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Mechanisms of *n*-butane isomerization over superacidic sulfated metal oxides

Tien-Syn Yang [a], Tsong-Huei Chang [b], Chiu-Hsun Lin [c], Chuin-Tih Yeh [a, *]

[a] *Department of Chemistry, Tsing-Hua University, Hsinchu, 300 Taiwan*
[b] *Department of Chemical Engineering, Ming-Hsin Institute of Technology and Commerce, Hsinfeng, Hsinchu, 304 Taiwan*
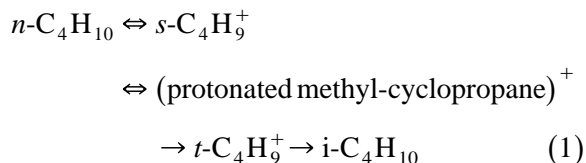[c] *Union Chemical Laboratories / ITRI, Hsinchu, 300 Taiwan*

Abstract

Superacidic sulfated metal oxides were prepared by impregnating different metal oxides (or hydroxides) with sulfuric acids. The superacidic strength of prepared samples were compared by temperature-programmed desorption of ammonia (NH_3-TPD) and showed a trend of $HS/ZrO_2 > HS/MgAl_2O_4 > HS/Al_2O_3 > HS/Fe_2O_3$. Catalytic properties of these superacidic samples towards isomerization of *n*-butane to isobutane were subsequently pursued. Both the activity and the isobutane selectivity increased with the superacidic strength of catalysts. Observed variation in the selectivity was interpreted with a difference in the reaction mechanism: A high selectivity was obtained from strong superacid sites that catalyze the isomerization through a revised monomolecular mechanism; while a low selectivity became dominated on weak superacid sites that favored a bimolecular mechanism. The relative importance of these two mechanisms was kinetically controlled by formation of different butyl carbenium ions (primary or secondary) while the *n*-butane reactant adsorbed on superacidic sites. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Butane isomerization; Mechanism; Sulfated metal oxide; Superacid; NH_3-TPD

1. Introduction

Methyl butyl ether (MTBE) and C_4 alkylates are being used to boost gasoline octane ratings. One of precursors for MTBE production is isobutane (i-C_4), which comes mainly from *n*-butane isomerization. Alkylation also requires i-C_4 as one of the reactants. Sulfated zirconia [1–6] and mordenite zoelite [7,8] have been suggested as acceptable solid superacid catalysts for *n*-butane isomerization in the literature. Two

kinds of reaction mechanisms, i.e., monomolecular (intramolecular) and bimolecular (intermolecular), have been proposed. The classical monomolecular mechanism is a sequence that involves at least three different butyl cations, i.e.,

$$n\text{-}C_4H_{10} \Leftrightarrow s\text{-}C_4H_9^+$$
$$\Leftrightarrow (\text{protonated methyl-cyclopropane})^+$$
$$\to t\text{-}C_4H_9^+ \to i\text{-}C_4H_{10} \qquad (1)$$

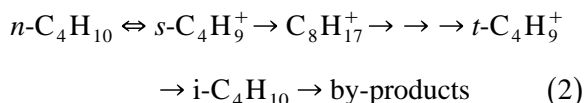The *sec*-butyl carbenium ions (s-$C_4H_9^+$) are suggested to be generated directly from adsorp-

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* Corresponding author.

tion of *n*-butane on superacidic catalysts of Lewis type (on sulfated zirconia [9]). On superacidic sites of Bronsted type (such as mordenites [8,10]), *sec*-butyl carbonium ions (s-$C_4H_{11}^+$) should be formed, but would convert consequently into s-$C_4H_9^+$ through a decomposition of hydrogen molecules. The involvement of the cyclic intermediate (protonated methyl-cyclopropane) in Sequence 1 was suggested by an isotope observation of *n*-butane-1-^{13}C to *n*-butane-2-^{13}C by carbon-scrambling [11].

