Catalysis Letters 3~~4~~6 (1996) 125–128

Preparation of superacid of iron-supported zirconia for reaction of butane to isobutane ☆

Makoto Hino

Hakodate Technical College, Tokura-cho, Hakodate 042, Japan

and

Kazushi Arata

Department of Science, Hokkaido University of Education, Hachiman-cho, Hakodate 040, Japan

Received 10 July 1995; accepted 22 September 1995

A highly active superacid of 2 wt% Fe-supported ZrO_2 for the skeletal isomerization of butane to isobutane was obtained by exposing Fe_2O_3/ZrO_2 to 1 N H_2SO_4 followed by calcining in air at 700°C for more than 24 h; the Fe_2O_3/ZrO_2 was prepared by impregnating zirconia gel with a solution of $Fe(NO_3)_3$ followed by drying at 300°C (2 wt% Fe). A much lower activity was observed with the opposite procedure, where the first impregnation was sulfation of the gel, followed by a second impregnation with the iron compound. It was proved from analysis of the sulfur content in the catalysts that residual sulfur species were not related with generation of the superacidic sites. XPS showed the catalyst to be Fe_2O_3 supported on ZrO_2.

Keywords: superacid; solid superacid; iron oxide; zirconium oxide; butane; isobutane

Among the solid superacids studied so far [1–4], sulfate-supported zirconia (SO_4/ZrO_2) is highest in acid strength ($H_o \leqslant -16.04$) with relative ease for preparation and thus it has been applied to various reactions. The superacid is, however, not sufficiently stable; reduction or elimination of the sulfate is sometimes observed during reaction. Thus it is hoped that superacids can be synthesized by the system of metal oxides. However, the acid strength of tungsten oxide supported on zirconia (WO_3/ZrO_2), which is highest in acidity among the superacids synthesized by metal oxides, is not satisfactorily high ($H_o \leqslant -14.52$) and also much inferior in acid strength than liquid superacids such as $HSO_3F–SbF_5$ and $HF–SbF_5$. The SO_4/ZrO_2 material is recently used with the addition of platinum, usually less than 0.5 wt%, for stabilizing the catalyst [5–9].

For one of the means of solving the above problem it is hoped to synthesize a superacid with acidity higher than that of the SO_4/ZrO_2 catalyst, where much milder conditions can be applied in order to avoid conversion of the surface sulfate. If this would be achieved by the system of metal oxides, it would be much better. We discovered very recently that the SO_4/ZrO_2 material impregnated with noble-metal salts, Ir, Pt, Rh, Ru, Os, and Pd, showed pronounced activity for the reaction of butane to isobutane, much more than the SO_4/ZrO_2, the metal concentration being equivalent to Pt of 7–8 wt%; the catalyst with Pt was highest in activity for the reaction [10,11].

Following the above observations we found that iron-supported zirconia with the iron concentration equivalent to 7 wt% Pt showed remarkable activity for the reaction of butane to isobutane, much more than that of the SO_4/ZrO_2 as well as the WO_3/ZrO_2 catalyst. Here, we report the preparation method of a new solid superacid by the system of metal oxides.

The catalyst was prepared as follows. Fe_2O_3/ZrO_2 was obtained by impregnating zirconia gel with an aqueous solution of $Fe(NO_3)_3$ followed by evaporating water and calcining at 300°C for 3 h, the concentration being 2 wt% Fe based on the gel. The gel was obtained by hydrolyzing $ZrOCl_2$ with aqueous ammonia to pH 8.0 followed by washing, drying at 100°C for 24 h, and powdering to below 100 mesh. The dried Fe_2O_3/ZrO_2 (2 g) was exposed to 1 N H_2SO_4 (30 ml) on a filter paper followed by atmospheric drying, calcining in air in a quartz crucible and finally sealing in an ampoule until use to avoid humidity.

Reactions for butane were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst (flow rate of He carrier gas 20 ml/min; catalyst 0.2 g; pulse size 0.05 ml). Gaseous reactants were introduced via a syringe and passed through the catalyst bed. The catalyst was again heated at 300°C for 1 h in the He flow before reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (VZ-7, 6 m,

---

☆ Superacids by metal oxides, VIII. For previous publications VI and VII in this series see refs. [10,11].

