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Synthesis of Highly Acidic Catalysts of Tungsten Oxide Supported on Tin Oxide, Titanium Oxide, and Iron Oxide[1]

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Synopsis. Solid superacid catalysts, which were active for the skeletal isomerization and cracking of isopentane, were obtained by impregnating hydroxides or amorphous oxides of Sn, Ti, and Fe with ammonium metatungstate and then calcining in air; the maximum activity was observed with calcination at 1000 °C for the material of Sn and 700 °C for those of Ti and Fe (11—13 wt% W).

Acids stronger than $H_o=-12$, which corresponds to the acid strength of 100% H_2SO_4, are known as superacids. We have synthesized solid superacid catalysts with an acid strength of up to $H_o\leqq-16.04$ by exposing hydroxides or oxides of Zr, Sn, Ti, and Fe to sulfate ion followed by calcination in air over 500 °C; the surface was shown to be SO_4 co-ordinated to the metals.[2,3] The superacid catalysts were satisfactorily active in a heterogeneous system for reactions which are generally catalyzed by a strong acid, especially a superacid: the skeletal isomerization of butanes and pentanes, the acylation of aromatics with acetic and benzoic acids, synthesis of esters from acids with alcohols, and others.

We have then synthesized another type of superacid, which was WO_3 supported on ZrO_2 with an acid strength of $H_o\leqq-14.52$.[4,5] The catalyst was more stable than the sulfate-treated materials; in the case of the latter catalyst the elimination of sulfate ion was sometimes observed according to types of reaction and condition, especially in a solid–liquid system, though it was still slight. This preparation method of catalyst was applied to other supports, and WO_3 supported on SnO_2, TiO_2, and Fe_2O_3, as observed with the sulfate superacids, were found to show high acidity on their surface; the catalysts were active for the skeletal isomerization and cracking of isopentane.

Experimental

The catalysts were prepared as follows. $Sn(OH)_4$, H_4TiO_4, and $Fe(OH)_3$ were obtained by hydrolyzing guaranteed grade reagents of $SnCl_4$, $TiCl_4$, and $Fe(NO_3)_3$, respectively, with aqueous ammonia, washing, drying at 300 °C, and powdering the precipitates (32—60 mesh). The hydroxides were impregnated with aqueous ammonium metatungstate [$(NH_4)_6(H_2W_{12}O_{40})$, Nippon Inorganic Color & Chemical Co.] followed by evaporating water, drying, calcining in air for 3 h. The concentration was 15wt% W based on the hydroxides [11—13 wt% after calcination (Table 2)]. A commercially available SiO_2–Al_2O_3 (Shokubai Kasei Co., Al_2O_3 13 wt%) was calcined at 500 °C.

Reactions for ethanol were carried out by a microcatalytic flow method using helium as carrier gas; helium saturated with ethanol vapor at 15 °C was passed through the fixed-bed catalyst (0.2 g) at flow rate of 20 ml min^{-1}. Conversions were obtained from the product yields 1 h after the start of reaction.

Reactions for isopentane were carried out in a microcatalytic pulse reactor with a fixed-bed catalyst [flow rate of He carrier gas 10 ml min^{-1}; catalyst 0.5 g; pulse size 0.05 ml (gas)].

Effluent products for both reactions were directly introduced into gas chromatographic columns for analysis (Porapak R-2 m for ethanol; VZ 7-4 m for isopentane). The catalyst was again heated at 350 °C for 1.5 h in the He flow before reaction.

X-ray powder diffraction spectra were obtained with a X-ray diffractometer (Rigaku 2013) by using Cu radiation.

Results and Discussion

The dehydration of ethanol to ethylene and ethyl ether, one of the typically acid-catalyzed reactions, was carried out at 190 °C over the catalysts which were obtained by impregnating $Sn(OH)_4$, H_4TiO_4, and $Fe(OH)_3$ with ammonium metatungstate and then calcining in air at various temperatures; the results are shown in Table 1. The catalysts showed high activities, much higher than that of SiO_2–Al_2O_3 which is well known as one of the catalysts with the highest surface acidity. The maximum activity was observed with calcination at the surprisingly high temperature, 1000 °C, for WO_3/SnO_2; that was 700 °C for WO_3/TiO_2 and WO_3/Fe_2O_3. Ethyl ether was predominantly formed as products in most cases. The relative activity of WO_3/SnO_2 heated at 1000 °C [WO_3/SnO_2 (1000 °C)], WO_3/TiO_2 (700 °C), WO_3/Fe_2O_3 (700 °C), and SiO_2–Al_2O_3 (500 °C) for the dehydration is approximately 4 : 4 : 2 : 1. The relative activity among the catalysts used was examined in the dehydration under milder conditions, at 160 °C; the maximum activity was again observed with calcination at 1000 °C for WO_3/SnO_2 and 700 °C for WO_3/TiO_2 and WO_3/Fe_2O_3.

