Vanadium oxide catalyst supported on TiO$_2$-ZrO$_2$ has been prepared by adding Ti(OH)$_4$-Zr(OH)$_4$ powder to an aqueous solution of ammonium metavanadate followed by drying and calcining at high temperatures. The characterization of the prepared catalysts was performed using solid-state $^{51}$V NMR and FTIR. In the case of calcination temperature at 773 K, vanadium oxide was in a highly dispersed state for the samples containing low loading V$_2$O$_5$ below 25 wt %, but for samples containing high loading V$_2$O$_5$ equal to or above 25 wt %, vanadium oxide was well crystallized due to the V$_2$O$_5$ loading exceeding the formation of monolayer on the surface of TiO$_2$-ZrO$_2$. The ZrV$_2$O$_7$ compound was formed through the reaction of V$_2$O$_5$ and ZrO$_2$ at 773-973 K, whereas the V$_7$Ti$_6$O$_{17}$ compound was formed through the reaction of V$_2$O$_5$ and TiO$_2$ at 973-1073 K. The V$_7$Ti$_6$O$_{17}$ compound decomposed to V$_2$O$_5$ and TiO$_2$ at 1173 K, which were confirmed by FTIR and $^{51}$V NMR.

**Introduction**

Vanadium oxides are widely used as catalysts in oxidation reactions, e.g., the oxidation of sulfur dioxide, carbon monoxide, and hydrocarbons.\textsuperscript{1-5} These systems have also been found to be effective catalysts for the oxidation of methanol to methylformate.\textsuperscript{6,7} Vanadia catalysts supported on titania-alumina mixed oxide and titania modified with alumina were found to exhibit superior activities in selective catalytic reduction of NOx.\textsuperscript{8-11} Much research has been done to understand the nature of active sites, the surface structure of catalysts and 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.\textsuperscript{12-14} Silica, titania, zirconia and alumina\textsuperscript{15-22} have been commonly employed as vanadium oxide supports, and comparatively few studies have been reported on binary oxide TiO$_2$-ZrO$_2$ as a support for vanadium oxide.

It is well known that the dispersion and structural features of supported species can depend strongly on the support. The promoting effect of a TiO$_2$ support on the oxidation of o-xylene on V$_2$O$_5$ has been ascribed to an increase of the number of surface V=O bonds on the V$_2$O$_5$/TiO$_2$ catalysts and the weakening of these bonds.\textsuperscript{23} In many studies concerning the mechanism involved in the catalytic reactions on vanadium oxide, the V=O species have been considered to play a significant role as active sites for the reactions.\textsuperscript{24} Structure and other physicochemical properties of the supported metal oxides are considered to be in different states compared with bulk metal oxides because of their interaction with the supports. Solid-state nuclear magnetic resonance (NMR) methods represent a novel and promising approach to these systems. Since only the local environment of a nucleus under study is probed by NMR, this method is well suited for the structural analysis of disordered systems such as the two-dimensional surface vanadium oxide phases that is of particular interest in the present study. In addition to the structural information provided by NMR methods, the direct proportionality of the signal intensity to the number of contributing nuclei makes NMR be useful for quantitative studies. In the present investigation, the techniques of solid-state $^{51}$V NMR and Fourier transform infrared (FTIR) have been utilized to characterize a series of V$_2$O$_5$ samples supported on TiO$_2$-ZrO$_2$ with various vanadia loadings.

**Experimental Section**

**Catalyst Preparation.** The coprecipitate of Ti(OH)$_4$-Zr(OH)$_4$ was obtained by adding slowly aqueous ammonia into a mixed aqueous solution of titanium tetrachloride and zirconium oxychloride at room temperature with stirring until the pH of the mother liquor reached about 8. The ratio of titanium tetrachloride to zirconium oxychloride was 1 : 1. The coprecipitate thus obtained was washed thoroughly with distilled water until chloride ion was undetectable, and then dried at 383 K for 12 h. The dried coprecipitate was powdered below 100 mesh.

The catalysts containing various vanadium oxide content were prepared by adding the Ti(OH)$_4$-Zr(OH)$_4$ powder into an aqueous solution of ammonium metavanadate (NH$_4$VO$_3$) followed by drying and calcining at high temperatures for 3 h in air. This series of catalysts are denoted by their weight percentage of V$_2$O$_5$. For example, 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$ indicates the catalyst containing 10 wt % V$_2$O$_5$.

