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Acidity and Catalytic Activity of Zirconium and Titanium Sulfates Heat-Treated at High Temperature. Solid Superacid Catalysts§

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Synopsis. Acidity and catalytic activity of $Zr(SO_4)_2$ and $Ti(SO_4)_2$ calcined at 500—800 °C were studied. The products obtained by calcination at 725 °C for $Zr(SO_4)_2$ and at 625 °C for $Ti(SO_4)_2$ showed the highest activity for the cracking of cumene among samples calcined at other temperatures; the former showed an acid strength of $-13.16<H_0\leqq-12.70$ and the activity for the reaction of pentane.

In the previous papers, Friedel–Crafts reactions catalyzed by heat-treated iron sulfates were reported; both iron(II) and iron(III) sulfates calcined in air at 700 °C showed the highest activities for benzylation,[1] benzoylation,[2] and isopropylation[3] of toluene. The acidity and catalytic activity of $FeSO_4$ calcined at 500—900 °C were also studied; the product obtained by calcination at 700 °C showed the maximum acid amount at $H_0\leqq1.5$ and the activity for isomerization of *d*-limonene, polymerization of isobutyl vinyl ether, and dehydration of 2-propanol, and the product showed no acidity or activity when calcined at 750 °C.[4] We have, afterwards, synthesized solid superacid catalysts with an acid strength of up to $H_0\leqq-16.04$ by supporting oxides of Fe,[5] Zr,[6] and Ti[7] with sulfate ion followed by calcination in air over 500 °C. We also studied the catalytic action of titanium and zirconium sulfates treated at high temperatures, over 500 °C, and found that the materials calcined in the vicinity of 700 °C showed exceedingly high surface acidity and catalytic activity, much higher than that of SiO_2–Al_2O_3 which is well-known as one of the solid catalysts with the highest surface acidity.

Experimental

Catalysts were prepared by heating $Zr(SO_4)_2\cdot4H_2O$ (Mitsuwa Chemical Co.) and $Ti(SO_4)_2\cdot xH_2O$ (Nakarai Chemical Co.) at 250 and 350 °C, respectively, followed by powdering below 100 mesh. Calcination was then carried out in air in Pyrex glass tubes (quartz tubes for temperatures over 700 °C) for 3 h. The catalysts were stored in sealed ampoules.

Reactions of cumene, hexane, and ethanol were carried out by using a microcatalytic pulse reactor. The catalyst was heat-treated in a reactor in He flow at 400 °C for 1.5 h before the reactions. The effluent products were directly introduced into a gas chromatographic column for analysis (Silicon SE30-2 m, 90 °C for cumene: Porapak R-2 m, 130 °C for ethanol: VZ7-4 m, RT for pentane). X-Ray powder diffraction spectra were obtained with a X-ray diffractometer (Rigaku 2013) by using Cu radiation.

Results and Discussion

Catalytic activities of $Ti(SO_4)_2$ and $Zr(SO_4)_2$ for the cracking of cumene, a typical acid-catalyzed reaction, were examined, and the results of the first pulse are shown as a function of calcination temperature of the catalysts in Fig. 1 (catalyst amount: 0.20 g, flow rate of He carrier gas: 20 ml min^{-1}, pulse size: 0.4 μl, reaction temperature: 180 °C). The activities were remarkably dependent on the calcination temperature; the maximum activity was observed with calcination at 625 °C for $Ti(SO_4)_2$ [$Ti(SO_4)_2$(625 °C)] and 725 °C for $Zr(SO_4)_2$ [$Zr(SO_4)_2$(725 °C)], rapid decrease being seen by calcination of the higher temperatures. The products were benzene and propylene in the ratio 1:1.

SiO_2–Al_2O_3 (Shokubai Kasei Kogyo Ltd., 13% Al_2O_3, heat-treated at 500 °C), whose acid strength is in the range $-12.70<H_0\leqq-11.35$, was totally inactive under the same conditions (54% conversion at 250 °C). The acid strength of $Zr(SO_4)_2$(725 °C) was examined using Hammett indicators; vapor of the indicators was adsorbed on the catalyst surface in a vacuum apparatus at room temperature. The catalyst distinctly changed the basic forms (colorless) of *p*-nitrotoluene ($pK_a=-11.35$) and *p*-nitrochlorobenzene (−12.70) to the conjugate acid forms (yellow), but did not change the color of *m*-nitrochlorobenzene (−13.16). Thus, the acid strength is estimated to be $-13.16<H_0\leqq-12.70$. Since acid stronger than $H_0=-12$ is known as superacid, the present catalysts are concluded to be superacid.

