CHEMISTRY LETTERS, pp. 1141-1144, 1993.

Skeletal Isomerization of n-Butane Catalyzed by an Acidic Cesium Salt of 12-Tungstophosphoric Acid

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A salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, catalyzed efficiently the skeletal isomerization of n-butane to isobutane at 300 °C. The activity and selectivity were much higher than those of SO_4^{2-}/ZrO_2. H-ZSM-5 was more active than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, but the selectivity was very low.

The skeletal isomerization of straight-chain alkanes has become important for the enhancement of the octane number of light petroleum fractions.1) While the isomerization of n-butane to isobutane is the slowest among those of alkanes in acid-catalyzed systems, this reaction has attracted much attention because isobutane is an important feedstock for alkylation with alkenes and synthesis of methyl *tert*-butyl ether as a high octane gasoline additive.2)

It is known that the skeletal isomerization of n-butane is catalyzed by strong acids such as SbF_5-HF3) and oxide-supported SbF_5 catalysts.4) Arata et al. reported that sulfate-treated zirconium oxides (SO_4^{2-}/ZrO_2) function even at room temperature.5)

Heteropoly compounds are excellent solid acids for both gas-solid and liquid-solid reaction systems.6,7) Ono et al. reported that $H_3PW_{12}O_{40}$ and its Pd salts catalyzed pentane and hexane isomerizations.8) However, there have been no reports as for the butane isomerization catalyzed by heteropoly compounds. Here we wish to report that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, which we previously found to be a very active solid-acid catalyst,7) was much more efficient for the isomerization than SO_4^{2-}/ZrO_2 at a nearly stationary state.

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated by Cs2.5) was prepared by the titration of the aqueous solution of $H_3PW_{12}O_{40}$ by an aqueous solution of Cs_2CO_3.7) For reference, H-ZSM-5 (obtained from Na-ZSM-5, which was supplied from Tosoh Corporation, HSZ-820NAA), SO_4^{2-}/ZrO_2 (prepared from $Zr(OH)_4$ and H_2SO_4),9) and H-Y zeolite (Reference Catalyst, JRC-Z-Y 4.8, Catalysis

Society of Japan) were tested. The reaction was performed in a flow reactor (Pyrex tube, 8 mm of I.D.) under an atmospheric pressure at 300 °C. The feed gas was composed of 5% n-butane and 95% nitrogen (balance). The total flow rate was 10 or 20 $cm^3 \cdot min^{-1}$ and the catalyst weight was 1 or 2 g. Prior to the reaction, the catalysts were pretreated at elevated temperatures (heteropoly compounds; 300 °C, H-ZSM-5; 535 °C, and SO_4^{2-}/ZrO_2; 370 °C) in an N_2 flow for 2 h. The gases at the outlet of the reactor were analyzed with a gas chromatograph (FID) with VZ-10 and SE-30 columns.

Figure 1 shows the typical time courses of n-butane isomerization over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5), $H_3PW_{12}O_{40}$, and SO_4^{2-}/ZrO_2 at 300 °C. For SO_4^{2-}/ZrO_2, the initial activity was very high, but the %-conversion decreased considerably at the initial stage of the reaction as has been pointed out already.[10)] On the other hand, the extent of the decrease was relatively small for Cs2.5. When the %-conversion of n-butane was compared at 5 h of the reaction time, the value for Cs2.5 was about 3 times as high as that of SO_4^{2-}/ZrO_2.

In Table 1, the catalytic activities and the product distributions are summarized. The activity for the formation of isobutane was in the following order, H-ZSM-5 > Cs2.5 > SO_4^{2-}/ZrO_2 > $H_3PW_{12}O_{40}$ > H-Y. On the other hand, the selectivity to isobutane was in the following order, Cs2.5 (83%) > $H_3PW_{12}O_{40}$ (81%) > SO_4^{2-}/ZrO_2 (61%) > H-ZSM-5 (14%) > H-Y (11%), where the figures in the parentheses are the selectivity to isobutane in mol% (after 5 h). These results indicate that Cs2.5 is a prominent catalyst for the selective formation of isobutane from n-butane.

Figure 2 provides the changes in the selectivity to isobutane as a function of the %-conversion of n-butane. In this figure, the data after 1 h of the reaction were collected, since the selectivities were almost unchanged and the carbon balances were about 100% after 1 h for all the catalysts. It was found that the high selectivity to isobutane of Cs2.5 was retained at least up to about the 20% conversion, where the equilibrium conversion is about 50% under these conditions.[2)] The changes in the selectivity were not significant also for SO_4^{2-}/ZrO_2 and H-ZSM-5. As shown in Fig. 2, the selectivity for H-ZSM-5 was also low at 200 °C.