Path (a) in Fig. 1 presents an energy profile theoretically calculated [9] for three carbenium intermediates in Sequence 1. According to this profile, activation energy around 35 kJ mol^{-1} is required for converting s-$C_4H_9^+$ to t-$C_4H_9^+$ by way of the protonated methyl-cyclopropane intermediate.

Some 2-butene molecules may exist in the reaction system through dehydrogenation of *n*-butane. The 2-butene molecule may combine with a s-$C_4H_9^+$ to form an intermediate of octyl carbenium ($C_8H_{17}^+$) [5,6]. This intermediate may subsequently decompose, in cooperating with

sequentially methyl and hydride shifts, into a *tert*-butyl carbenium according to the following bimolecular mechanism:

$$n\text{-}C_4H_{10} \Leftrightarrow s\text{-}C_4H_9^+ \to C_8H_{17}^+ \to \to \to t\text{-}C_4H_9^+$$

$$\to i\text{-}C_4H_{10} \to \text{by-products} \qquad (2)$$

In the bimolecular mechanism, the 35 kJ mol^{-1} of activation energy required for the formation of protonated cyclopropane intermediate in Sequence 1 is avoided (path (b) in Fig. 1), hence, a high conversion of *n*-butane may therefore be achieved. However, the selectivity towards isobutane from this bimolecular mechanism should be lower than that from the monomolecular mechanism because some additional fragments ($C_3H_7^+$ and $C_5H_{11}^+$) can form through branching transfer and scission steps following the formation of $C_8H_{17}^+$.

The main role of platinum is to produce activated hydrogen. The activated hydrogen inhibits the formation of coke (carbonaceous deposit), which affects the strong acid sites and is the cause of the catalyst deactivation. However, Garin et al. [3] proposed that Pt had no influence on the catalyst activity and stability under the existence of H_2. Yori et al. [4] demonstrated that Pt supported on SO_4^{2-}/ZrO_2 had the same activity as SO_4^{2-}/ZrO_2 because of sulfur poison on Pt and strong metal–support interaction. The poison on Pt was believed to proceed during the isomerization of *n*-butane for the identification of sulfur-containing species formed by hydrogen reduction of sulfate during the reaction at 250°C [12]. Therefore, to observe undisturbed the influence of acidity on the initial activity and i-C_4 selectivity, we use the catalysts without Pt addition. In this study, four sulfated metal oxides are prepared to catalyze *n*-butane isomerization. Their catalytic conversions and isobutane selectivities are compared and interpreted in a fixed reaction condition, and a revised reaction mechanism is suggested to proceed on these superacidic catalysts.
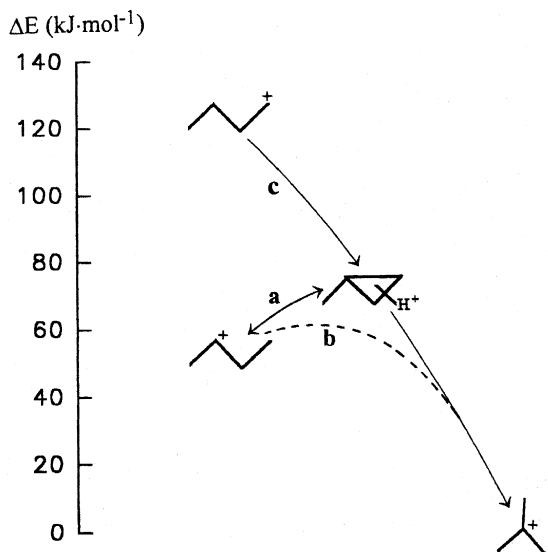

Fig. 1. The potential energy diagrams for (a) monomolecular mechanism (b) bimolecular mechanism and (c) the revised monomolecular mechanism of *n*-butane isomerization.