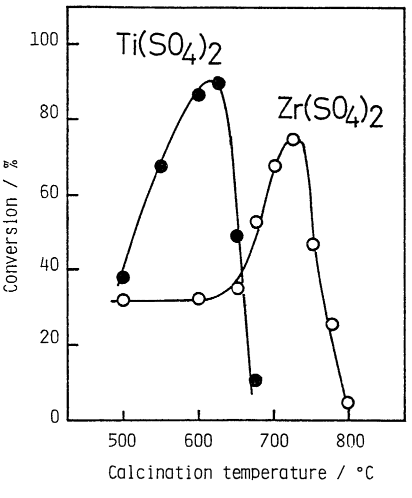

Fig. 1. Catalytic activities of $Ti(SO_4)_2$ and $Zr(SO_4)_2$ for reaction of cumene at 180°C.

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The present catalyst was also examined in the reaction of pentane, which is generally catalyzed by strong acid, especially superacid. The $Zr(SO_4)_2$(725 °C) catalyst converted pentane into 1.5% a mixture of methane and ethane, 8.1% propane, 2.0% butane, 6.4% isobutane, and 4.3% isopentane for the first pulse at 300 °C [catalyst: 0.3 g, He flow: 20 ml min^{-1}, pulse size: 0.1 ml (gas)]; $Ti(SO_4)_2$(625 °C) and SiO_2-Al_2O_3 were inactive under the same conditions, also being inactive for hexane.

The acidity of $NiSO_4$ shows a maximum at ca. 350 °C,[8] revealing its acidity on the sulfate configuration between the monohydrate and anhydrous forms.[9] Other metal sulfates, $Al_2(SO_4)_3$, $ZnSO_4$, $MgSO_4$, and $CdSO_4$, also show surface acidity on the sulfate structure, the maxima appearing at 180—400 °C calcination.[8] The present sulfates appear to be decomposed if calcined at high temperatures over 500 °C. The decomposition was examined using TGA; the TGA data of $Ti(SO_4)_2$ and $Zr(SO_4)_2$ treated at 350 °C for 3 h to remove their water of crystallization showed weight decrease at 500—800 °C. This decrease would be caused by decomposition of the sulfates to form SO_3 and the corresponding metal oxides. On the basis of reaction $Ti(SO_4)_2 \rightarrow TiO_2 + 2SO_3$ or $Zr(SO_4)_2 \rightarrow ZrO_2 + 2SO_3$, the percentage weight decrease was 9.1, 10.2, 27.7, 37.4, and 96.5% by calcination at 500, 550, 600, 625, and 650 °C for $Ti(SO_4)_2$, and 1.7, 3.5, 33.8, 66.6, and 97.8% at 500, 600, 700, 725, and 750 °C for $Zr(SO_4)_2$, respectively.

X-Ray diffraction measurement of the catalysts was performed; the spectra are shown in Fig. 2. The XRD pattern shows an anatase form of TiO_2 for $Ti(SO_4)_2$ (650 °C) and a monoclinic system of ZrO_2 for $Zr(SO_4)_2$(750 °C), while the materials prepared by calcining $Ti(SO_4)_2$ at 600—625 °C and $Zr(SO_4)_2$ at 700—725 °C show the diffraction peaks based on the sulfate forms in addition to those oxide systems. Thus, $Ti(SO_4)_2$(625 °C) and $Zr(SO_4)_2$(725 °C), which showed the highest activity, are concluded to be a mixture of their crystallized oxides and sulfate forms. The specific surface areas of $Ti(SO_4)_2$(625 °C) and $Zr(SO_4)_2$ (725 °C) were 48 and 58 m^2 g^{-1}, respectively.