Reaction was carried out for the less reactive isopentane (i-C_5) and the results on the short contact time by means of the pulse-reaction method are shown in Table 2. The catalysts were active for the skeletal isomerization and cracking of isopentane. Pentane (C_5), hexane (C_6), and heptane (C_7) were observed as products in addition to propane (C_3), isobutane (i-C_4), and butane (C_4). The maximum activity was again observed with calcination at 1000 °C for WO_3/SnO_2. The SiO_2–Al_2O_3 catalyst was completely inactive for the reaction.

Table 1. Activities of the Catalysts for Dehydration of Ethanol at 190 °C

Catalyst	Calcination temp/°C	Conversion/%
WO_3/SnO_2	700	22
	800	31
	900	47
	1000	67
	1000	32[a)]
	1100	55
	1200	23
WO_3/TiO_2	500	43
	600	62
	700	73
	700	32[a)]
	800	60
	900	17
WO_3/Fe_2O_3	500	14
	600	24
	700	33
	700	14[a)]
	800	21
	900	2
SiO_2–Al_2O_3	500	18
WO_3/ZrO_2	800	47[a)]

a) Reaction at 160 °C.

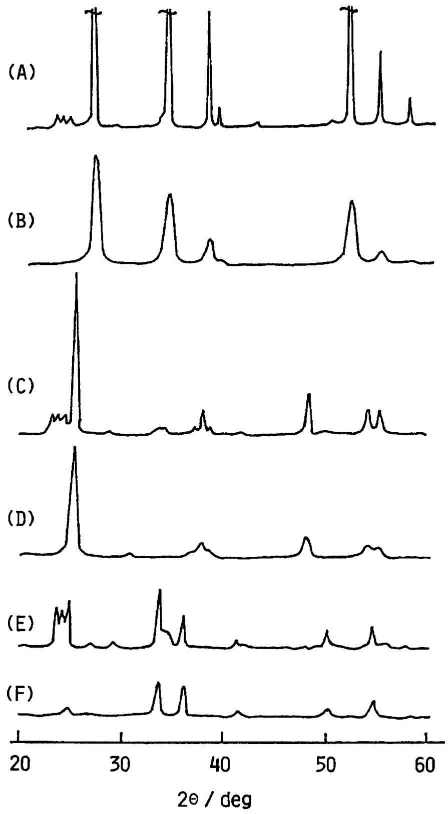

Fig. 1. XRD profiles of WO_3/SnO_2 (1000 °C) (B), WO_3/TiO_2 (700 °C) (D), and WO_3/Fe_2O_3 (700 °C) (F) superacids. (A), (C), (E): WO_3/SnO_2 (1000 °C) (A), WO_3/TiO_2 (700 °C) (C), and WO_3/Fe_2O_3 (700 °C) (E) prepared by impregnation of the tungstate on the crystallized oxides followed by calcination.

It is of interest that the WO_3/SnO_2 catalyst, even when heat-treated at quite a high temperature of 1200 °C, is still active for the reaction.

The oxidation of isopentane to give carbon oxides were observed with WO_3/SnO_2 and WO_3/Fe_2O_3 catalysts; CO and CO_2 were mainly formed on WO_3/SnO_2 (800 °C) and WO_3/Fe_2O_3 (700 °C). The activity enhancement of oxidation by the sulfate addition was observed with the SO_4/SnO_2 and SO_4/Fe_2O_3 superacids when reaction was performed at temperatures above 100 °C;[6,7)] butanes were converted into CO and CO_2 at 300 °C over SO_4/Fe_2O_3.[7)] The present results show that the oxidation effect can be also brought about by supporting WO_3 as well as SO_4 on SnO_2 and Fe_2O_3. The effect, however, vanished with calcination at elevated temperatures for preparation, over 1000 °C for WO_3/SnO_2.

Acid strength of SiO_2–Al_2O_3 used was in the range of $-12.70 < H_o \leqq -11.35$, determined by the visual color change method of the Hammett indicators.[8)] The present catalysts were themselves colored, brown for WO_3/Fe_2O_3 and yellow for WO_3/TiO_2 and WO_3/SnO_2; the acid strength was not estimated by the visual color change method. Since activities of the present catalysts for both reactions are much higher than that of SiO_2–Al_2O_3, whose acid strength nearly corresponds to superacidity of $H_o \leqq -12$, the present catalysts would be solid superacids.

