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Selective Conversion of 4-Isopropenyl-1-methylcyclohex-1-ene to 4-Isopropylidenyl-1-methylcyclohex-1-ene over SO_4^{2-}/ZrO_2

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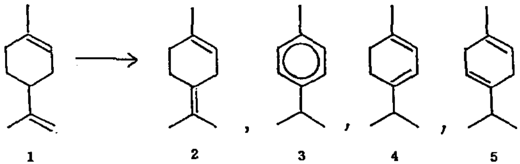
Isomerization of limonene **1** was carried out over various metal oxides and a metal phosphate at 60°C and a normal pressure to identify catalysts over which terpinolene **2** is preferentially formed. It has been found that strong acid catalysts such as SO_4^{2-}/ZrO_2 and SiO_2–Al_2O_3 are active and of these SO_4^{2-}/ZrO_2 is capable of catalyzing the reaction selectively. The SO_4^{2-} promotion of SiO_2–Al_2O_3 brought about the depression of the activity of bare SiO_2–Al_2O_3. These results suggest that both Brønsted and Lewis acid sites are active sites. Selectivity to terpinolene **2** is better on the strong Lewis sites. However, SO_4^{2-}/Fe_2O_3, a strong Lewis solid acid, was inactive for the reaction, suggesting that isomerization of limonene **1** to terpinolene **2** is not dominated only by the strong Lewis acidity. Effects of SO_4^{2-} promotion to ZrO_2 and Fe_2O_3 are discussed.

4-Isopropylidenyl-1-methylcyclohex-1-ene **2** (terpinolene), a beneficial compound as an intermediate material for herbicide, can be synthesized by isomerization of 4-isopropenyl-1-methylcyclohex-1-ene **1** (limonene) catalyzed by acids in the homogeneous system. A liquid SO_2 and organic acids are used as a catalyst in homogeneous systems (*1*). However, severe reaction conditions are required to catalyze the reaction selectively: a high pressure for the liquid SO_2 and a high temperature for organic acids. The reaction involving transfer of the C=C double bond proceeds accompanied by the formation of 4-isopropyl-1-methylbenzene **3** (*p*-cymene), 4-isopropyl-1-methylcyclohexa-1,3-diene **4** (α-terpinen), and 4-isopropyl-1-methylcyclohexa-1,4-diene **5** (γ-terpinen), resulting in low selectivity to **2** even at a low level conversion of **1**.



1 **2** **3** **4** **5**

In the present work, we carried out the reaction over various acid, base, and acid–base catalysts to find a highly selective catalyst effective under mild conditions. We wish to report here that zirconium oxide treated with SO_4^{2-} ions (*2*) is capable of catalyzing the reaction selectively at a relatively low temperature and a normal pressure.

EXPERIMENTAL

Solid metal oxides used as catalysts were MgO (Merck), Al_2O_3 (JRC-ALO2, reference catalyst supplied from Catalysis Society Japan), ZrO_2 prepared by hydrolysis of $ZrO(NO_3)_2$, TiO_2–ZrO_2 prepared by coprecipitation from $ZrOCl_2$ and $TiCl_4$ solution by addition of NH_4OH solution (final pH 10), $AlPO_4$ (*3*), $Nb_2O_5 \cdot nH_2O$ (CBMM), SiO_2–Al_2O_3 (JRC-SAH1), SO_4^{2-}/ZrO_2 (*2*), SO_4^{2-}/Fe_2O_3 (*4*), and SO_4^{2-}/SiO_2–Al_2O_3 prepared in the same way as SO_4^{2-}/ZrO_2. The catalyst samples were activated by evacuation at various temperatures before each run, as given in Table 1. The powdered catalyst was placed in a quartz reactor maintained at 333 K without exposure to air and 3.0 ml of **1** was added under atmospheric

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TABLE 1

Activity of Various Metal Oxides for Conversion of **1**[a]