The base strength of $Zr(SO_2)_2$(725 °C) was estimated using the Hammett indicators to be $H_- \leqq 22.3$, whose value is markedly basic; the catalyst in dried benzene changed the acid form (colorless) of diphenylamine (pK_a=22.3) to the conjugate base form (greenish blue). In order to study both acid and base characters of the present catalysts, the reaction of ethanol was carried out (catalyst: 30 mg, He flow: 30 ml min^{-1}, pulse size: 0.4 µl, temperature: 250 °C); the results for the first pulse are shown in Table 1. Acetaldehyde was observed as a product in addition to ethylene and diethyl ether, which were formed by the acid-catalyzed reaction. Acetaldehyde, formed by the base-catalyzed reaction, was observed without formation of other products when the catalyst was poisoned with pyridine;

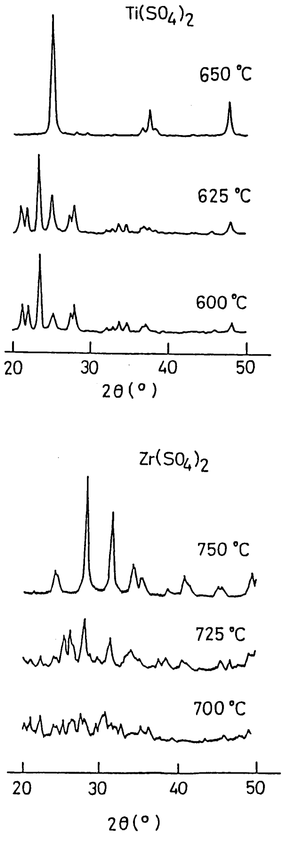

Fig. 2. XRD profiles of calcined $Ti(SO_4)_2$ and $Zr(SO_4)_2$.

Table 1. Reaction of Ethanol at 250 °C

Catalyst	Calcn. temp/°C	Conversion	Products/%[a]		
		%	E	EE	A
$Zr(SO_4)_2$	675	74	49	17	8
	725	85	58	18	9
	725[b]	11	0	Trace	11
	750	77	36	32	9
$Ti(SO_4)_2$	575	60	22	26	12
	625	75	44	19	12
	650	57	19	26	12
$TiOSO_4$[c]	625	81	50	21	10
$Ti_2(SO_4)_3$[c]	625	86	57	17	12

a) E: ethylene, EE: diethyl ether, A: acetaldehyde. b) The catalyst was poisoned by injection of pyridine (1 µl) before reaction. c) Nakarai Chemical Co.

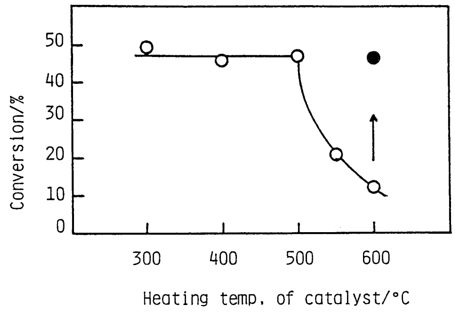

Fig. 3. Catalytic activities of $Zr(SO_4)_2$(725 °C) preheated at various temperatures in a He flow before reaction (reaction of cumene at 180 °C). (●): After reaction of the first pulse, water (1 µl) was injected at 120 °C followed by heating the catalyst at 400 °C for 1.5 h and performing the reaction at 180 °C.

the existence of basic sites is also supported. $TiOSO_4$ and $Ti_2(SO_4)_3$ also showed the same catalytic action as that of $Ti(SO_4)_2$ after calcination in air.

In order to locate the active sites of the catalyst the relation between the preheating temperature of $Zr(SO_4)_2$ (725 °C) in the reactor before reaction and the catalytic activity for the reaction of cumene was examined; the results are shown in Fig. 3. The activities were almost steady when heated at 300—500 °C, and decreased by heating at 550 to 600 °C. It is considered that Brönsted sites, created by adsorption of water on Lewis sites, were decreased by heating at high temperatuers in the He flow, thus the reaction of cumene catalyzed by Brönsted acid was restrained. In fact, the activity on heating at 600 °C was raised to that at 400 °C by regeneration of the Brönsted sites (● mark in the figure), where the catalyst was treated by moistening with water at 120 °C after the reaction followed by heating again in the He flow at 400 °C for 1.5 h and performing the reaction at 180 °C. It is indicative that Lewis and Brönsted sites on the present catalysts are easily changeable by adsorption or desorption of water molecules, the reaction of cumene being also catalyzed by Brönsted site as is well-known.

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