A highly active solid superacid catalyst for *n*-butane isomerization: persulfate modified Al_2O_3–ZrO_2

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A new solid superacid catalyst of persulfate modified Al_2O_3–ZrO_2 has been prepared for the first time; it displays extraordinarily high catalytic activity and stability for the isomerization of *n*-butane.

In recent years, sulfated zirconia superacids have attracted increasing attention because they can give high activity at low temperature for *n*-butane isomerization, which has recently become a very important reaction in the petrochemical industry owing to growing environmental constraints and requirements for high-octane-number gasoline.[1–3] However, a rapid deactivation of this catalyst has often been observed at high temperature. In order to improve the lifetime of SO_4^{2-}/ZrO_2 catalysts for *n*-butane isomerization, the presence of hydrogen and/or addition of a small amount of Pt or Ni have been suggested.[4,5] Although Fe- and Mn-promoted sulfated zirconia are *ca.* three orders of magnitude more active than SO_4^{2-}/ZrO_2 for *n*-butane isomerization at low temperature,[6] they are deactivated quickly at 250 °C in the presence of hydrogen or at 60 °C in the presence of nitrogen.[7,8] We found that sulfated oxides of Cr–Zr, Fe–Cr–Zr and Fe–V–Zr were 2–3 times more active than sulfated Fe–Mn–Zr for *n*-butane isomerization, but these transition metal-doped sulfated zirconias also deactivated rapidly in the presence of hydrogen at high temperature.[8,9] In our previous results,[10,11] the addition of Al to sulfated zirconia significantly enhanced the activity and stability of the catalyst for *n*-butane isomerization at 250 °C in the presence of H_2. Persulfate modified zirconia is more active than sulfated zirconia for the isomerization of *n*-butane. The main problem in this research area is the durability of the catalyst during isomerization of *n*-butane. Here, we report a new solid superacid catalyst that is more active and stable for *n*-butane isomerization than any sulfated zirconia-based catalysts yet reported.

The new catalyst was prepared as follows: aqueous ammonia was added dropwise to a mixed solution of $ZrOCl_2\cdot 8H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ until pH = 9–10. After washing the mixed hydroxide and drying at 383 K overnight it was immersed in 0.5 M ammonium persulfate solution for 30 min. The persulfated $Al(OH)_3$–$Zr(OH)_4$ was then filtered off, dried at 383 K overnight and calcined at 923 K in static air for 3 h. The new catalyst, a white solid, had a surface area of 80.8 $m^2\ g^{-1}$ and contained 3.0 mol% Al_2O_3 and 3.5 wt% sulfate. Sulfated zirconia was made for comparison in the same manner by immersing dried $Zr(OH)_4$ in 0.5 M sulfuric acid, followed by calcination at 923 K in static air for 3 h. The sulfated zirconia, also a white solid, had a surface area of 113.0 $m^2\ g^{-1}$ and contained 4.0 wt% sulfate. *n*-Butane isomerization on the catalysts was carried out at 523 K in a fixed-bed continuous flow reactor under ambient pressure with WHSV = 0.3 h^{-1} and an H_2 : butane molar ratio of 10 : 1. Before testing, each catalyst was pretreated *in situ* in dry air at 723 K for 3 h. The products were analyzed with an on-line gas chromatograph equipped with a flame ionization detector.

The major reaction product of *n*-butane isomerization at 523 K is isobutane and by-products are propane and isopentane. The selectivity to isobutane for the SO_4^{2-}/ZrO_2 and $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalysts is > 95%. Table 1 shows the variation of the conversion of *n*-butane at 523 K with time on stream for both catalysts. During the initial 1 h of reaction both catalysts are rapidly deactivated. After being on stream for 2 h the conversions of both catalysts then drop more slowly. The $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalyst reaches a steady state for *n*-butane isomerization after 2 h on stream (although it deactivates more rapidly than SO_4^{2-}/ZrO_2 during the initial 1 h of reaction), indicating that it is more stable than SO_4^{2-}/ZrO_2 for the reaction of *n*-butane isomerization. Both the initial and steady state activities of the $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalyst are much higher than those of SO_4^{2-}/ZrO_2. As compared with SO_4^{2-}/ZrO_2, $S_2O_8^{2-}/Al_2O_3$–ZrO_2 is 2.1 times more active after being on stream for 6 h.

The stability of the $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalyst has been investigated by running the reaction at 523 K continuously for 200 h. As illustrated in Fig. 1, the initial conversion on $S_2O_8^{2-}/Al_2O_3$–ZrO_2 is 51.8%, dropping to 37.8% after 2 h, and then remaining constant at *ca.* 37.4% up to 200 h without further observable deactivation. In other words, *n*-butane isomerization proceeds steadily on $S_2O_8^{2-}/Al_2O_3$–ZrO_2 at a level of 72% of its equilibrium conversion. In view of its high isomerization activity and stablity, $S_2O_8^{2-}/Al_2O_3$–ZrO_2 can be regarded as an excellent candidate for a commercial-scale *n*-butane isomerization catalyst.