Catalysts	Activation[b] (K)	Conversion[c] (%)	Selectivity[d] (%)			
			2	**3**	**4**	**5**
MgO	1073	0.0	—			
ZrO_2	803	0.0	—			
Al_2O_3	773	0.0	—			
$AlPO_4$	973	0.0	—			
TiO_2–ZrO_2	823	0.0	—			
$Nb_2O_5 \cdot nH_2O$	373	0.0	—			
SiO_2–Al_2O_3[e]	773	17.2	59.0	4.6	12.9	17.1
SiO_2–Al_2O_3	773	87.7	30.0	7.9	22.1	20.7
SO_4^{2-}/ZrO_2	903	20.4	83.9	0.2	8.9	8.4
SO_4^{2-}/ZrO_2[f]	903	51.8	69.3	0.2	15.8	11.0
SO_4^{2-}/SiO_2–Al_2O_3	773	5.4	45.6	13.4	13.1	14.2
96% H_2SO_4[g]	—	27.0	33.3	1.1	23.0	31.6
SO_4^{2-}/Fe_2O_3	643–943	0.0	—			

[a] **1**, 3.0 ml; catalyst amount, 200 mg; reaction temperature, 333 K; reaction time, 1 h.
[b] Activation temperature of catalyst.
[c] Conversion of **1** based on initial amount of **1**.
[d] Selectivity to **2**, **3**, **4**, and **5**.
[e] This run was carried out at 323 K.
[f] The reaction time was 3 h.
[g] 0.4 ml of 96% sulfuric acid was added to 3 ml of **1**.

dried oxygen-free nitrogen. During a reaction, the reaction mixture was continually stirred. A small portion of the reaction mixture was periodically withdrawn and filtered for analysis by GLC.

RESULTS AND DISCUSSION

Isomerization of Limonene over Various Catalysts

Table 1 summarizes the results of the reaction over various catalysts. A base catalyst (MgO), acid–base catalysts (ZrO_2, Al_2O_3, and TiO_2–ZrO_2), and relatively weak acid catalysts ($AlPO_4$ and $Nb_2O_5 \cdot nH_2O$) were completely inactive although MgO and ZrO_2 have been reported previously to convert **1** at 273 K in a pulse reaction (*5*). On the other hand, strong acids such as SO_4^{2-}/ZrO_2 and SiO_2–Al_2O_3 showed fairly high activities. It should be noted that SO_4^{2-}/ZrO_2 exhibited much higher selectivity than SiO_2–Al_2O_3.

The selectivities to **2** are plotted against conversion for SO_4^{2-}/ZrO_2 in Fig. 1. The data were obtained by changing the reaction temperature and activation temperature of the catalyst. A good correlation between the selectivity and the conversion

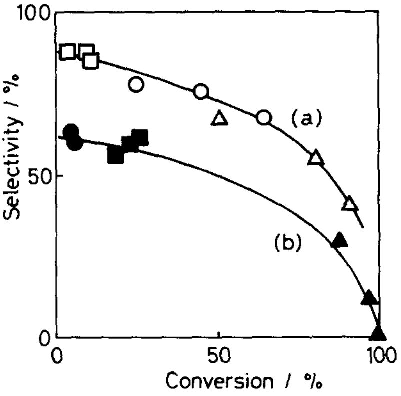


FIG. 1. Plots of conversions of **1** vs selectivities to **2** over (a) SO_4^{2-}/ZrO_2 pretreated at 743 K (△), 903 K (○), and 973 K (□), and (b) SiO_2-Al_2O_3 pretreated at 773 K carried out at 313 K (●), 323 K (■), and 333 K (▲).

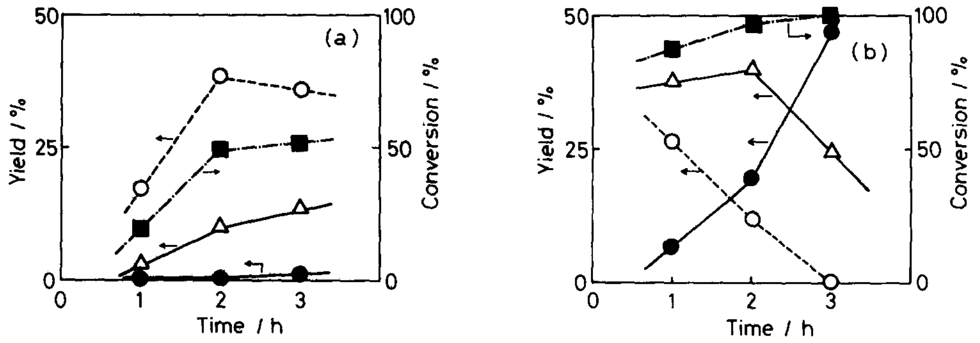
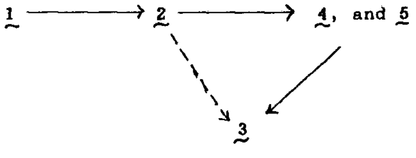


