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CATALYTIC ACTIVITY OF TiO_2 TREATED WITH HEXAFLUOROACETONE IN THE ISOMERIZATION OF 1-BUTENE

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The catalytic activity of TiO_2 is markedly enhanced by treatment with hexafluoroacetone. The IR spectrum of pyridine adsorbed on treated TiO_2 and the selectivity of 2-butene indicate that the active sites are Brönsted acid formed by the interaction between hexafluoroacetone and the TiO_2 surface.

Hexafluoroacetone (HFA) is known to have remarkable electrophilic properties,[1,2) and to be easily adsorbed on rutile[3) and alumina.[4) However, no study has been made yet on the catalytic activity of a metal oxide treated with HFA.

In this communication, we wish to report our results concerning the catalytic activity of TiO_2 in the double bond isomerization of 1-butene. A marked enhancement of activity was observed after treatment with HFA. The active sites were elucidated to be Brönsted acid sites which were formed by the interaction of HFA with surface OH groups. The catalytic activities of other metal oxides treated with HFA were also investigated for comparison with TiO_2.

The TiO_2 was prepared by the hydrolysis of titanium tetraisopropoxide (Wako Chemical Co.) at room temperature, followed by washing, drying and calcination at a high temperature (500°C) for 3 h. The MgO and ZrO_2 were prepared by calcination of $Mg(OH)_2$ (G.R., Kanto Chemical Co.) and $Zr(OH)_4$ (pure reagent, Daiichikigenso Co.), respectively. The SiO_2 was prepared from colloidal silica, "SNOW TEX" (Nissan Chemical Co.). The Al_2O_3 was prepared by the hydrolysis of $Al(NO_3)_3$ (G.R., Wako Chemical Co.) with a 28 % ammonia solution, followed by washing, drying and calcination at 500°C for 3 h. The SiO_2-Al_2O_3 used as a standard Brönsted acid was N-631 (Al_2O_3 15 wt %) supplied by Nikki Chemical Co., while HFA was supplied by Allied Chemical Co. Gas chromatography showed no detectable amounts of impurities in the HFA reagent. The treatment with HFA was performed by contact with HFA vapor at 200°C for 1 h in a circulation system having a volume of 0.43 l. The initial pressure of HFA was adjusted to 200 torr in the treatment. In order to avoid the effects of moisture, the isomerization reactions were carried out in the same circulation system just after treatment with HFA and/or evacuation of the metal oxides.

The results obtained for the isomerization reactions over various metal oxides before and after treatment with HFA are shown in Table 1. The selectivity, i.e., the ratio of cis-2-butene to trans-2-butene was determined by extrapolation to zero conversion of the reaction. For reference, the adsorbed amount of HFA, which was measured by use of a gravimetric method, and the decrease in the pressure of butene (possibly due to polymerization) are also tabulated. While the metal oxides by themselves are also inactive as catalysts for the isomerization under the conditions used, the catalytic activities are enhanced by the treatment with HFA. The order of the catalytic activity for the treated metal oxide is

$$TiO_2 > ZrO_2 > Al_2O_3 > SiO_2 \approx MgO$$

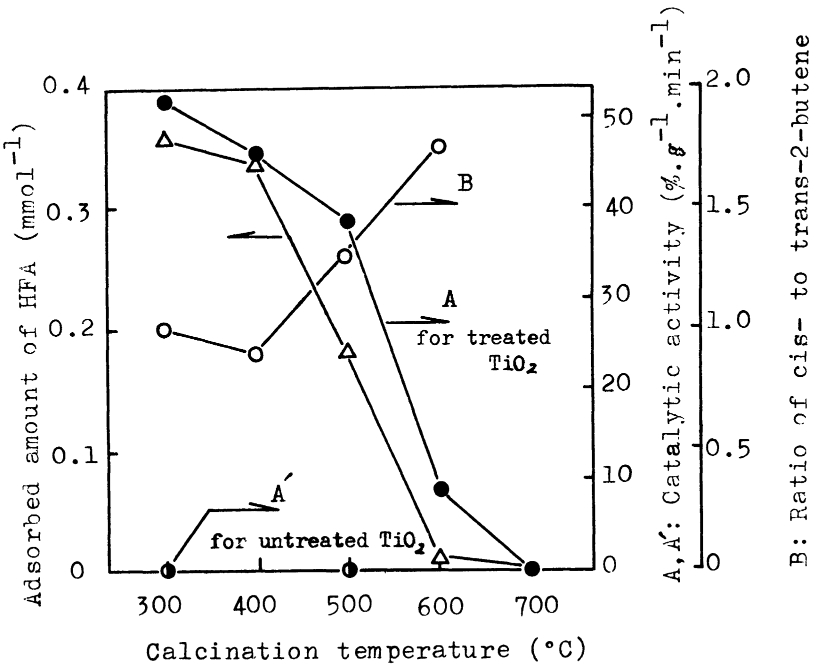
Except for SiO_2, this order almost coincides with that of the electronegativity of the metal ion.