After running on stream for 6 h, the amount of coke deposited on the $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalyst is 1.0 wt%, which is

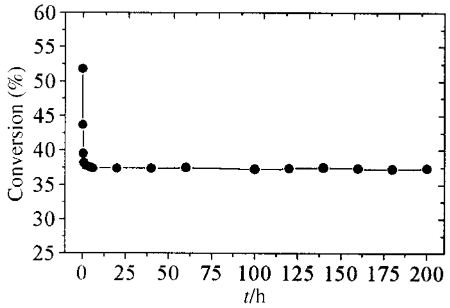

Fig. 1 Long-term test of $S_2O_8^{2-}/Al_2O_3$–ZrO_2 catalyst for *n*-butane isomerization at 523 K.

Table 1 Activities of solid superacid catalysts for *n*-butane isomerization at 523 K

	Conversion (%)							
Catalyst	2 min	10 min	60 min	120 min	180 min	240 min	300 min	360 min
SO_4^{2-}/ZrO_2	27.7	25.2	23.5	21.6	20.4	19.3	18.1	17.5
$S_2O_8^{2-}/Al_2O_3$–ZrO_2	51.8	43.7	38.2	37.8	37.7	37.7	37.4	37.3

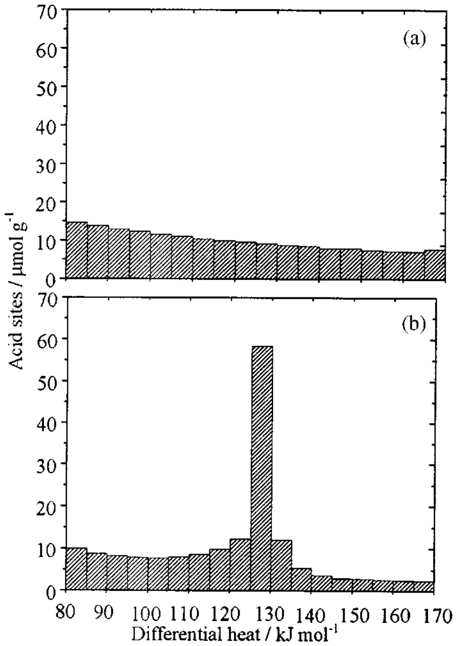

Fig. 2 Histograms of acid strength distributions for (a) SO_4^{2-}/ZrO_2 and (b) $S_2O_8^{2-}/Al_2O_3–ZrO_2$ catalysts.

slightly less than that on SO_4^{2-}/ZrO_2 (1.3 wt%). Furthermore, the amount of coke deposited on $S_2O_8^{2-}/Al_2O_3–ZrO_2$ remained almost unchanged from 6 to 200 h, showing that the initial drop in activity during 0–2 h is probably caused by catalyst coking; after this time coking and deactivation slowed down. Both catalysts can recover their activities completely after treatment in air at 723 K and can be used repeatedly, further demonstrating that the fast deactivation of the catalysts during the initial period of the reaction is mainly caused by coking.

Microcalorimetric measurements of NH_3 adsorption on SO_4^{2-}/ZrO_2 and $S_2O_8^{2-}/Al_2O_3–ZrO_2$ catalysts were conducted. The differential heat of adsorption (*i.e.* heat generated after microadsorption on the adsorption system which has already reached equilibrium) decreases with increasing NH_3 coverage, indicating a distribution of acid site strength in both catalysts. Fig. 2 shows histograms of the distribution of acid site strengths. The strengths of the acid sites on SO_4^{2-}/ZrO_2 are more evenly distributed than for $S_2O_8^{2-}/Al_2O_3–ZrO_2$. Although the total amount of acid sites with a differential adsorption heat above 80 kJ mol^{-1} for $S_2O_8^{2-}/Al_2O_3–ZrO_2$ (174.2 μmol g^{-1}) is nearly the same as that for SO_4^{2-}/ZrO_2 (178.2 μmol g^{-1}), the former posseses 2.9 times more acid sites with a differential heat between 125 and 140 kJ mol^{-1}, which have been reported in an earlier study[12] as being the effective active sites for *n*-butane isomerization. Hence, the abundance of sites with intermediate acid strengths on $S_2O_8^{2-}/Al_2O_3–ZrO_2$ is the main reason for its remarkable activity and stability for the *n*-butane isomerization reaction. Our recent study[11] has shown that the characteristic stretching frequency of covalent S=O bonds for persulfate modified zirconia is at 1398 cm^{-1}, which is different from that for SO_4^{2-}/ZrO_2 at 1388 cm^{-1}; we postulate that $S_2O_7^{2-}$ is responsible for this stretching frequency in agreement with earlier studies.[13,14] On the persulfate modified oxide superacid, the main structure of the active sites is **II** (Fig. 3), whereas active site **I** predominates on the sulfated oxide superacid. The difference in the structure of the active sites for each of the catalysts is probably another reason why the catalytic activity and stability of $S_2O_8^{2-}/Al_2O_3–ZrO_2$ for the isomerization of *n*-butane are much higher than those of SO_4^{2-}/ZrO_2.

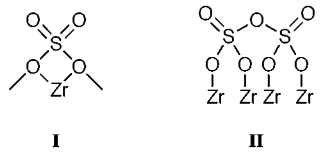

Fig. 3 Structure of active sites **I** and **II**.

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