MoO_3로 개질된 Zirconia에 담지된 V_2O_5 촉매의 분광학적인 연구

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Spectroscopic Study of V_2O_5 Supported on ZrO_2 and Modified with MoO_3

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INTRODUCTION

Vanadium oxides are widely used as catalysts in oxidation reactions, e.g., the oxidation of sulfur dioxide, carbon monoxide, and hydrocarbons[1]. Much research has been done to understand the nature of active sites, the surface structure of catalysts as well as the role played by the promoter of the supported catalysts, using infrared (IR), X-ray diffraction (XRD), electron spin resonance (E.S.R) and Raman spectroscopy[2]. This paper describes spectroscopic study of vanadium oxide supported on zirconia and modified with MoO_3. The characterization of the samples was performed by means of solid-state ^{51}V nuclear magnetic resonance(^{51}V NMR) and Fourier transform infrared (FTIR).

EXPERIMENTAL

Precipitate of $Zr(OH)_4$ was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride(Aldrich) at room temperature with stirring until the pH of mother liquor reached about 8. The catalysts containing various vanadium oxide content and modified with MoO_3 were prepared by adding $Zr(OH)_4$ powder into a mixed aqueous solution of ammonium metavanadate (NH_4VO_3) (Aldrich) and ammonium molybdate $[(NH_4)_6(Mo_7O_{24})(4H_2O)$ (Aldrich) followed by drying and calcining at high temperatures for 1.5 h. $3V_2O_5$-$15MoO_3/ZrO_2(773)$ indicated the catalyst containing 3 wt% V_2O_5 and 15 wt% MoO_3 calcined at 773 K. FTIR absorption spectra of V_2O_5-MoO_3/ZrO_2 powders were measured by KBr disk method over the range 1200-400 cm^{-1}. ^{51}V NMR spectra were measured by a Varian Unity Inova 300 spectrometer with a static magnetic field strength of 7.05 T.

RESULTS AND DISCUSSION

Fig. 1 shows IR spectra of V_2O_5-$15MoO_3/ZrO_2$ (773) catalysts with various V_2O_5 content calcined at 773 K for 1.5 h. Although with samples below 15 wt % of V_2O_5, definite peaks were not observed, the absorption bands at 1022 and 818 cm^{-1} appeared for $15V_2O_5$-$15MoO_3/ZrO_2$, $20V_2O_5$-$15MoO_3/ZrO_2$, $25V_2O_5$-$15MoO_3/ZrO_2$ and pure V_2O_5 containing high V_2O_5 content. The band at 1022 cm^{-1} was assigned to the V=O stretching vibration, while that at 818 cm^{-1} was attributable to the coupled vibration between V=O and to V-O-V. Generally, the IR band of V=O in crystalline V_2O_5 showed at 1020-1025 cm^{-1} and the Raman band at 995 cm^{-1}[3]. This observation suggests that vanadium oxide below 15 wt % is in a highly dispersed state.

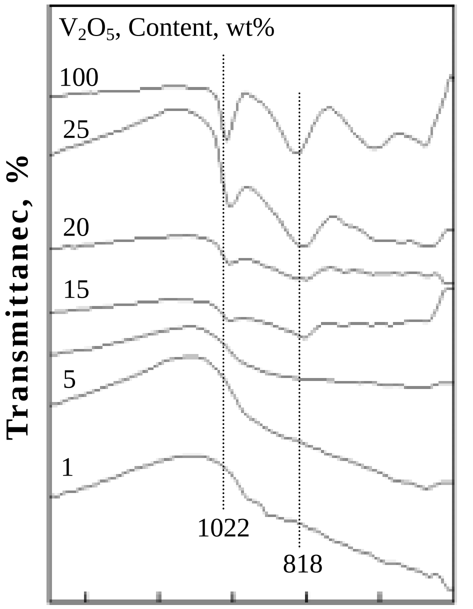

Fig. 1. Infrared spectra of V_2O_5-$15MoO_3/ZrO_2$ (773) catalysts with different V_2O_5 contents.

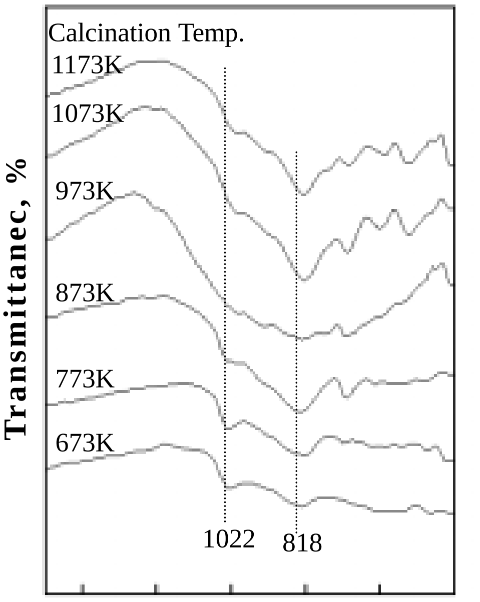

Fig. 2. Infrared spectra of $20V_2O_5$-$15MoO_3/ZrO_2$ catalysts calcined at different temperatures.

