Conversion of propane into butanes catalyzed by sulfated zirconia mixed with Pt/ZrO_2

Makoto Hino[a] **and Kazushi Arata***[b]

[a] *Hakodate Technical College, Tokura-cho, Hakodate 042-8501, Japan*
[b] *Department of Science, Hokkaido University of Education, Hachiman-cho, Hakodate 040-8567, Japan. E-mail: karata@hak.hokkyodai.ac.jp*

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An active catalyst for the conversion of propane into butanes is obtained by mechanically mixing sulfated ZrO_2 and Pt/ZrO_2.

Among conversion of light alkanes by cracking, coupling, or isomerization in heterogeneous catalytic sytems much attention has been focused on the coupling of methane, but the catalytic systems still require high temperatures to obtain satisfactory activity and selectivity.[1] Sulfated zirconia and related catalysts have received attention because of their high activities for butane isomerization.[2,3] Cheung and Gates tested Fe–Mn-promoted sulfated ZrO_2 for conversions of ethane and propane, but conversions were low, being only 0.6% for the highest propane conversion observed at 300 °C.[4–6] We have demonstrated that impregnation of sulfated ZrO_2 with noble metals such as Pt and Ir leads to pronounced activity for butane conversion, the Pt concentration being 7–8 wt%; the catalyst with Pt showed highest activity for the reaction.[7,8] These noble metal-added sulfated zirconias were applied to propane, but the conversions were still low. However, the conversion was found to be promoted by simply mechanically mixing Pt-supported zirconia (Pt/ZrO_2) with sulfated zirconia (SO_4/ZrO_2).

SO_4/ZrO_2 and 0.5 wt% Pt/ZrO_2 catalysts were prepared as described elsewhere.[3,8,9] The thus-prepared catalysts, 0.3 g SO_4/ZrO_2 and 0.3 g Pt/ZrO_2, were mixed well by kneading with a mortar and pestle. Other catalysts of sulfated Al_2O_3, TiO_2, and Fe_2O_3, together with WO_3/ZrO_2, were prepared as described elsewhere.[9]

Reactions of propane were carried out in a microcatalytic pulse reactor as described elsewhere.[8] The catalyst was heated at 300 °C for 1 h in an He flow before reaction. A slightly continual gain of conversion was observed with pulse number, and thus conversions were calculated on the basis of mol fraction as the average of the 6th–10th pulse values.

Table 1 Activities of the catalysts for the reaction of propane

Catalyst	T/°C	Conversion (%)	Products (%) C_1	C_2	C_4	C_5
SO_4/ZrO_2	200	0.1	Tr[a]	Tr	0.1	0
$Pt–SO_4/ZrO_2$[b]	200	0.2	0	Tr	0.2	0
$Pt–SO_4/ZrO_2$[c]	250	0.3	Tr	0.2	0.1	0
$SO_4/ZrO_2–Pt/ZrO_2$	200	3.2	Tr	0.2	3.0	Tr
$SO_4/ZrO_2–Pt/ZrO_2$[d]	200	4.2	0.1	0.7	3.4	Tr
$SO_4/ZrO_2–Pt/ZrO_2$[e]	200	4.6	0.3	1.2	3.1	0
$SO_4/ZrO_2–Pt/ZrO_2$	225	6.1	0.3	1.6	4.1	0.1
$SO_4/ZrO_2–Pt/ZrO_2$	250	10.6	1.8	4.9	3.8	0.1
$SO_4/Al_2O_3–Pt/ZrO_2$	250	8.4	2.1	6.3	Tr	0
$SO_4/TiO_2–Pt/ZrO_2$	250	8.9	2.4	6.4	0.1	0
$SO_4/Fe_2O_3–Pt/ZrO_2$	250	13.3	3.9	9.4	0	0
$WO_3/ZrO_2–Pt/ZrO_2$	250	14.0	3.3	10.7	0	0
$SO_4/ZrO_2–Pt/ZrO_2$[f]	250	5.8	5.5	0.3[g]	0	0
$SO_4/ZrO_2-Pt/ZrO_2$[f]	300	16.3	16.2	0.1[g]	0	0