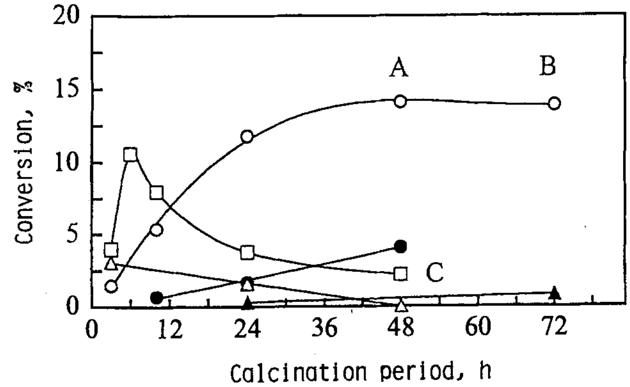

Fig. 1. Activities of Fe-supported ZrO_2 with calcination period for reaction of butane at 60°C. Calcination temperature: (▲) 650°C, (○) 700°C, (□) 725°C, (△) 750°C. (●) Catalyst prepared by impregnation of zirconia gel with 1 N H_2SO_4 followed by a second impregnation with a solution of $Fe(NO_3)_3$ and calcination at 700°C. Quantity of S: (A) 0.39, (B) 0.31, (C) 0.2 wt%.

0–30°C). Activities were compared with the tenth pulse value.

The reaction of butane (C_4) was carried out at temperatures below 100°C over the catalysts which were obtained by exposure of Fe_2O_3/ZrO_2 to aqueous sulfuric acid followed by calcination in air at 600–800°C. A continual gain of conversion was observed with the pulse number, and thus the catalytic activities were compared with the tenth pulse value. The results at 60°C of reaction are shown in fig. 1 as a function of calcination period (3–72 h) of the catalysts. The conversions were largely dependent on the calcination temperature and period; the maximum conversion was observed with calcination at 700°C (Fe_2O_3/ZrO_2(700°C)) after 24 h, continuous increase of the conversion being seen up to 24 h of calcination. Such high conversion was obtained by calcination for 6 h when heated at 25°C higher temperature, 725°C.

Table 1 shows the reaction results over the Fe_2O_3/ZrO_2 catalysts calcined at various temperatures for 24 h together with their surface areas and sulfur amounts. The chief product was isobutane (i-C_4), which was formed from C_4 by skeletal isomerization; propane (C_3) and pentane (C_5) were negligible as products. In the absence of hydrogen or without any reduction before reaction the Fe_2O_3/ZrO_2(700°C) catalyst gave sufficient conversion into isobutane at 50°C and almost 100% selectivity for the skeletal isomerization with 19.3% conversion at 80°C. The SO_4/ZrO_2(650°C) catalyst with the highest acid strength of up to $H_0 \leqslant -16.04$ among the sulfated superacids was inactive under the present conditions; the catalyst was prepared by exposing zirconia gel to 1 N H_2SO_4 followed by drying and calcining in air at 650°C [1,2]. SO_4/ZrO_2(700°C) and unsulfated Fe_2O_3/ZrO_2(700°C) were also completely inactive even at reaction temperature of 130°C; the latter material was similarly prepared by calcination of Fe_2O_3/ZrO_2 without the sulfate compound at 700°C after impregnation of zirconia gel with a solution of $Fe(NO_3)_3$ followed by drying at 300°C.

From the table no relationship between the catalytic activities and quantities of sulfur in the catalysts can be observed, though the sulfated zirconia generates superacidic sites by strong interaction of the sulfate species with zirconia [1,2], the S quantity of SO_4/ZrO_2(650°C) being 1.27 wt%. The quantity of S decreases with increasing calcination temperature; the Fe_2O_3/ZrO_2 (750°C) catalyst with 0.18 wt% S is still active for the reaction. The catalyst calcined at 700°C, highest in activity, also showed rather small amounts of sulfur after 48 h of calcination, 0.39 and 0.31 wt% for the samples of 48 and 72 h, respectively; the active catalyst of Fe_2O_3/ZrO_2(725°C) heated for 48 h was 0.2 g in quantity (fig. 1). Thus, it appears that the generation of superacidic sites is different from the case of SO_4/ZrO_2.

