

CATALYTIC ACTIVITY OF ZrO_2 AND ThO_2 FOR H-D EXCHANGE REACTION BETWEEN METHYL GROUP OF ADSORBED ISOPROPYL ALCOHOL- d_8 AND SURFACE OH GROUP

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The H-D exchange reaction of methyl group of adsorbed isopropyl alcohol- d_8 with surface OH group was studied over several metal oxides by means of reflectance IR spectroscopy. Zirconium oxide and ThO_2 showed a significant catalytic activity for the exchange reaction, though SiO_2 , Al_2O_3 , TiO_2 , and $\text{SiO}_2\text{-Al}_2\text{O}_3$ were all inactive.

Zirconium oxide,¹⁾ ThO_2 ,²⁾ and rare earth metal oxides²⁾ are known as dehydration catalysts which show a specific selectivity for the formation of 1-olefin from 2-alkanol. Lundeen et al. suggested that a preferential interaction of terminal methyl group adjacent to the carbon attached to OH group of 2-alkanol with surface O^{2-} takes place over ThO_2 .²⁾

In order to characterize the nature of catalytic property of ZrO_2 and ThO_2 , the exchange reaction was studied over various metal oxide catalysts in the present work. For the purpose, diffuse reflectance IR spectroscopy was employed, since ThO_2 is hardly pervious to infrared.

Zirconium oxide and ThO_2 were prepared by calcining the hydroxides in air at 500°C for 6 hr, which were obtained from zirconium oxychloride (Wako Pure Chem. Ind., Ltd., GR) and thorium nitrate (Wako Pure Chem. Ind., Ltd., GR), respectively. Titanium oxide and SiO_2 prepared by hydrolysis of TiCl_4 (Wako Pure Chem. Ind., Ltd., EP) and ethyl orthosilicate (Wako Pure Chem. Ind., Ltd., GR), respectively, and activated Al_2O_3 (Kishida Chemical Co.) and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Nikki Chemical Co., N631L) were calcined in air at 500°C for 6 hr. Isopropyl alcohol- d_8 (99 % purity) purchased from Merck Co. was purified by repeating a freezing-thawing cycle and dried over a molecular sieve evacuated at 500°C after treatment with D_2O .

Infrared spectra were recorded with a JASCO-DS-701G spectrometer by using a reflection attachment. Samples were evacuated in a reflectance cell at 500°C for several hours before adsorption. Mass spectral analysis was carried out with a NEVA NAG-515 Mass filter.

Typical reflectance spectra of isopropyl alcohol- d_8 adsorbed on ZrO_2 are shown in Fig. 1. On ZrO_2 evacuated at 500°C, two bands of OH group were observed at 3740 and 3660 cm^{-1} . After admission of isopropyl alcohol- d_8 on the surface, those bands of surface OH group slightly decreased and the bands of OD group at 2750 and 2700 cm^{-1} appeared. A sharp band at 2230 cm^{-1} is due to C-D vibration band, while small bands at 2970 and 2940 cm^{-1} are due to C-H bands. After trapping of residual

alcohol by liquid nitrogen the intensity of the C-D band decreased, while that of the C-H bands formed by hydrogen exchange increased as seen in b)-e) of Fig. 1. By mass spectral analysis of gas phase, the formation of propylene was observed, but the rate of formation was very slow compared to the H-D exchange. The results for ThO_2 were almost the same as those for ZrO_2 .

On the other hand, the H-D exchange reaction did not take place over SiO_2 , Al_2O_3 , TiO_2 or $\text{SiO}_2\text{-Al}_2\text{O}_3$ which are known to form 2-olefins as major products in the dehydration of 2-alkanols.^{3,4)}

These results confirm the specific character of ZrO_2 and ThO_2 which activate methyl group of alcohols. Thus, these catalysts are capable of abstracting both OH^- and H^+ of terminal methyl group to form 1-olefins from 2-alkanols. Strongly acidic catalysts such as $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Al_2O_3 do not activate methyl group of alcohols, while strongly basic catalysts such as MgO , CaO , etc. cause the dehydrogenation of alcohols to form ketones.⁵⁾ It is suggested that ZrO_2 and ThO_2 have both moderately acidic and basic strength and would be used as potential acid-base bifunctional catalysts.

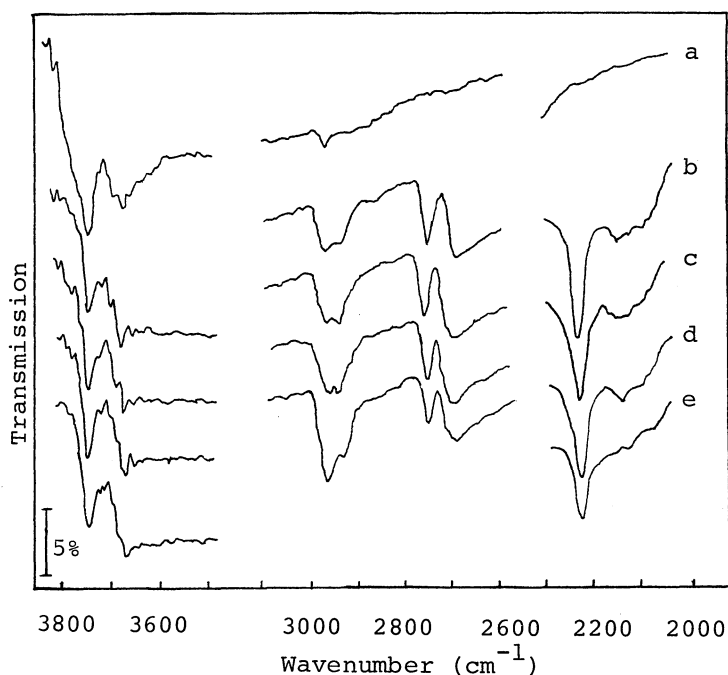


Fig. 1. IR spectral change of isopropyl alcohol- d_8 adsorbed on ZrO_2 evacuated at 500°C after removal of residual alcohol in gas phase.
a) before adsorption,
b) 3 min. after,
c) 14 min. after,
d) 30 min. after,
e) 15 hr. after.

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