[a] Trace. [b,c] Prepared by sulfation of zirconia gel followed by platinization and calcination ([b] 0.5, [c] 2 wt% Pt). [d,e] Reaction with [d] 0.6 or [e] 1.2 g of 0.5% Pt/ZrO_2 and 0.3 g of SO_4/ZrO_2. [f] Reaction of ethane. [g] Yield of C_3.

The reaction of propane (C_3) was carried out at 200 °C and 20 ml min^{-1} of He carrier over 0.3 g of SO_4/ZrO_2, but the conversion was only 0.1%. The addition of platinum (0.5 or 2 wt%), $Pt-SO_4/ZrO_2$ (0.3 g), was ineffective even at 250 °C as shown in Table 1. The addition of Pt was, however, effective when Pt/ZrO_2 was mechanically mixed with SO_4/ZrO_2. A mixture of 0.3 g of SO_4/ZrO_2 and 0.3 g of 0.5 wt% Pt/ZrO_2, where the Pt quantity was equivalent to that in 0.3 g of 0.5 wt% $Pt-SO_4/ZrO_2$, gave 3.2% conversion. The major product was butanes (C_4); trace amounts of pentanes (C_5) were observed in addition to ethane (C_2) and methane (C_1). Dehydrogenated materials were not observed, though ethylene and propylene were formed over Fe–Mn-sulfated ZrO_2.[5,6]

The catalysts were then examined in butane; the Pt co-impregnated catalyst, $Pt–SO_4/ZrO_2$[c] in Table 1, gave 48% conversion for the first pulse at 80 °C (catalyst amount: 0.1 g), while the mixture of SO_4/ZrO_2 and Pt/ZrO_2 only gave 8% conversion. Thus, the catalyst which is effective for butane is not efficient for propane and *vice versa*.

The effect of mixing was examined further at temperatures of 225 and 250 °C; the yields of C_4 were $\approx 4\%$ with higher conversions of C_3, but showing lower selectivity for the formation of C_4 (Table 1). In terms of preparation temperature of the catalysts the highest activity was observed upon calcination at 600 °C for SO_4/ZrO_2 and 750°C for Pt/ZrO_2.

The effect of modifying the proportion of platinum in the catalyst was studied. Catalysts with 0.6 and 1.2 g of Pt/ZrO_2 showed 4.2 and 4.6% propane conversion at 200 °C, with 3.4 and 3.1% C_4 yields, respectively. This indicates that the effect of concentration of platinum is relatively small. In terms of isomers of C_4 the selectivity for isobutane was 60–65% in each case.

The effect of mixing of Pt/ZrO_2 for the reaction of propane was examined for other sulfated metal oxides, Al_2O_3, TiO_2, and Fe_2O_3 in addition to WO_3/ZrO_2, the acidities of which are lower relative to SO_4/ZrO_2.[3] These materials showed a noticeable effect upon mixing for the conversion reaction of butane to isobutane.[9,10] Remarkable conversions of C_3 over these substances mixed with Pt/ZrO_2 were obtained at 250 °C, but the yield of C_4 was low, at most 0.1%. Thus, high superacidity is needed to form C_4 products.

XPS experiments were carried out in order to elucidate the surface properties of Pt/ZrO_2. The binding energy of Pt 4f was 72.6 eV, which was far from that of the metallic state (71.7 eV), but close to that of cationic Pt species.[11]

The formation of higher molecular weight alkanes is brought about by catalysis of the cracking ability in addition to the protonation of propane by a superacid to form a carbonium ion.[5] This behavior was also shown by the formation of propane from ethane in the present system, although the yield was low (Table 1).

Notes and references

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