FIG. 2. Time courses of the product distribution and conversion of reaction of **1** over (a) SO_4^{2-}/ZrO_2 pretreated at 903 K and (b) SiO_2–Al_2O_3 pretreated at 773 K. (■) Conversion of **1**; (○) **2**; (●) **3**; (△) **4** and **5**. Both reactions were carried out at 333 K.

was obtained regardless of the differences in the reaction temperature and pretreatment temperature. At all conversions, SO_4^{2-}/ZrO_2 gave higher selectivities than SiO_2–Al_2O_3.

Figure 2a shows a time course of the reaction on SO_4^{2-}/ZrO_2 carried out at 333 K. With increasing conversion of **1**, the yield of **2** increased and then decreased accompanied by the production of **3**, **4**, and **5**. The increment of the yields of **4** and **5** reduced with reaction time while the increment of the yield of **3** slightly increased. On SiO_2–Al_2O_3, **1** was converted faster than on SO_4^{2-}/ZrO_2 as shown in Fig. 2b and the conversion became nearly constant after 1 h. By contrast, the yield of **2** monotonously decreased with reaction time after 1 h and the yield of **4** and **5** increased and then decreased. The increment of the yield **3** corresponds to the change of the sum of the yields of **2**, and **4** and **5**. These results suggest that the reaction proceeds through the intermediate **2** to the dehydrogenated compound **3**, presumably through mentadienes **4** and **5** as presented in previous work (*5*). Thus the difference in the selectivity between SO_4^{2-}/ZrO_2 and SiO_2–Al_2O_3 is considered to be related to the stability of **2** over the catalysts. It is supposed that the adsorbed species **2** on SiO_2–Al_2O_3 undergoes isomerization to **4** and **5** and dehydrogenation to **3** faster than those on SO_4^{2-}/ZrO_2. As the active sites on SO_4^{2-}/ZrO_2, either the sulfate ions or Lewis acid sites generated on ZrO_2 by interaction with SO_4^{2-} are possible. To examine the possibility of sulfate ions alone being active sites, we carried out the reactions catalyzed by sulfuric acid and SO_4^{2-}-modified SiO_2–Al_2O_3. The results are shown in Table 1. Both homogeneous and heterogeneous reactions gave lower selectivities than those over SO_4^{2-}/ZrO_2. In particular, the selectivity and the activity of SO_4^{2-}/SiO_2–Al_2O_3 were lower than those of SiO_2–Al_2O_3, suggesting that loaded sulfate ions block the Brønsted acid sites of SiO_2–Al_2O_3, which are recognized as the active sites. These results also suggest that active sites other than sulfate ions play a significant role, e.g., strong Lewis acid sites generated by interaction between ZrO_2 and SO_4^{2-} (*6*). It has been proposed that like SO_4^{2-}/ZrO_2, strong Lewis acid sites can be generated on iron oxide when $Fe(OH)_3$ is treated with SO_4^{2-} ions, followed by calcination (*7, 8*). Since the generation mechanism of the strong acid sites of SO_4^{2-}/



SCHEME 1

Fe_2O_3 is explained in the same way as that for SO_4^{2-}/ZrO_2 (*6*) and its acid strength is thought to be higher than SiO_2–Al_2O_3 (*8*), considerable activity and selectivity for SO_4^{2-}/Fe_2O_3 is expected. However, thus prepared SO_4^{2-}/Fe_2O_3 was completely inactive for the activation at temperatures ranging from 643 to 943 K as given in Table 1.

