Direct evidence of intramolecular rearrangement in skeletal isomerization of *n*-butane over bifunctional catalysts

Tetsuo Suzuki and Toshio Okuhara *

Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan
E-mail: oku@ees.hokudai.ac.jp

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Mechanisms of skeletal isomerization of *n*-butane over bifunctional catalysts, Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Pt-sulfated ZrO_2, as well as the corresponding solid acids were studied using 1,4-$^{13}C_2$-*n*-butane. The isotopic distributions of the reactant and product were analyzed with field ionization mass spectrometry, by which the parent peak patterns were obtained. It was found that 1,4-$^{13}C_2$-*n*-butane was selectively isomerized to $^{13}C_2$-isobutane over these catalysts in the presence of H_2 at 423–523 K, while the corresponding solid acids gave isobutane with binomial distributions of ^{13}C. These results clearly demonstrate that the skeletal isomerization of *n*-butane proceeded mainly via a monomolecular path with intramolecular rearrangement on both the bifunctional catalysts, while it occurred through a bimolecular path with intermolecular rearrangement on the solid acids. This difference in reaction mechanism is reflected on that in the selectivity to isobutane.

KEY WORDS: skeletal isomerization; *n*-butane; ^{13}C-butane; heteropoly compounds

1. Introduction

Skeletal isomerizations of *n*-alkanes are of industrially importance because the branched alkanes are useful as clean fuels. Among these reactions, the skeletal isomerization of *n*-butane is the slowest one, since this reaction must proceed through a primary carbenium ion [1]. However, isobutane is a raw material in the alkylation process to clean gasoline and in MTBE synthesis through isobutylene. The isomerization of *n*-butane has thus attracted much attention. Strong solid acids; such as mordenite [2], sulfated ZrO_2 [3–5] and heteropoly compounds [6,7]; are effective catalysts for this reaction. Furthermore, it has been known that the addition of Pt (that is, formation of bifunctional catalysts) enhanced the activity and selectivity in the presence of H_2 [8–11].

Recent mechanistic studies of *n*-butane isomerization using ^{13}C-*n*-butane [12,13] pointed out that there are two possible pathways, that is, a bimolecular pathway which is accompanied with intermolecular rearrangement and a monomolecular pathway with intramolecular rearrangement. Some studies about the mechanism were reported [12,13]. However, there is a controversy on the mechanism over sulfated ZrO_2 and quantitative discussion as for the reaction pathways has not been performed. Adeeva et al. [12] claimed by using 1,4-$^{13}C_2$-*n*-butane that the skeletal isomerization occurred through the bimolecular mechanism, since the ^{13}C-distribution of the product isobutane formed on sulfated ZrO_2 at 353 K was close to the binomial one. On the other hand, Garin et al. [13] reported using 1-$^{13}C_1$-*n*-butane that intramolecular rearrangement (monomolecular mechanism) was preferential over sulfated ZrO_2 at 523 K in the presence of H_2. More recently, we preliminarily inferred that over a pure protonic solid acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, both the monomolecular and bimolecular pathways coexisted in the *n*-butane isomerization, the latter being dominant [14]. Here we wish to report the direct evidence for the preferential operation of the monomolecular mechanism over typical bifunctional catalysts, Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Pt-sulfated ZrO_2, in the presence of H_2 at various reaction temperatures. Field ionization mass spectrometry made quantitative analysis of the isotopic composition possible.

2. Experimental

1.0 wt% Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Pt–Cs2.5) was prepared according to the literature [9]. An aqueous solution (12.06 cm^3) of H_2PtCl_6 (Wako Chemical, Co., 40.9 mmol dm^{-3}) was added to an aqueous solution (20 cm^3) of $H_3PW_{12}O_{40}$ (Nippon Inorganic Color and Chemicals, Co., 0.148 mol dm^{-3}) at room temperature. Then an aqueous solution (34.6 cm^3) of Cs_2CO_3 (Aldrich, 0.108 mol dm^{-3}) was added with vigorous stirring to form a milky suspension (yellow). After evaporation to solid, the resulting solid was calcined at 573 K in air for 2 h. The surface area of Pt–Cs2.5 was 80 $m^2\,g^{-1}$. 1.0 wt% Pt-sulfated ZrO_2 was prepared by incipient wetness impregnation using sulfated ZrO_2 and the aqueous solution of H_2PtCl_6, where sulfated ZrO_2 was obtained from H_2SO_4 and $Zr(OH)_4$ by calcination at 893 K for 5 h [8]. The obtained 1.0 wt% Pt-sulfated ZrO_2 has a surface area of 85 $m^2\,g^{-1}$ after the calcination at 573 K for 2 h. This sample will be denoted as Pt-SZ. As references, the corresponding non-promoted solid

* To whom correspondence should be addressed.