As reported previously, the acid strength measurements by Hammett indicators and NH_3-TPD showed that Cs2.5 was a strong acid similar to $H_3PW_{12}O_{40}$, of which the acid strength was a little higher than H-ZSM-5, but lower than SO_4^{2-}/ZrO_2.[7d)] The strong acidity of SO_4^{2-}/ZrO_2 is probably responsible for the high initial activity (Fig. 1), and for the coke formation which deactivates the catalyst. It is considered that the superiority of Cs2.5 in activity to the parent $H_3PW_{12}O_{40}$ is due to the

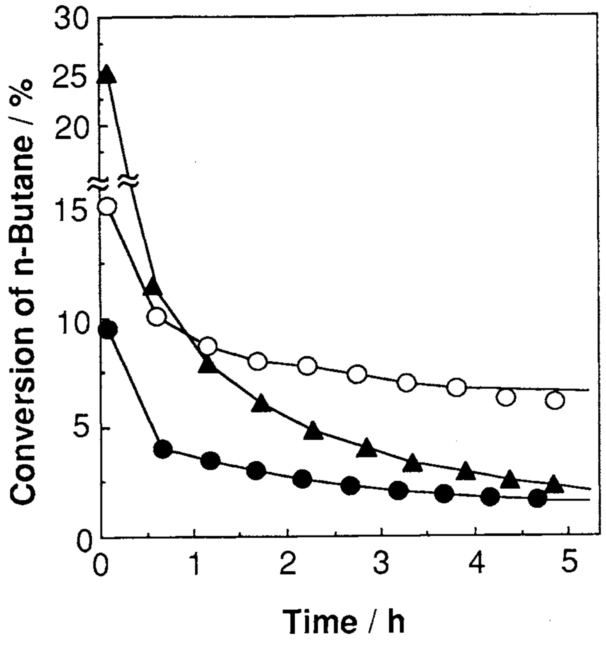

Fig. 1. Time courses of n-butane isomerization at 300 °C.
(○):Cs2.5, (▲):SO_4^{2-}/ZrO_2,
(●):$H_3PW_{12}O_{40}$.
(W/F = 41 g·h·mol^{-1})

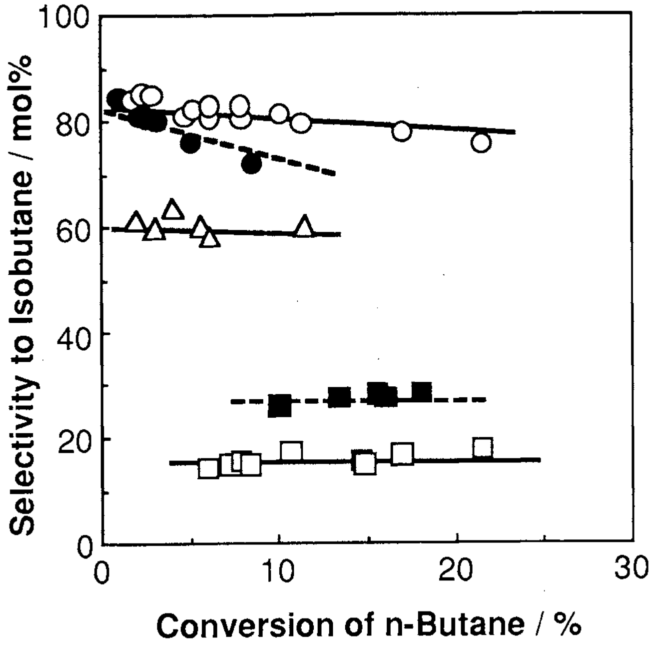

Fig. 2. Changes in the selectivity as a function of the %-conversion of n-butane.
(○):Cs2.5 at 300 °C, (●):$H_3PW_{12}O_{40}$ at 300 °C, (△):SO_4^{2-}/ZrO_2 at 300 °C, (□):H-ZSM-5 at 300 °C, (■):H-ZSM-5 at 200 °C.

Table 1. Activity and Selectivity for Skeletal Isomerization of n-Butane$^{a)}$

Catalyst	Rate$^{b)}$	Selectivity/mol%$^{c)}$					
		C_1	$C_2 + C_2^=$	$C_3 + C_3^=$	Isobutane	$C_4^=$	$C_5(+)$
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	2.0	1.1	2.0	8.5	83.1	0.8	4.5
$H_3PW_{12}O_{40}$	0.4	1.1	2.4	11.7	80.9	0	3.9
SO_4^{2-}/ZrO_2	0.4	3.1	9.1	23.0	60.8	0	4.0
H-ZSM-5	2.9	0.7	2.3	74.5	14.1	0.4	8.0
H-Y$^{d)}$	0.03	15.8	33.3	18.1	11.1	18.8	2.9

a) 300 °C, butane 5%. b) Formation of isobutane; 10^{-8} mol·g^{-1}·s^{-1}. c) C_1; CH_4, $C_2 + C_2^=$; $C_2H_4 + C_2H_6$, $C_3 + C_3^=$; $C_3H_6 + C_3H_8$, $C_4^=$; C_4H_8, $C_5(+)$; hydrocarbons containing more than 5 carbons. d) 400 °C.

larger quantity of the surface proton than that of $H_3PW_{12}O_{40}$.[7d] The protonic acidity on the surface can be estimated by multiplying the formal concentration of proton on the surface by the specific surface area, {(3-x)·(BET surface area/surface area of one Keggin unit) for $Cs_xH_{3-x}PW_{12}O_{40}$}, since all protons are randomly distributed throughout the bulk as was deduced from ^{31}P solid-state NMR.[7d,11] Due to the high surface area of Cs2.5 (140 $m^2 \cdot g^{-1}$), its surface acidity became greater than that of $H_3PW_{12}O_{40}$ (6 $m^2 \cdot g^{-1}$). This is the probable reason for the superiority of Cs2.5 to $H_3PW_{12}O_{40}$.

The authors thank Tosoh Corporation for the supply of Na-ZSM-5.

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(Received April 13, 1993)