Fig. 2 shows IR spectra of $20V_2O_5$-$15MoO_3/ZrO_2$ catalysts calcined at 673-1173 K for 1.5h. Unlike $3V_2O_5$-$15MoO_3/ZrO_2$ and $10V_2O_5$-$5MoO_3/ZrO_2$ catalysts, for $25V_2O_5$-$15MoO_3/ZrO_2$ crystalline V_2O_5 appeared at a lower calcination temperature from 673 K to 873 K and consequently V=O stretching band was observed at 1022 cm^{-1}. This is because V_2O_5 loading exceeding the formation of monolayer on the surface of ZrO_2 is well crystallized. However, at 973 K all V_2O_5 reacted with ZrO_2 and changed into ZrV_2O_7 so that V=O stretching at 1022 cm^{-1} disappeared completely, as shown in Fig. 2.

The solid state ^{51}V NMR spectra of V_2O_5-MoO_3/ZrO_2 catalysts calcined at 773 K followed by exposing to air are shown in Fig. 3. There are three types of signals in the spectra of catalysts with varying intensities depending on V_2O_5 content. At low loadings up to 10 wt% V_2O_5 a shoulder at about –260 ppm and intense peak at -590 ~ -650 ppm are observed. The former is assigned to the surface vanadium-oxygen structures surrounded by a distorted octahedron of oxygen atoms, while the latter is attributed to the tetrahedral vanadium-oxygen structures[4,5].

Increasing the V_2O_5 content on the zirconia surface changes the shape of the spectrum to a rather intense and sharp peak at about –300 ppm and a broad low-intensity peak at about –1250 ppm, which are due to the crystalline V_2O_5 of square pyramid coordination[4]. These observations of crystalline V_2O_5 for samples containing high V_2O_5 content above or equal to 15 wt% are in good agreement with the results of the IR spectra in Fig. 1. Moreover, the increase in V_2O_5 content resulted in the appearance of an additional signal with a peak at –800 ppm. Different peak positions normally indicate the differences of the spectral parameters and are observed due to different local environments of vanadium nuclei[5]. Thus species at –590 ~ -650 ppm and –800 ppm can be attributed to two types of tetrahedral vanadium complexes with different oxygen environments.

The spectra of $20V_2O_5$-$15MoO_3$/ZrO_2 containing higher vanadium oxide content than monolayer loading and calcined at various temperatures are shown in Fig. 4. Unlike $3V_2O_5$-$15MoO_3$/ZrO_2 for $20V_2O_5$-$15MoO_3$/ZrO_2 calcined even at lower temperatures (773 K) a sharp peak due to crystalline V_2O_5 appeared at –300 ppm together with peaks at –800 ppm due to the tetrahedral surface species. However, for samples calcined at 873 K, in addition to a peak at –300 ppm due to crystalline V_2O_5, a sharp peak at –800 ppm due to ZrV_2O_7 compound appeared.

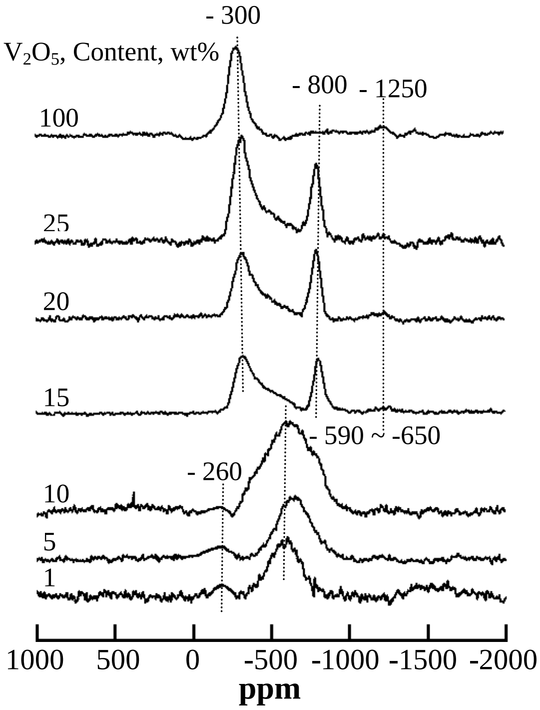

Fig. 3. Solid state ^{51}V NMR spectra of V_2O_5-15MoO_3/ ZrO_2(773) catalysts with different V_2O_5 contents.

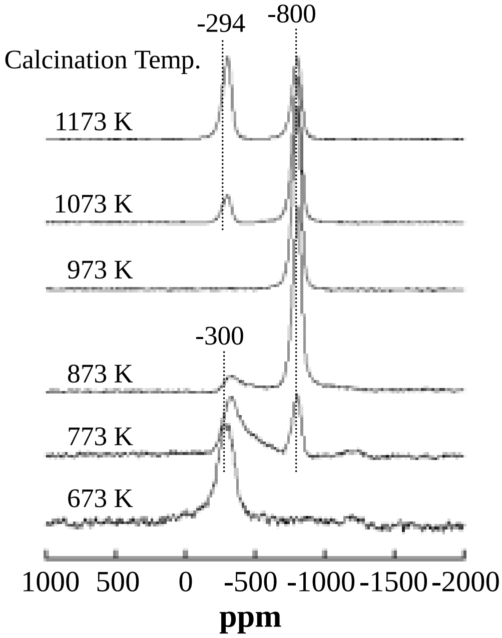

Fig. 4. Solid state ^{51}V NMR spectra of 20V_2O_5-15MoO_3/ ZrO_2 catalysts calcined at different temperatures.

CONCLUSIONS

On the basis of the results of FTIR, solid state ^{51}V NMR and XRD, at low calcination temperature of 773 K vanadium oxide up to 10 wt% was well dispersed on the surface of zirconia. However, high V_2O_5 loading (equal to or above 15 wt%) exceeding the formation of monolayer on the surface of zirconia was well crystallized.

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