2. Experimental

2.1. Preparation of superacidic sulfated metal oxides

Four kinds of sulfated metal oxides (HS/MO), designated in this report as HS/Fe_2O_3, HS/ZrO_2, HS/γ-Al_2O_3 and HS/$MgAl_2O_4$, were prepared by impregnating 1 g of powdered metal hydroxides or oxides (i.e., $Fe(OH)_3$, $Zr(OH)_4$, γ-Al_2O_3 or $MgAl_2O_4$, respectively) with 10 ml of 0.5 M sulfuric acid. After filtration, the obtained pastes were subsequently dried in ambient air for 24 h and calcined at 550°C for 3 h before being stored as sulfated samples. Part of the sulfated samples were further converted into bifunctional samples by an additional impregnation of $PtCl_4$ solution. These bifunctional samples were designated as Pt-HS/MO in this report and had a platinum content around 2.25wt.%.

2.2. Desorption of ammonia

The relative acid strengths of sulfated samples were compared with the temperature-programmed desorption of ammonia (NH_3-TPD) in a fixed-bed flow reactor [13,14]. Each sample was dehydrated by an evacuation at 300°C for 1 h before being exposed to a flow of dry NH_3 gas at 100°C. Excessive and physically adsorbed ammonia were then purged away at the same temperature with an Ar flow (100 ml min^{-1}). The NH_3-TPD was then performed on raising the system temperature from 100°C to 600°C in the Ar flow. After trapping in a boric acid/ammonium chloride solution, the amount of evolved ammonia was titrated by sulfamic acid using an on-line automatic pH titrator.

2.3. Isomerization test

n-Butane isomerization reaction was carried out in a flow system with a fixed-bed reactor. A superacidic sample was precalcined in the reactor before each reaction test with flowing air at 550°C to burn out hydrocarbons possibly adsorbed on the superacidic sites. The catalytic isomerization was performed in ambient pressure at 300°C with an *n*-butane feed of 1 h^{-1} in WHSV and a hydrogen/*n*-butane molar ratio of 6. The reaction products were analyzed with an on-line gas chromatograph using an FID detector and a 30-m capillary column of SE-30.

3. Results and discussions

Fig. 2 exhibits NH_3-TPD traces from four sulfated metal-oxides prepared in this study. Each trace contained two peaks indicating desorption of ammonia molecules from two kinds of sites of different acidic strengths [13,14]. Weakly adsorbed ammonia molecules desorbed approximately around 250°C, while the desorption temperature of the strongly adsorbed ammonia varied with the metal oxide of superacidic samples, and increased in the order of:

$$HS/Fe_2O_3 < HS/\gamma\text{-}Al_2O_3 < HS/MgAl_2O_4$$
$$< HS/ZrO_2 \qquad (3)$$

This acidic sequence is consistent with their order in the H_o values (12.5, 13.8, 14.5 and
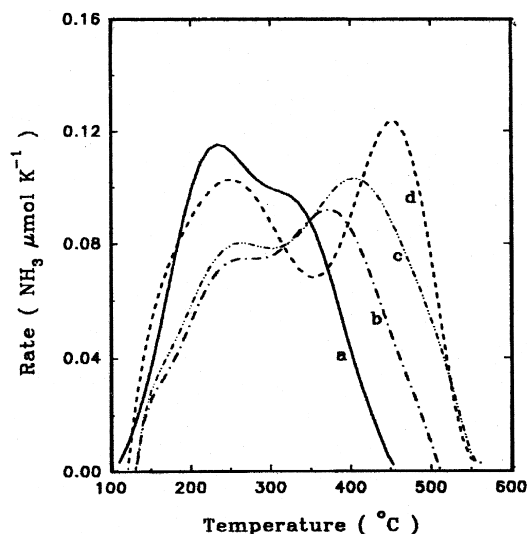

Fig. 2. NH_3-TPD traces obtained from four superacidic samples: (a) HS/Fe_2O_3 (b) HS/Al_2O_3 (c) HS/$MgAl_2O_4$ and (d) HS/ZrO_2.

16.0, respectively) measured from the Hammett indicator method [13]. The four sulfated metaloxides in Sequence 3 were then used as superacid catalysts to catalyze the isomerization of n-butane.