SO_4^{2-}-Promoted Metal Oxides

Acid strength of SO_4^{2-}/Fe_2O_3 has not been evaluated directly to our knowledge; the dark color of SO_4^{2-}/Fe_2O_3 prevents the determination of its Hammett function by color indicator methods (*9*). However, to try to evaluate the acidity of SO_4^{2-}/Fe_2O_3, we have summarized in Table 2 the earlier results, reported by Hino (*10*), of acid-catalyzed reactions over related catalysts. Acid strength for SO_4^{2-}/Fe_2O_3 is slightly weaker than that for SO_4^{2-}/ZrO_2 ($H_0 < -16.04$) (*11*) but somewhat stronger than that for SiO_2–Al_2O_3 ($-12.7 < H_0 < -11.35$) (*8*). The results suggest that the acid strength of SO_4^{2-}/Fe_2O_3 is presumably within the range of $-12.7 < H_0 < -16.04$ and that the activity for the present reaction is dependent on factors in addition to the acid strength of the catalyst. A similar effect of sulfate-promotion has been reported by Itoh and Tada (*12*). They found that sulfate-promotion to $AlPO_4$ does not cause an increase in acid strength but influences its catalytic activity and selectivity for 1-butanol dehydration.

TABLE 2

Summary of Acid-Catalyzed Reactions over the Related Catalysts[a]

Reaction	Conversion		
	SO_4^{2-}/Fe_2O_3	SO_4^{2-}/ZrO_2	SiO_2–Al_2O_3
n-Butane isomerization[b]	18[c]	30.5[d]	0.0
Dehydration of ethanol[e]	40–59	78–82	12.0

[a] Taken from Ref. *10*.

[b] Carried out in closed circulating system at 298 K. Catalyst amount, 1.0 g. Initial amount of *n*-butane, 0.35 mmol.

[c] 20 h.

[d] 24 h.

[e] Carried out with a pulse reactor at 343 K. Catalyst amount, 30 mg. Pulse size, 0.4 μl.

Active sites for both the sulfate-promoted metal oxide catalysts are thought to be Lewis acid sites, the acidity of which is enhanced by strong electron transfer to sulfate ion(s). Isomerization of olefin like the present reaction is initiated by abstraction of an allylic hydrogen as hydride by Lewis acid sites. In such cases, it is probable that a bulky olefin molecule is adsorbed and stabilized by interactions with plural sites of the catalyst surface (*13*). Thus, the surface structure of the catalyst should have an effect on the reactivity of the olefin isomerization.

It is often the case that a zirconium ion is surrounded by seven to eight oxygens in the bulk oxide and the Zr–O bondlength is longer than the length between 3*d* metal and oxygen atoms. SO_4^{2-}-promoted ZrO_2 has a tetragonal ZrO_2 phase while unpromoted ZrO_2 has a monoclinic one (*14*). In a tetragonal phase of zirconium oxide, the Zr–O bond lengths are reported to be 2.07 and 2.46 Å (*15*) while SO_4^{2-}/Fe_2O_3 has an α-Fe_2O_3 phase in which Fe–O bond lengths are 1.99 and 2.06 Å (*16*). The difference in bond lengths for each oxide is expected to appear for each surface structure. In addition, it has been found by means of TPD methods using carbon dioxide that weak basic sites are also present on SO_4^{2-}/ZrO_2 (*17*) but not at all on SO_4^{2-}/Fe_2O_3. This is an unexpected result because there exists one SO_4^{2-} ion per 15–30 Å^2 on the surfaces for both of the metal oxides and this is almost the same level of population of surface metal cations. At such a high population of sulfate, most of the surface oxygen anions can "see" and "feel" sulfate ions through neighboring zirconium cations. Therefore, weak basic sites are possibly located at the sites adjacent to strong Lewis acid sites generated by coordination of sulfate ions. In catalysis by solid acid and/or base, the importance of the concept of acid–base bifunctionality has been emphasized (*18*); not only the acid and base strength but also the orientation of acid and base are important. The high selectivity observed for SO_4^{2-}/ZrO_2 may be attributed to the stabilization of surface intermediate on strong acid and base sites, although at present we have no evidence that the reactant molecule interacts with the base site.

Therefore, the high activity and selectivity observed for SO_4^{2-}/ZrO_2 can be due to the particular nature of SO_4^{2-}/ZrO_2 deficient to other SO_4^{2-}-promoted superacids: strong Lewis acidity, high coordination number of zirconium cations, long Zr–O bonds, and the presence of base sites adjacent to acid sites.

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