion, while selectivity for C_5 remains low with the ratio of $C_3/C_5 \gg 1$ on Pt/HBEA(11)

at 20.4 atm. That is an additional proof that these light alkanes may be formed as primary products. It appears that low conversion and low pressure are preferable for high isomerization selectivity on Pt/HBEA(11) as well as on Pt/SZ. Product distribution of n-butane transformation seems to be dependent on the pore structure of zeolite and the reaction pressure.

3.4. Hydrogenolysis and cracking

Since increasing the H_2 pressure can help the removal of surface coke and olefin species and thus enhances the function of Pt, the less i-C_4 and more C_1–C_3 alkanes production at high pressure may be expected from the participation of hydrogenolysis on Pt/Hzeolite (as shown in Table 2). By studying the n-C_4H_{10} hydrogenolysis on PtNaHY [25], Gallezot et al. found that the activation energy of C_2H_6 formation was higher than that of CH_4 and C_3H_8. Besides metal catalyzed hydrogenolysis, C_1–C_3 products can be obtained either by direct protolytic cleavage of C–C bond in butane or by dimerization of butane with subsequent β-scission on protonic acid sites. For Pt/SZ, enhancement of C_1–C_3 production with $C_2/C_3 > 1$ and the small amount of CH_4 with decreased i-C_4 yield at high pressure (Table 2) may be caused by the unimolecular protolytic cracking. This process occurs as a primary reaction to give very small variation in C_2H_6 and C_3H_8 productions with conversion at 240°C as shown in Fig. 1a. The Arrhenius plots of rate constants of C_1, C_2 and C_3 yields with temperatures of 240–300°C under conversion of 6–35 wt% on Pt/SZ (the result of our previous study) [2] are shown in Fig. 2. The activation energies of CH_4, C_2H_6 and C_3H_8 formations are 37, 26 and 37 kcal/mol, respectively, and they are similar to that for C–C bond rupture of carbenium ions on solid acid catalysts [24]. Based on the study of n-butane cracking on HZSM-5 by Krannila et al. [24] and Ono et al. [26], monomolecular protolytic breaking of C–C bond (the activation energy of ~ 33 kcal/mol) is assumed to occur as a dominate cracking pathway with catalyst having low hydrogen transfer activity due to the steric hindrance in zeolitic micropores of medium size, low dehydrogenation capability to give very low olefin concentration in the absence of Pt on HZSM-5 at 430–520°C. By investigating the cracking of isobutane on de-Al Y zeolite at 400–500°C [27], Corma et al. found that the selectivity of bimolecular process to unimolecular process on cracking was increased with decreasing the reaction temperature. In the present reaction condition the equilibrium between butene and butane is easily established, Pt/HBEA and Pt/HMOR seem to be less active for
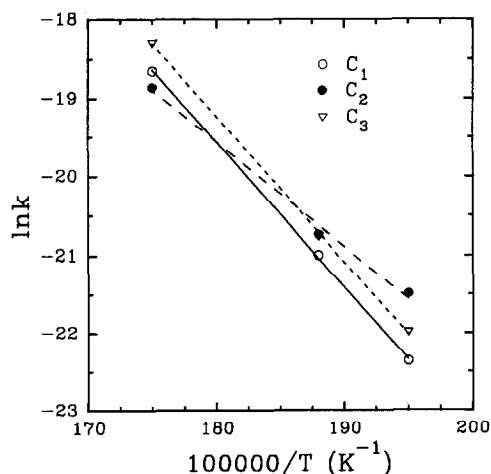

Fig. 2. Arrhenius plots of yields of CH_4, C_2H_6 and C_3H_8 over Pt/SO_4^{2-}–ZrO_2 at WHSV = 2 h^{-1} and H_2 / n-C_4 = 0.9.

primary protolytic cracking of butane than for secondary cracking of disproportionation products to give the mole ratio of $C_2/C_3 < 1$ as listed in Table 1 while $C_2/C_3 > 1$ has been found on Pt/SZ.

4. Conclusions

Acid-type unimolecular mechanism plays a more important role on protolytic cracking and skeletal isomerization of *n*-butane over Pt/SZ than over Pt/Hzeolites. For Pt/Hzeolites, hydrogenolysis and intermolecular isomerization are the predominant processes in the formation of cracking products and *i*-butane product, respectively, at a low conversion level under high reaction pressure.

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