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acids, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as $Cs_{2.5}$) and sulfated ZrO_2 (SZ), were also used.

The catalytic reaction was carried out at 423–523 K in a closed circulation system (300 cm^3) with an on-line GC. The bifunctional catalysts were pretreated in a vacuum at 573 K for 2 h (for Pt–Cs2.5) or at 673 K for 4 h (for Pt-SZ). Then a mixture of 40 Torr (1 Torr = 133 Pa) of 1,4-$^{13}C_2$-*n*-butane (Isotec Inc., ^{13}C 99%) and 200 Torr of H_2 was introduced to the reaction system at the reaction temperature. In the cases of Cs2.5 and SZ, the reaction was performed in the absence of H_2. It was already shown that the presence of H_2 gave no effect on the activity and selectivity in the case of Cs2.5, as described previously [9]. The product isobutane and reactant *n*-butane were separated with a GC column (VZ-7) to be analyzed with a field ionization mass spectrometer (FI-MASS, Jeol JMS-SX102A) for ^{13}C-distribution. It should be emphasized that FI MASS gave the parent peak patterns of isobutane and *n*-butane.

3. Results and discussion

Figure 1 shows the isotopic distributions of isobutane formed over Pt–Cs2.5 and Cs2.5 at 423 K. Contrasting isotopic distributions were obtained between Pt–Cs2.5 and Cs2.5. Pt–Cs2.5 gave exclusively $^{13}C_2$-isobutane (figure 1(A)), but Cs2.5 brought about a spread distribution containing $^{13}C_0$-isobutane to $^{13}C_4$-isobutane. The isotopic distribution of isobutane formed over Cs2.5 (solid rectangles in figure 1(B)) was very close to the binomial distribution (open rectangles). Binomial patterns of ^{13}C-isobutane were calculated by using the ratio in the content of ^{13}C to that of ^{12}C, r, assuming binomial distribution, $1 : 4r : 6r^2 : 4r^3 : r^4$, where r was determined by the optimization between the observed and the calculated fractions for $x = 0$, 1, 3 and 4 in $^{13}C_x{}^{12}C_{4-x}H_{10}$ of isobutane. It is noted that the fraction of $^{13}C_2$-isobutane in the observed pattern over Cs2.5 (figure 1(B)) was slightly higher than that of the calculated binomial distribution. It was confirmed that the reactant *n*-butane after the reaction was exclusively $^{13}C_2$-*n*-butane (not shown here) for all cases.

If the reaction proceeds through the monomolecular pathway involving a protonated cyclopropane intermediate (scheme 1), the product isobutane would be $^{13}C_2$-isobutane, if the 1,4-$^{13}C_2$-*n*-butane was used as reactant. In addition, the high selectivity (100%) to isobutane is expected in this mechanism. On the other hand, the bimolecular mechanism would proceed accompanied with intermolecular rearrangement; a variety of isobutanes having different numbers of ^{13}C would be formed from 1,4-$^{13}C_2$-*n*-butane (scheme 1), because octyl cations readily undergo various rearrangements involving methyl shifts to give *tert*-carbenium ions. As a matter of fact, the pattern close to the binomial distribution was observed over Cs2.5. Thus we can estimate the contribution of each pathway from the difference between the observed fraction of $^{13}C_2$-isobutane and that of the binomial distribution, assuming that the bimolecular path gives

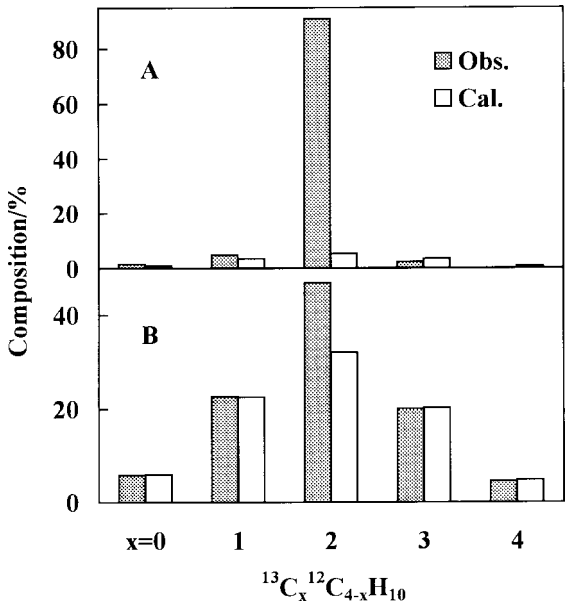
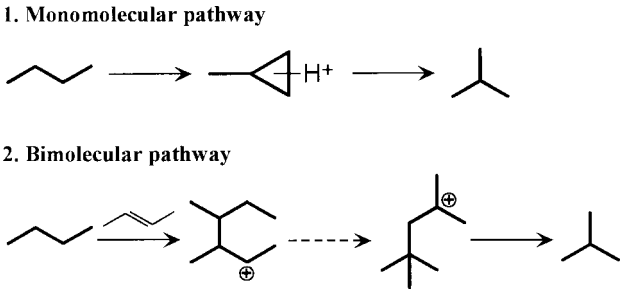


Figure 1. ^{13}C-distribution of isobutane in the isomerization of 1,4-$^{13}C_2$-*n*-butane over (A) 1.0 wt% Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (B) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 423 K. Conversions are 10 and 12% for (A) and (B), respectively.