**Characterization.** FTIR absorption spectra of V$_2$O$_5$/TiO$_2$-ZrO$_2$ powders were measured by the KBr disk method over the range 1200-400 cm$^{-1}$. The samples for the KBr disk method were prepared by grinding a mixture of the catalyst and KBr powders in an agate mortar and pressing them in the usual way. FTIR spectra of ammonia adsorbed on the catalyst were obtained in a heatable gas cell at room temperature using a Mattson Model GL 6030E spectrophotometer. The self-supporting catalyst wafers contained about 9 mg/cm$^2$. Before obtaining the spectra the samples were heated...
under vacuum at 673-773 K for 2 h.

$^{51}$V NMR spectra were measured by a Varian Unity Inova 300 spectrometer with a static magnetic field strength of 7.05 T. Larmor frequency was 78.89 MHz. The ordinary single pulse sequence was used in which the pulse width was set at 2.8 s and the acquisition time was 0.026 s. The spectral width was 500 kHz. The number of scans was adjusted from 200 to 15,000, depending on the concentration of vanadium. The signal was acquired from the time point 4 $\mu$s after the end of the pulse. The sample was static, and its temperature was ambient (294 K). The spectra were expressed with the signal of VOCl$_3$ being 0 ppm, and the higher frequency shift from the standard was positive. Practically, solid NH$_4$VO$_3$ (-571.5 ppm) was used as the second external reference.

Results and Discussion

Infrared Spectra. Figure 1 shows IR spectra of V$_2$O$_5$/TiO$_2$-ZrO$_2$ catalysts with various content calcined at 773 K for 3 h. Although with samples below 25 wt % of V$_2$O$_5$ the definite peaks were not observed, the absorption bands at 1022 and 820 cm$^{-1}$ appeared for 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$, 33-V$_2$O$_5$/TiO$_2$-ZrO$_2$, and pure V$_2$O$_5$ containing high V$_2$O$_5$ content. The band at 1022 cm$^{-1}$ is assigned to the V=O stretching vibration, whereas the band at 820 cm$^{-1}$ is attributed to the coupled vibration between V=O and to V-O-V. Generally, the IR band of V=O in crystalline V$_2$O$_5$ shows at 1020-1025 cm$^{-1}$ and the Raman band at 995 cm$^{-1}$. The intensity of the V=O absorption gradually decreased with decreasing V$_2$O$_5$ content, although the band position did not change. As shown in Figure 1, the catalysts at vanadia loadings below 25 wt % gave no absorption bands from crystalline V$_2$O$_5$. This observation suggests that vanadium oxide below 25 wt % is in a highly dispersed state. It is reported that V$_2$O$_5$ loading exceeding the formation of monolayer on the surface of support is well crystallized and observed in the spectra of IR and $^{51}$V solid state NMR.

As shown in Figure 1, for samples below 25 wt% of V$_2$O$_5$ calcined at 773 K the crystalline V$_2$O$_5$ was not observed in their IR spectra, suggesting the monolayer dispersion of V$_2$O$_5$ on the surface of TiO$_2$-ZrO$_2$ as the amorphous phase. However, it is necessary to examine the formation of crystalline V$_2$O$_5$ as a function of calcination temperature. Variations of IR spectra against calcination temperature for 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$ are shown in Figure 2. For the sample, there are no V=O stretching bands at 1022 cm$^{-1}$ from the calcination temperature of 673 K to 1073 K, indicating no

![Figure 1](image1.png)  
Figure 1. Infrared spectra of catalysts calcined at 773 K: (a) TiO$_2$-ZrO$_2$, (b) 5-V$_2$O$_5$/TiO$_2$-ZrO$_2$, (c) 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$, (d) 15-V$_2$O$_5$/TiO$_2$-ZrO$_2$, (e) 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$, (f) 33-V$_2$O$_5$/TiO$_2$-ZrO$_2$, and (g) V$_2$O$_5$.

![Figure 2](image2.png)  
Figure 2. Infrared spectra of 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$ calcined at (a) 673 K, (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K, and (f) 1173 K.
formation of crystalline V$_2$O$_5$. However, as shown in Figure 2, V=O stretching bands due to crystalline V$_2$O$_5$ at 1173 K appeared at 1022 cm$^{-1}$ together with lattice vibration bands of V$_2$O$_5$ and TiO$_2$-ZrO$_2$ below 900 cm$^{-1}$. The formation of crystalline V$_2$O$_5$ at 1173 K can be explained in terms of the decomposition of V$_3$Ti$_6$O$_{17}$ compound, which was formed through the reaction of V$_2$O$_5$ and TiO$_2$ at 973-1073 K. In the present work, the triclinic phase of crystalline V$_3$Ti$_6$O$_{17}$ was confirmed by X-ray diffraction. X-ray diffraction patterns showed the triclinic phase of V$_3$Ti$_6$O$_{17}$ (2$\theta$: 27.6, 28.3, 28.4, 36.2, and 41.4$^o$) in the samples calcined at 973-1073 K, and for sample calcined at 1173 K the V$_3$Ti$_6$O$_{17}$ phase disappeared due to the decomposition of V$_3$Ti$_6$O$_{17}$, leaving the V$_2$O$_5$ phase and the rutile phase of TiO$_2$. These results are in good agreement with those of $^{51}$V solid state NMR described later.