Activities of the catalysts were also compared with that of WO_3/ZrO_2 (800 °C) with an acid strength of $H_o \leqq -14.52$,[4,5)] estimated using the Hammett indicators; the latter catalyst was prepared following the literature, the results being shown in Tables 1 and 2. Even though acid strength of the present catalysts was not determined by the visual color change method using the Hammett indicators, the highest strength can be estimated to be $H_o = -13$—-14, ca. -13, and -13—-12 for WO_3/SnO_2 (1000 °C), WO_3/TiO_2 (700 °C), and WO_3/Fe_2O_3 (700 °C), respectively, judging from the relative activity of the catalysts together with SiO_2–Al_2O_3 and WO_3/ZrO_2 (800 °C) for both reactions and from comparison with the catalytic activities of other superacids.[2—5)]

Superacid sites were not created by impregnation of the tungstate on the crystallized oxides, but on the amorphous form followed by calcination to the crystallization. Namely, the catalysts prepared by calcining $Sn(OH)_4$ at 1000 °C and H_4TiO_4 and $Fe(OH)_3$ at 700 °C to the crystallization, impregnating each with the tungstate and finally calcining at the same temperature were not active at all for the skeletal isomerization and cracking of isopentane (under 1/10 in activity for the dehydration of ethanol). The same

Table 2. Activities of the Catalysts for the Skeletal Isomerization and Cracking of Isopentane at 250 °C

Catalyst	Conversion	Products/%$^{a)}$						Quantity
	%	$CO+CO_2$	C_3	i-C_4	C_4	C_5	C_6+C_7	of W/wt%
WO_3/SnO_2 (800°C)	3.8	2.4	T$^{b)}$	0.8		0.6		
(900°)	3.1	0.3	0.1	1.0	T	1.7	T	
(1000°C)	9.4		0.2	5.3	0.1	3.0	0.8	13.2
(1100°C)	3.7		T	1.6	T	2.0	0.1	
(1200°C)	1.2			0.2		1.0		12.1
WO_3/TiO_2 (700°C)	5.9		0.1	2.0	T	3.2	0.6	11.3
WO_3/Fe_2O_3 (700°C)	4.4	3.8		T		0.6		13.4
SiO_2–Al_2O_3 (500°C)	0							
WO_3/ZrO_2 (800°C)	19.0		1.5	10.1	0.7	3.7	3.0	

a) The 3rd pulse values. b) Trace.

phenomenon was also observed with the WO_3/ZrO_2 superacid.[4,5] The relation between the precalcination temperature of $Zr(OH)_4$ before the impregnation and the catalytic activities, together with XRD analyses, showed that superacid sites could be created by impregnation on the amorphous form followed by calcination to the crystallization.[4]

X-Ray diffraction measurement of the catalysts was performed; the spectra are shown in Fig. 1. XRD pattern of the material prepared from the crystallized oxide, whose superacidity was not observed, was completely different from that prepared from the hydroxide. The former of WO_3/SnO_2 showed the degree of crystallization to be much higher than that of the latter. The crystallographic phase transformation of TiO_2 is known to be from an anatase form to a rutile one by calcination. The pattern of WO_3/TiO_2 with superacidity was anatase system, while that of the catalyst prepared from the crystallized oxide was rutile one. Thus, it is seen that the crystallization or the phase transformation of anatase to rutile form is quite low in degree when prepared from the amorphous form of TiO_2. Similarly in the case of the WO_3/ZrO_2 superacid, XRD analysis of the catalyst showed that tungsten oxide combines with zirconium oxide to create superacid sites at the time when a tetragonal system is formed;[4] the crystallographic phase transformation of ZrO_2 is from a tetragonal form to monoclinic one by calcination. The degree of crystallization of the WO_3/Fe_2O_3 superacid was also lower than that of the catalyst prepared from the crystallized iron oxide, the pattern of Fe_2O_3 being α-Fe_2O_3. Strong peaks of the crystallized WO_3 are observed at degrees below 25°.[4] The remarkable spectra of crystallized WO_3 can be seen for the catalysts without superacidity, prepared from the crystallized oxides, WO_3 being formed in the state of crystallized aggregation, while the catalysts with superacidity are not. Thus, WO_3 is highly dispersed into the supports in the case of the latter.

Specific surface areas of the catalysts were much larger than those of the oxides without impregnation of the tungstate.[9] Experiments using XPS showed the catalysts to be WO_3 supported on SnO_2, TiO_2, and Fe_2O_3.[9]

To the best of our knowledge this is the first synthesis of solid superacid which is prepared by calcination at temperatures above 1000 °C, whose temperature is in the range of calcination to prepare stable materials, ceramics. It is also concluded that solid superacids can be synthesized by supporting WO_3 as well as SO_4 on oxides of Zr, Sn, Ti, and Fe.

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