Scheme 1. Reaction pathways for skeletal isomerization of *n*-butane.

a binomial distribution and the monomolecular path brings about only $^{13}C_2$-isobutane.

In figure 2, the contributions of the monomolecular pathway estimated from the above method are plotted against the reaction temperature. It was found that the contribution of the monomolecular pathway was higher than 80% at 423 K over both the bifunctional catalysts and declined gradually as the reaction temperature increased. In contrast, the contribution of the monomolecular pathway was much less at 423 K over both the non-promoted solid acids and increased gradually as the temperature increased. The catalytic activities were in the following order at 523 K: Pt-SZ (23.0) > Pt–Cs2.5 (1.5) = SZ (1.5) > Cs2.5 (1.3), where the figures in parentheses are the reaction rates in the unit of 10^{-8} mol g^{-1} s^{-1}.

The selectivities to isobutane at 423 K were 96.3% (10% conversion) and 94.9% (10% conversion) on Pt–Cs2.5 and Pt-SZ, respectively, while they were 86.8% (13% conversion) and 86.4% (11% conversion) on Cs2.5 and SZ, respectively. A similar difference in the selectivity between Pt–Cs2.5 and Cs2.5 was confirmed in a flow system [9].

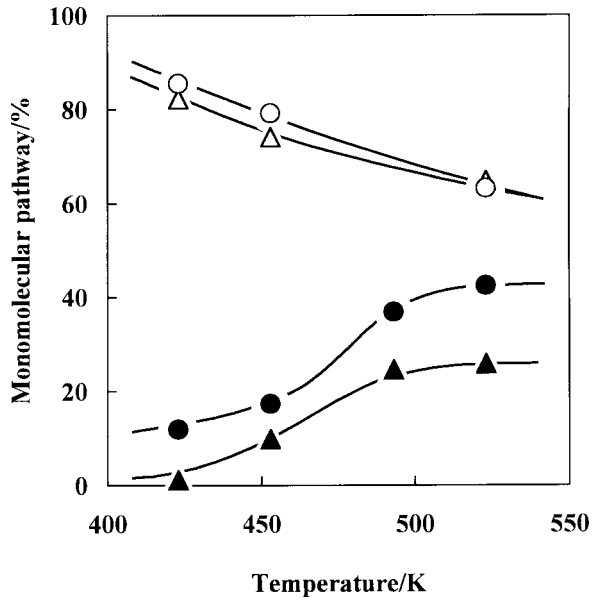


Figure 2. Contribution of the monomolecular pathway in skeletal isomerization of *n*-butane at 423 K: (○) 1 wt% Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$, (△) 1.0 wt% Pt-sulfated ZrO_2, (●) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and (▲) sulfated ZrO_2.

These differences in selectivity are reasonably understood by a switching of the mechanism. The contribution of the monomolecular pathway was significant on the bifunctional catalysts and the monomolecular pathway would exhibit 100% selectivity (scheme 1). These are responsible for the higher selectivity of the bifunctional catalysts. The presence of Pt and H_2 might greatly suppress the formation of olefins and thus the bifunctional pathway would be intercepted. On the other hand, the bimolecular pathway which would lead to side reactions was dominant over the non-promoted solid acids (figure 2). In conclusion, the switching of the reaction mechanism from bimolecular on non-promoted solid acids to monomolecular on bifunctional catalysts is the reason for the enhancement of selectivity.

4. Conclusion

The reaction mechanism of the skeletal isomerization of *n*-butane to isobutane catalyzed by the typical bifunctional catalysts Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and Pt–SO_4^{2-}/ZrO_2 was elucidated by an isotopic study. 1,4-$^{13}C_2$-*n*-butane was selectively isomerized to $^{13}C_2$-isobutane in the presence of H_2 over these catalysts. The quantitative analysis of the isotopic distribution demonstrated that the contribution of intramolecular rearrangement became more than 80% at 423 K over both the bifunctional catalysts. The higher selectivity obtained over the bifunctional catalysts in the presence of H_2 than over the corresponding acid catalysts can be explained by the different contribution of the reaction paths.

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