Analysis of sulfur in the catalysts calcined at 700°C for 3–72 h was carried out with thermal gravimetrical analysis (TGA), where samples were heated in air with a temperature programmed rate of 10°C/min. The results

Table 1
Activities of Fe-supported ZrO_2 catalysts calcined at various temperatures for 24 h for reaction of butane at 60°C

Catalyst	Conversion (%)	Products (%)			Quantity of S (wt%)	Surface area (m^2/g)
		C_3	i-C_4	C_5		
Fe_2O_3/ZrO_2 (650°C)	0.3	0	0.3	0	1.07	84
(675°C)	4.9	0	4.9	0	0.76	64
(700°C)	11.8	trace	11.8	0	0.52	45
(700°C)^{a}	4.9	0	4.9	0		
(700°C)^{b}	19.3	trace	19.3	trace		
(725°C)	3.8	0	3.8	0	0.31	31
(750°C)	1.6	0	1.6	0	0.18	20
(775°C)	0.0				0.06	11
SO_4/ZrO_2 (650°C)	0.0				1.27	123
SO_4/ZrO_2 (650°C)	0.0^{c}				0.44	44
Fe_2O_3/ZrO_2 (700°C)^{d}	0.0^{c}					17

[a] Reaction at 50°C. [b] Reaction at 80°C. [c] Reaction at 130°C.
[d] Prepared by impregnation of zirconia gel with iron nitrate and calcination without sulfation.

of SO_4/ZrO_2(700°C), together with those of $Fe_2(SO_4)_3$(700°C) and $Zr(SO_4)_2$(700°C) for comparison, are shown in table 2. The TGA data showed a weight decrease at 750–1000°C caused by the decomposition of sulfur species on the surface to form SO_3. It was shown from the initiation–termination temperature of decomposition that the temperature region of decomposition shifted to a high temperature as the period of calcination was prolonged. It seems that the species move into the inner part or interact gradually stronger with the support during calcination. These temperatures were coincident with those of the weight decrease of $Fe_2(SO_4)_3$ and $Zr(SO_4)_2$ heat-treated at 700°C. These sulfate materials do not show any superacidity, and thus the sulfur species that remained in the present catalysts are not related with generation of superacidity.

Determination of the catalytic strengths of these orange-colored catalysts was tried by temperature/conversion comparisons with the SO_4/ZrO_2 materials; the results are shown in fig. 2. The conversions of catalysts prepared by calcination at 700°C for 48 h were compared with those of the SO_4/ZrO_2 catalysts with $Ho = -16.04$ and -14.52, the difference in Ho values being 1.5; the SO_4/ZrO_2 samples were obtained by hydrolyzing $ZrOCl_2$ and $ZrO(NO_3)_2$, respectively, with ammonia followed by exposure to 1 N H_2SO_4 and calcination at 650°C [1,2]. The temperature difference to show 10% conversion (100% i-C_4 in selectivity) between the present catalyst and SO_4/ZrO_2 with $Ho = -16.04$ is 89°C; the catalytic activity corresponds to $Ho = -20$ based on the assumption that the activity difference is due to the Hammett acidity.

Hsu and co-workers prepared a new catalyst of 1.5 wt% Fe–0.5 wt% Mn–SO_4/ZrO_2 by impregnation of $Zr(OH)_4$ with aqueous $Fe(NO_3)_3$, $Mn(NO_3)_2$, and $(NH_4)_2SO_4$ [12,13]; this catalyst was much lower in activity than the present catalysts.

XPS investigation of Fe_2O_3/ZrO_2(700°C) yielded a value of 711.4 eV for the Fe 2p binding energy, which was close to 710.7 eV for the Fe 2p binding energy of Fe_2O_3. The single peak of S 2p was observed at 169–170 eV, which value agreed with that of metal sulfate. The sample also gave a peak at 530 eV showing metal oxide in addition to a shoulder peak at 531.7 eV, which was similar to that of metal sulfate. All the spectra were unchangeable while calcination was carried out from 3 to 72 h.

