CHEMISTRY LETTERS, pp. 57-60, 1979. Published by the Chemical Society of Japan

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

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The catalytic activity of TiO_2 is markedly enhanced by the treatment with hexafluoropropylene oxide. The IR spectrum indicates that the adsorbed state of hexafluoropropylene oxide on TiO_2 coincides with that of hexafluoroacetone on TiO_2. The isomerization of hexafluoropropylene oxide to hexafluoroacetone is elucidated to be remarkably catalyzed by TiO_2.

Previously, we reported that the catalytic activity of TiO_2 in the isomerization of 1-butene was pronouncedly enhanced by the pretreatment with hexafluoroacetone (HFA).[1] Hexafluoropropylene oxide (HFPO), one of the isomers of HFA, is now industrially produced as a raw material of the excellent ion-exchanging membrane, commercially named as "NAFION".[2] It is expected that HFPO is more active than HFA in the reaction with surface OH groups owing to the unstable epoxy ring and to the positive carbon atom of the central CF group surrounded by electronegative CF_2 and CF_3 groups. However, no study on the reaction between HFPO and surface OH groups on metal oxides has been made.

In this communication, we wish to report the pronounced effect of the pretreatment with HFPO on the catalytic activity for the double bond isomerization of 1-butene. In the investigation concerning the activated state of TiO_2 surface, it was found that HFPO remarkably isomerized to HFA over TiO_2.

The metal oxides such as TiO_2, ZrO_2, Al_2O_3, SiO_2 and MgO were prepared according to the previously outlined procedure.[1] HFPO was kindly supplied by Daikin Kogyo Co., and was used without further purification. A gas chromatographic analysis showed no detectable amount of impurities in this reagent. The treatment of metal oxides with HFPO was performed by contacting with 200 torr of HFPO vapor at 100°C for 1 h and evacuating at 100°C for 0.5 h in a circulation system having a volume of 0.43 l. Since the isomerization reactions were carried out in the same circulation system just after the treatment with HFPO and/or evacuation of the metal oxides, the effect of moisture on the active sites of the treated metal oxides may be ignored. In the treatment of TiO_2 surface, the initial pressure was adjusted to 110 torr, and the reaction was carried out at 50°C or 100°C. In the isomerization of HFPO to HFA, the initial pressure was adjusted to 200 torr, and the reaction was carried out at 100°C for 1 h. The amounts of HFPO and HFA were determined with the intensities of the IR absorption bands assigned to CF_3 group at 1340 cm^{-1} (for HFPO) and 1367 cm^{-1} (for HFA).[3]

Table 1 shows the results obtained for the isomerization of 1-butene over

Table 1 Catalytic activities for isomerizations of 1-butene and HFPO

Catalyst *	Isomerization of 1-butene Activity(% $g^{-1}min^{-1}$)	Isomerization of 1-butene Selectivity(cis/trans)	Isomerization of HFPO Activity (% $g^{-1}min^{-1}$)
TiO_2	0.3	3	38.3 *** 24.0
TiO_2-HFPO	35.5 ** 60.8	1.3 ** 0.9	
ZrO_2	0	-	2.5
ZrO_2-HFPO	0	-	
Al_2O_3	0	-	5.2
Al_2O_3-HFPO	0.1	-	
MgO	0	-	
MgO-HFPO	0.1	-	
SiO_2	0	-	
SiO_2-HFPO	0	-	

* Metal oxide-HFPO denotes the metal oxide treated with HFPO.

** The isomerization was carried out at 50°C. (Other reactions were carried out at 100 °C.)

*** TiO_2 was heat-treated at 300°C before the use as a catalyst for this run. Metal oxides were heat-treated at 500°C for other runs.)

various metal oxides before and after the treatment with HFPO. The ratio of cis-2-butene to trans-2-butene, which is generally accepted as a measure of the surface acidity,[4)] was determined by extrapolating the data to zero conversion of the reaction. As shown in Table 1, the oxides are inactive as catalysts for the isomerization of 1-butene. However, the catalytic activity of TiO_2 is markedly enhanced by treatment with HFPO. The ratio of cis- to trans isomer nearly equals 1, a value which is indicative of the participation of Brönsted acid sites. The effect of the temperature of the treatment with HFPO on the catalytic activities of TiO_2 was examined (Fig. 1). In addition, the effect of the temperature for the treatment with HFA was examined for a comparison. A marked enhancement of activity was observed after a treatment with HFPO even at low temperature such as 50°C. The optimum temperature of the treatment with HFPO is lower than that with HFA by about 100°C. The lowering of the effective treatment temperature suggests that HFPO is more active in the reaction with surface OH groups. In order to study the surface structure, the IR spectra of TiO_2 treated with HFPO were recorded (Fig. 2). The absorption bands at about 1600 and 1480 cm^{-1} may be due to C-O stretching vibration and the bands at 1250 - 1150 cm^{-1} may be assigned to CF_3 groups.[3)] The band at about 1550 cm^{-1} may be