Table 1 Catalytic activities and selectivities [a)]
(Reaction temperature : 100°C ; Initial pressure of butene : 110 torr)

Catalyst[b)]	Activity (% $g^{-1}min^{-1}$)	Selectivity (cis/trans ratio)	Decrease in butene pressure[c)] (torr g^{-1})	Adsorbed amount of HFA (mmol g^{-1})
TiO_2	0.3	3	0	—
TiO_2-HFA	85.5	1	40.5	0.18
ZrO_2	0	–	0	—
ZrO_2-HFA	22.7	1	12.5	0.33
Al_2O_3	0	–	0	—
Al_2O_3-HFA	1.1	2	0	0.46
MgO	0	–	0	—
MgO-HFA	0	–	0	0.21
SiO_2	0	–	0	—
SiO_2-HFA	0	–	0	—
SiO_2-Al_2O_3	107.5	1	31.5	—

a) The data were taken 2 min after the begining of the reaction.
b) Metal oxide-HFA denotes the metal oxide treated with HFA.
c) The decrease in butene pressure was observed for the first 1 h.

In parallel with the adsorbed amount of HFA, the catalytic activity of treated TiO_2 decreased with an increase in the heat treatment temperature of TiO_2 (Fig. 1). It has been shown that the number of surface OH groups on TiO_2 is gradually reduced in accordance with a rise in treatment temperature.[5)] Therefore, the formation of active sites on TiO_2 treated with HFA might be due to the interaction of HFA with surface OH groups. The IR spectra of TiO_2 treated with HFA were recorded in order to study the surface structure. The behavior of the surface OH groups could not be examined because of the low transmittance in the range of 4000 – 3000 cm^{-1}. However, the absorption bands at about 1600 and 1480 cm^{-1} may be assigned to C-O stretching vibrations, and the bands at 1250 – 1150 cm^{-1} may be assigned to CF_3 groups[3)] (Fig. 2). These bands, due to C-O and C-F bands, remained after heat treatment at 200°C under reduced pressure. On the other hand, the band at about 1800 cm^{-1} due to C=O



(reaction temp.: 50°C)