The function of H_2 in n-butane isomerization was to hinder the deactivation of the reaction, but a high hydrogen pressure could inhibit the conversion [3,4]. We selected $H_2/n\text{-}C_4 = 6$ (condition as described in Section 2) to obtain the best initial conversion for each sulfated metal oxide although the conversion would decay gradually. Table 1 summarizes the initial conversion of n-butane and isobutane selectivity for the four catalysts. Interestingly, the conversion and selectivity both increased with the acidity of the catalysts. The increase in the catalytic activity (conversion) with the acidity may be expected from a high rate of sec-butyl carbenium formation on interaction of n-butane with catalysts, i.e.,

$$n\text{-}C_4H_{10}^{+\,*} \Leftrightarrow \left(s\text{-}C_4H_9^+ + H^- \right)^* \qquad (4)$$
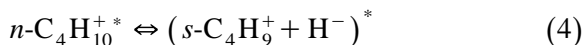
where * denotes a superacid site on catalysts.

Nevertheless, the observed increase in the isobutane selectivity with the acidity of catalyst is rather puzzling. Presumably, the isomerization prefers to proceed on strong superacid through the monomolecular mechanism of Sequence 1 which has a higher isobutane selectivity than the bimolecular mechanism of Sequence 2. However, this preference can hardly be expected from the potential energy diagram (a) shown in Fig. 1. The above rationale may be conceivable that the sec-butyl carbenium gradually become the primary intermediate ($n\text{-}C_4H_9^+$) during adsorption on sites of increasing superacidic strength:

$$n\text{-}C_4H_{10}^+ \Leftrightarrow \left(n\text{-}C_4H_9^+ + H^- \right)^* \qquad (5)$$
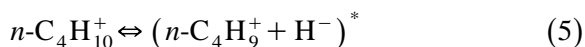
According to a theoretical calculation [15], the heterolytic dissociation energy (E_d) for decomposition of n-butane to a hydride ion (H^-) and an $n\text{-}C_4H_9^+$ is 1.11×10^3 kJ mol^{-1}. This energy is 70 kJ higher than the E_d required for a heterolytic dissociation of hydride ion from $n\text{-}C_4H_{10}$ to form $s\text{-}C_4H_9^+$. Accordingly, $s\text{-}C_4H_9^+$ species has been widely considered in literature as the preferred butyl carbenium ion primarily formed on adsorption of n-butane on superacids. However, the probability of reaction (5) during butane adsorption should depend heavily on the acidic strength of solid superacids. According to the Hammett equation, the concentration ratio of a neutral molecule (RH) to its conjugated acid (R +) varies with both the acidic strength of superacid and the acidity of the conjugated acid according to:

$$\log\{[R+]/[RH]\} = pKa - H_o \qquad (6)$$

where K_a is the acidic constant for the R + to associate a H^- to form RH, and the H_o represents the acidic strength (in the Hammett scale) of superacid. Reaction (5) may therefore proceed appreciably on acidic sites with a strong superacidic strength.

Experimentally, CH_3^+ carbeniums, which require an E_d of 1.31×10^3 kJ mol^{-1} (200 kJ mol^{-1} higher than that of $n\text{-}C_4H_9^+$) [15] to form from methane molecules, have been suggested from interactions of methane with liquid superacid [16] as well as with Fe–Mn promoted sulfated zirconia [17]. It is thus our expectation that reaction (5) may compete with reaction (4)
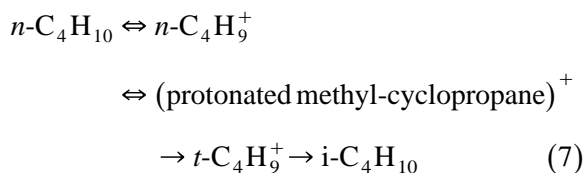
Table 1

Initial conversions[a] of n-butane isomerization on various SO_4^{2-}/MO_x samples