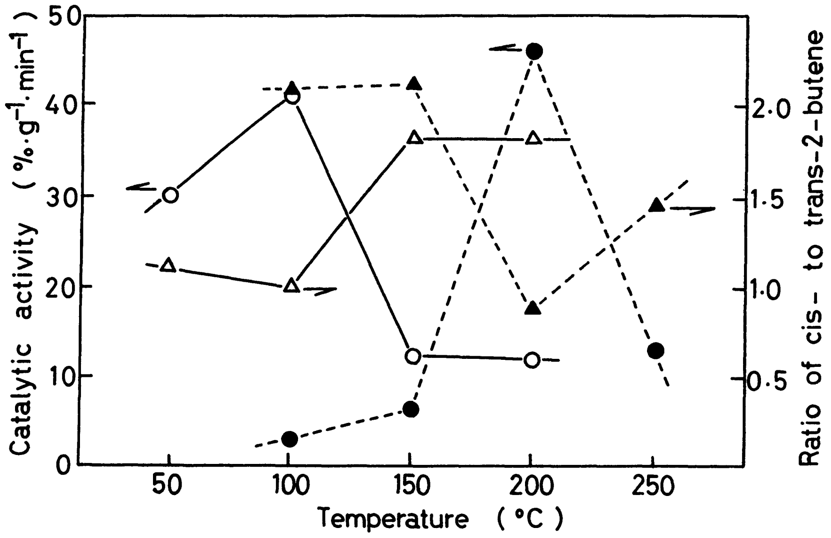


Fig. 1 Effects of treatment temperature on catalytic activity

○ , △ : HFPO, ● , ▲ : HFA

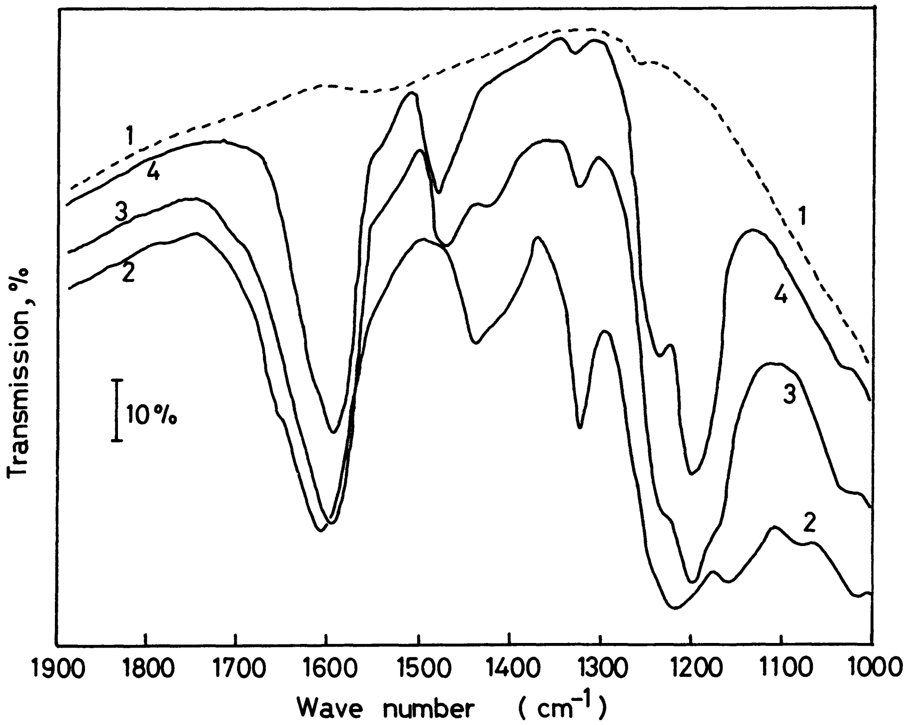


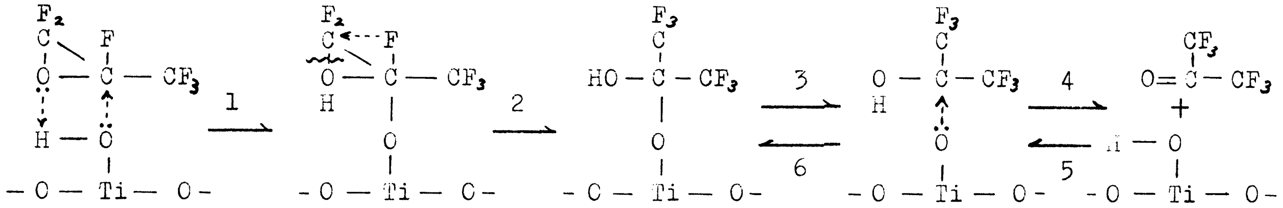
Fig. 2 IR spectra of HFPO adsorbed on TiO_2 at various temperatures.

1 : Background (TiO_2 heat-treated at 400°C, followed by evacuation at 200°C for 2 h)

2 : 50°C , 3 : 100°C , 4 : 150°C

attributed to epoxy ring in HFPO because the band is not found in the spectra of the similar compounds consisted of C, O and F atoms such as HFA, C_2F_5COF, CF_3OCF_3 and $C_2F_5OC_2F_5$.[5)] This band is scarcely observed in the spectra of TiO_2 treated with HFPO.

In general, the TiO_2 treated with HFPO gives spectra similar to that of the oxide treated with HFA, i.e., both spectra coincide with each other except the band at about 1340 cm^{-1} assigned to CF_3 groups of HFPO. This suggests that the structure of HFPO attached to TiO_2 is almost the same as that of HFA on TiO_2, and hence the interaction between HFPO and surface OH groups is considered to proceed through the pathways 1 and 2 in the following scheme.



In order to confirm the reaction scheme, the TiO_2 treated with HFPO at 50°C was evacuated at 100°C in the circulation system, and the evolved gas was analyzed. It was found that the gas is entirely constituted of HFA. Thus, it became clear that the surface product decomposed mainly through the pathways of 3 and 4. The route of decomposition is considered to be just in opposition to that of the interaction between HFA and surface OH groups,[1)] which is designated as 5→6. For further confirmation of the scheme, the isomerization of HFPO to HFA was carried out at 100°C, and it was assertained that the isomerization is markedly promoted by TiO_2 as shown in Table 1. It is highly probable that the isomerization proceeds through the route of 1 → 2 → 3 → 4, and the active compound which promotes the isomerization of 1-butene is the intermediate of the isomerization of HFPO to HFA.

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(Received October 27, 1978)