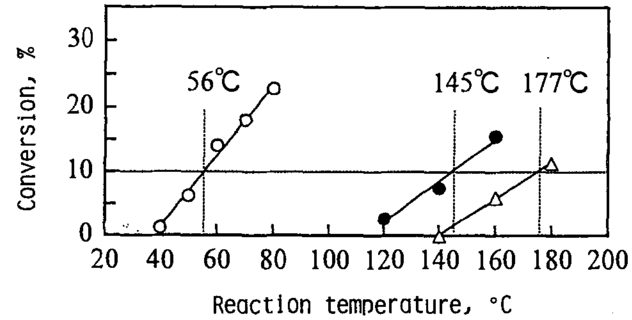

Fig. 2. Comparison of the activity of Fe_2O_3/ZrO_2 (○) with those of SO_4/ZrO_2 prepared from $ZrOCl_2$ (●) and from $ZrO(NO_3)_2$ (△). First pulse data for the SO_4/ZrO_2 catalysts.

The opposite procedure to the present one, in that the first impregnation of zirconia gel was with 1 N H_2SO_4 followed by a second impregnation of the sulfated zirconia with a solution of $Fe_2(NO_3)_3$, gave conversion much lower than that of the present procedure as shown in fig. 1. It is considered from the figure that the opposite manner needs a long period of calcination to get the same activity as that of the present case.

In the consideration of the results, it is proposed that highly active sites are created by interaction of iron with the support, ZrO_2, while chemical reactions such as oxidation or/and reduction takes place with sulfur oxides, originated from decomposition of the sulfate matter, during calcination [14]. In this point, it seems that the opposite preparation leads to difficult combination of the Fe compound onto the support because of the precedently strong interaction of SO_4 with ZrO_2.

Superacidity of SO_4/Fe_2O_3 is much lower than that of SO_4/ZrO_2 [1,2].

The specific surface areas of the catalysts are shown in table 1. It is obvious that the conversions are not related with the areas. A large increase of area is observed on the sulfated zirconia when superacidity is generated [1,2]. The area of the sulfated Fe_2O_3/ZrO_2(700°C), 45 m^2/g, was much larger compared with 17 m^2/g of the unsulfated Fe_2O_3/ZrO_2(700°C).

Table 2
Thermal gravimetrical analysis of sulfur in the catalysts

Catalyst	Calcination period (h)	Initiation–termination temperature of decomposition (°C)
Fe_2O_3/ZrO_2 (700°C)	3	775–893
	10	793–902
	24	813–910
	48	822–924
	72	831–934
$Fe_2(SO_4)_3$ (700°C)	3	743–867
$Zr(SO_4)_2$ (700°C)	3	815–968

References

[1] K. Arata, Adv. Catal. 37 (1990) 165.
[2] K. Arata and M. Hino, Mater. Chem. Phys. 26 (1990) 213.
[3] K. Arata and M. Hino, *Proc. 10th Int. Congr. on Catalysis*, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 2613.
[4] M. Hino and K. Arata, Bull. Chem. Soc. Jpn. 67 (1994) 1472.
[5] M.Y. Wen, I. Wender and J.W. Tierney, Energy Fuels 4 (1990) 372.
[6] E. Iglesia, S.L. Soled and G.M. Kramer, J. Catal. 144 (1993) 238.

[7] F. Garin, D. Andriamasinoro, A. Abdulsamad and J. Sommer, J. Catal. 131 (1991) 199.

[8] K. Ebitani, J. Tsuji, H. Hattori and H. Kita, J. Catal. 135 (1992) 609.

[9] K. Ebitani, T. Tanaka and H. Hattori, Appl. Catal. A 102 (1993) 79.

[10] M. Hino and K. Arata, Catal. Lett. 30 (1995) 25.

[11] M. Hino and K. Arata, J. Chem. Soc. Chem. Commun. (1995) 789.

[12] C.-Y. Hsu, C.R. Heimbuch, C.T. Armes and B.C. Gates, J. Chem. Soc. Chem. Commun. (1992) 1645.

[13] C.-H. Lin and C.-Y. Hsu, J. Chem. Soc. Chem. Commun. (1992) 1479.

[14] A. Sayari and A. Dicko, J. Catal. 145 (1994) 561.