Figure 3 shows IR spectra of 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$ catalysts calcined at 673-1173 K for 3 h. Unlike 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$ for 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$ crystalline V$_2$O$_5$ appeared at 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$_2$O$_5$ loading exceeding the formation of monolayer on the surface of ZrO$_2$ is well crystallized. However, at 973-1073 K all V$_2$O$_5$ reacted with ZrO$_2$ or TiO$_2$ and changed into ZrV$_2$O$_7$ or V$_3$Ti$_6$O$_{17}$, so that V=O stretching at 1022 cm$^{-1}$ disappeared completely, as shown in Figure 3. At the calcination temperature of 1173 K some of the V$_3$Ti$_6$O$_{17}$ decomposed into V$_2$O$_5$ and TiO$_2$, and then the V=O stretching band due to the crystalline V$_2$O$_5$ was again observed at 1022 cm$^{-1}$. These results are in good agreement with those of $^{51}$V solid state NMR.

$^{51}$V Solid State NMR Spectra. Solid state NMR methods represent a novel and promising approach to vanadium oxide catalytic materials. The solid state $^{51}$V NMR spectra of V$_2$O$_5$/TiO$_2$-ZrO$_2$ catalysts calcined at 773 K are shown in Figure 4. There are three types of signals in the spectra of catalysts, with varying intensities depending on V$_2$O$_5$ content. At low loadings or up to 15 wt% V$_2$O$_5$ a shoulder at about -260 ppm and the intense peak at -590 -730 ppm are observed. The former is assigned to the surface vanadium-oxygen structures surrounded by a distorted octahedron of oxygen atoms, and the latter is attributed to the tetrahedral vanadium-oxygen structures.

However, the surface vanadium oxide structure is remarkably dependent on the metal oxide support material. Vanadium oxide on TiO$_2$ (anatase) displays the highest tendency to be 6-coordinated at low surface coverages, whereas in the case of $\gamma$-Al$_2$O$_3$ a tetrahedral surface vanadium species is the favored. As shown in Figure 4, at low vanadium loading on TiO$_2$-ZrO$_2$ a tetrahedral vanadium species is exclusively dominant compared with a octahedral species. In general, it is known that low surface coverages favor a tetrahedral coordination of vanadium oxide, but at higher surface coverages vanadium oxide becomes increasingly octahedral-coordinated. As shown in Figure 4, the peak shapes for the vana-

![Figure 3](image-url)  
**Figure 3.** Infrared spectra of 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$ calcined at (a) 673 K, (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K, and (f) 1173 K.

![Figure 4](image-url)  
**Figure 4.** Solid state $^{51}$V NMR spectra of V$_2$O$_5$/TiO$_2$-ZrO$_2$ catalysts calcined at 773 K.
ium species on TiO$_2$-ZrO$_2$ are narrower and more symmetric compared with those of vanadium species on TiO$_2$ or $\gamma$-Al$_2$O$_3$ reported in other studies.\textsuperscript{32,33} It seems likely that the different physical and chemical properties of TiO$_2$-ZrO$_2$ compared with TiO$_2$ or $\gamma$-Al$_2$O$_3$ affect the symmetry of the surface vanadium-oxygen structures.

Increasing the V$_2$O$_5$ content on the TiO$_2$-ZrO$_2$ surface changes the shape of the spectrum to a rather intense and sharp peak at about -300 ppm ($\delta$) and a broad low-intensity peak at about -1400 ppm ($\delta$), which are due to the crystalline V$_2$O$_5$ of square pyramid coordination.\textsuperscript{32} These observations of crystalline V$_2$O$_5$ for samples containing high V$_2$O$_5$ content above 15 wt % are in good agreement with the results of the IR spectra in Figure 1. Namely, this is because V$_2$O$_5$ loading exceeding the formation of monolayer on the surface of TiO$_2$-ZrO$_2$ is well crystallized.\textsuperscript{28}