Fig. 1 Effect of calcination temperature of TiO_2

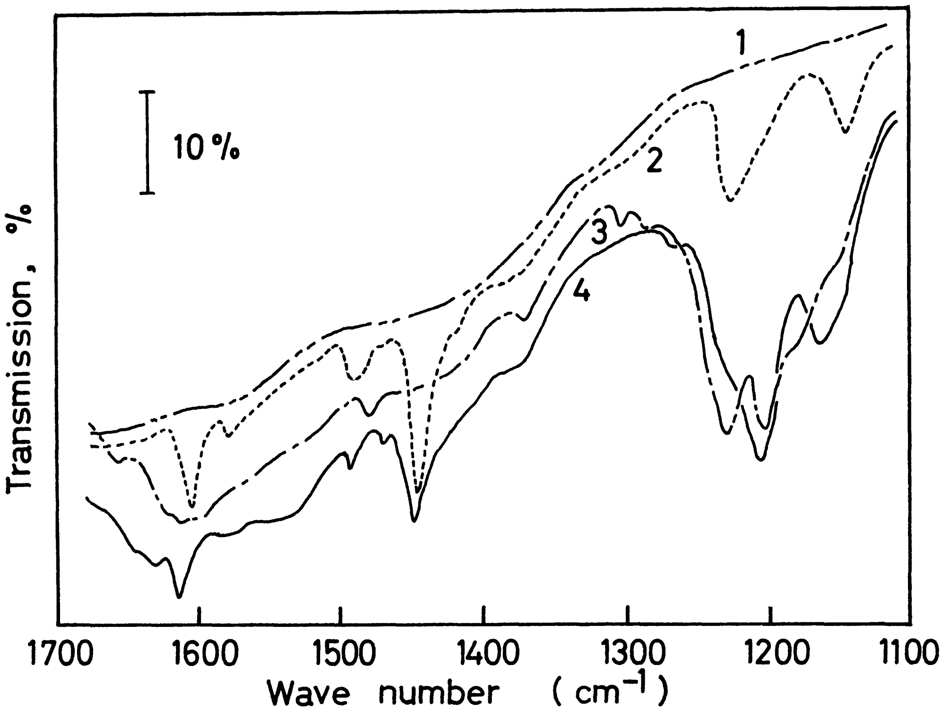


Fig. 2 IR spectra of pyridine and HFA on TiO_2 calcined at 400°C

(1) : Background (TiO_2 evacuated for 3 h at 200°C)

(2) : TiO_2(shown in (1)) treated with 8 torr of pyridine for 5 min at RT, then evacuated for 30 min at 200°C

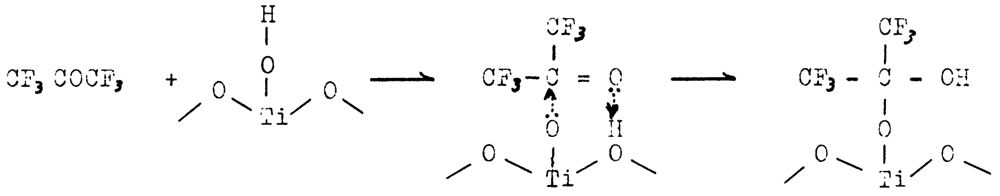
(3) : TiO_2(shown in (1)) treated with 200 torr of HFA for 1 h at 200°C, then evacuated for 30 min at 200°C

(4) : TiO_2(shown in (3)) retreated with 8 torr of pyridine for 5 min, then evacuated for 30 min at 200°C

stretching vibrations of HFA was not observed at all even when the sample was kept *in vacuo* at room temperature. These results suggest that HFA molecules attach to the surface not by physical adsorption, but by chemical bonds.

The titration with butylamine showed that there was a pronounced increase in the surface acidity due to the treatment with HFA. To determine whether the acid sites formed are Brönsted or Lewis type, the IR absorption spectra of pyridine adsorbed on treated TiO_2 were compared with that of untreated TiO_2. As also shown in Fig. 2, a weak band at 1540 cm^{-1} (assigned to the pyridinium ion) can be detected along with a band at about 1450 cm^{-1} (coordinated pyridine). Since there were only bands related to Lewis acids in the case when pyridine was adsorbed on untreated TiO_2, it is evident that the treatment with HFA causes the formation of Brönsted acid sites.

The formation of Brönsted acid sites is supported by the fact that the selectivity shown in Table 1 nearly equals 1, a value which is indicative of the participation of Bronsted acid sites.[6] The acid site may be formed on the TiO_2 surface through a reaction such as



The large electronegativity of the Ti^{4+} ion might promote the polarization of surface OH groups, and thus accelerate the reaction between HFA and surface OH groups. The polarization of the O-H bond of the surface compound may be promoted by the pronounced electroinductive effect of two CF_3 groups which attach to the same carbon atom. Thus, fairly strong Brönsted acid sites capable of promotion of the isomerization of 1-butene, even at rather low temperatures, may be formed.

References

1) C.G.Krespan and W.J.Middleton, Fluorine Chemistry Reviews, Vol.1, ed. by P.Tarrant, Marcel Decker, New York, 1967, p.145.

2) N.P.Gambaryan, E.M.Rokhlin, Yu V.Zeifman, C.Ching-Yun and I.L.Knynyants, Angew. Chem. Intern. Edit. 5, 947(1966)

3) D.M.Griffiths and C.H.Rochester, J. Chem. Soc. Farad. Inst. 1977, 1913.

4) F.P.Shirley and W.H.Wade, J. Colloid. Interface Sci. 38, 205(1972).

5) S.Okazaki and T.Kanto, Nippon Kagaku Kaishi, 1976, 404.

6) K.Tanabe, "Shokubai no hataraki," Kagakudozin, 1974, p.21.

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