Samples	Conversion (wt.%)	Molar selectivity (%)				
		C_1	C_2	C_3	i-C_4	C_5
HS/ZrO$_2$	23.2	7.1	19.5	25.9	38.3	9.2
HS/MgAl$_2$O$_4$	21.0	19.2	27.6	28.7	13.2	11.3
HS/Al$_2$O$_3$	15.0	6.1	20.3	50.2	9.2	14.2
HS/Fe$_2$O$_3$	4.2	0	52.1	32.6	4.9	10.4
0.25% Pt/ HS/ZrO$_2$	27.2	0.4	2.9	15.4	67.3	14.0
0.25% Pt/ HS/Al$_2$O$_3$	21.0	2.4	11.0	27.6	37.1	21.9

Condition: Flow rate of H_2 is 60 cm^3 min^{-1}, $n\text{-}C_4$ 10 cm^3 min^{-1}; $T = 300°C$; WHSV of $n\text{-}C_4 = 1$ h^{-1}.

[a] Initial conversion is measured at 5 min time on stream.

during adsorption of *n*-butane on the stronger superacidic sites. If the superacidic strength is strong enough, reaction (5) may become dominant because primary hydrogen atoms in *n*-butane molecules are more accessible, due to a less geometric hindrance, than secondary hydrogen atoms to react with bulky superacidic sites. Obviously, strong superacid sites tend to catalyze the isomerization of *n*-butane to isobutane through the following revised monomolecular mechanism:

$$n\text{-}C_4H_{10} \Leftrightarrow n\text{-}C_4H_9^+$$

$$\Leftrightarrow (\text{protonated methyl-cyclopropane})^+$$

$$\rightarrow t\text{-}C_4H_9^+ \rightarrow i\text{-}C_4H_{10} \qquad (7)$$

Path (c) in Fig. 1 displays the potential energy diagram for Sequence 7. The energies for the three intermediates decrease steeply in the reaction coordinate. Negligible activation energy is therefore expected from the conversion of these carbeniums step by step in the revised mechanism and its rate-determining step should be the initial adsorption of *n*-butane (reaction 5).

Although Liu et al. [5,6] considered *n*-butane isomerization to proceed by intermolecular (bimolecular) mechanism on platinum promoted sulfated zirconia catalysts, we believed that the mechanism of *n*-butane isomerization on sulfated metal oxide without Pt was different from those promoted by Pt because Pt has a good dehydrogenation activity, which would induce more butenes profitable to produce $C_8H_{17}^+$, the intermediate through intermolecular mechanism. We observed in our study that Pt could enhance the conversions and selectivities of *n*-butane isomerization on HS/ZrO_2 and HS/Al_2O_3 (Table 1). The functions of platinum on such a bifunctional catalyst have been discussed in literature [3,4,18]. Therefore, the compete contributions of Pt and superacidity to *n*-butane isomerization by which mechanism on these Pt promoted sulfated metal oxides deserve a detailed comparison and discussion in future work.

4. Conclusion

n-Butane isomerization is suggested in this report to proceed mainly by two different mechanisms, i.e., revised monomolecular (Sequence 7) and bimolecular (Sequence 2), on superacidic sites of sulfated metal-oxides. The superacidic strength of the sites determines the ratio of *n*-butyl carbeniums ($n\text{-}C_4H_9^+$) to *sec*-butyl carbeniums ($s\text{-}C_4H_9^+$) formed during the initial adsorption step and the subsequent isomerization mechanism proceeded. On strong superacid sites as HS/ZrO_2, $n\text{-}C_4H_9^+$ is preferentially formed on adsorption; a high isobutane selectivity is therefore obtained through the revised monomolecular mechanism (Path (c) in Fig. 1). On weak superacidic sites as HS/Fe_2O_3, low isobutane selectivity is found because the reaction proceeded mainly through the bimolecular mechanism (path (b) in Fig. 1) initiated by the *sec*-butyl carbeniums.

Acknowledgements

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