However, for 25-V$_2$O$_5$/TiO$_2$-ZrO$_2$ a sharp peak at -800 ppm due to crystalline ZrV$_2$O$_7$ appeared, indicating the formation of a new compound from V$_2$O$_5$ and ZrO$_2$. Other investigators\textsuperscript{22,31} reported the formation ZrV$_2$O$_7$ from V$_2$O$_5$ and ZrO$_2$ at the calcination temperature of 873 K for 1.5 h. In this case, since the sample was prepared by calcining for 3 h, it seems likely that the formation of ZrV$_2$O$_7$ occurred even at 773 K of calcination temperature. As discussed below, the cubic phase of ZrV$_2$O$_7$ was confirmed by X-ray diffraction. Moreover, the increase in V$_2$O$_5$ content resulted in the appearance of additional signals with a peak at -730 ppm. The intensity of the signal increases with increase in V$_2$O$_5$ loading. Different peak positions normally indicate differences in the spectral parameters and are observed due to different local environments of vanadium nuclei.\textsuperscript{32-36} Thus, species at -590 ppm and -730 ppm can be attributed to two types of tetrahedral vanadium complexes with different oxygen environments. Namely, the signals at -590 ppm can be attributed to the surface vanadium complexes containing OH groups or water molecules in their coordination sphere,\textsuperscript{33} because the evacuation treatment decreases the intensities remarkably. On the other hand, the signals at -730 ppm are due to the surface tetrahedral vanadium complexes, which do not contain OH groups or adsorbed water molecules.

It is necessary to examine the effect of calcination temperature on the surface vanadium oxide structure. The spectra of 10-V$_2$O$_5$/TiO$_2$-ZrO$_2$ containing lower vanadium oxide content and calcined at various temperatures are shown in Figure 5. The shape of the spectrum is very different depending on the calcination temperature. For the sample calcined at lower temperatures (673-773 K), there are two peaks at about -260 ppm and -590 ~ -730 ppm, a result of the octahedral and tetrahedral vanadium-oxygen structures, indicating the monolayer dispersion of V$_2$O$_5$ on the ZrO$_2$ surface, which are in good agreement with the results of IR spectra of Figure 1. Namely, this is because V$_2$O$_5$ loading exceeding the formation of monolayer on the surface of TiO$_2$-ZrO$_2$ is well crystallized.\textsuperscript{28} For sample calcined at 873 K, only a sharp peak at -800 ppm, due to crystalline ZrV$_2$O$_7$, appeared, indicating that most of V$_2$O$_5$ on the surface of TiO$_2$-ZrO$_2$ was consumed to form the ZrV$_2$O$_7$ compound. For sample calcined at 873 K, X-ray diffraction patterns for the cubic phase of ZrV$_2$O$_7$ ($2\theta$: 20.0, 33.9, 46.3, 52.8, and 54.5°) were observed. At 973-1073 K calcination temperatures, we also observed only a sharp peak at -800 ppm. For samples calcined at 973-1073 K, X-ray diffraction patterns of V$_3$Ti$_6$O$_{17}$ were observed. In previous work\textsuperscript{22} it was known.
that the \( \text{ZrV}_2\text{O}_7 \) compound decomposed completely to \( \text{V}_2\text{O}_5 \) and \( \text{ZrO}_2 \) at 1073 K. Therefore, on the basis of previous work and the present result it is clear that a sharp peak at -800 ppm for 10-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) calcined at 1073 K is due to the crystalline \( \text{V}_3\text{Ti}_6\text{O}_{17} \) phase formed by the reaction between \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \). However, at 1173 K of calcination temperature we observed only the peaks of crystalline \( \text{V}_2\text{O}_5 \) at -300 ppm and about -1400 ppm, indicating the decomposition of \( \text{V}_3\text{Ti}_6\text{O}_{17} \). These results are in good agreement with those of IR spectra in Figure 2.

The spectra of 25-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) containing higher vanadium oxide content than monolayer loading and calcined at various temperatures are shown in Figure 6. Unlike 10-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \), for 25-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) calcined even at the lower temperature of 673 K a sharp peak due to crystalline \( \text{V}_2\text{O}_5 \) appeared at -300 ppm and -1400 ppm together with a peak at -590 ~ -730 ppm due to the tetrahedral surface species. However, the for sample calcined at 773 K, in addition to a peak at -300 ppm due to crystalline \( \text{V}_2\text{O}_5 \), a sharp peak at -800 ppm due to \( \text{ZrV}_2\text{O}_7 \) compound appeared. As shown in Figure 6, the peak intensity of \( \text{ZrV}_2\text{O}_7 \) increased with an increase in calcination temperature, consuming the content of crystalline \( \text{V}_2\text{O}_5 \). Consequently, at 973 K of calcination temperature only a peak due to the \( \text{ZrV}_2\text{O}_7 \) and \( \text{V}_3\text{Ti}_6\text{O}_{17} \) phases appeared at -800 ppm. As mentioned above, since at 1073 K the \( \text{ZrV}_2\text{O}_7 \) decomposes completely to \( \text{V}_2\text{O}_5 \) and \( \text{ZrO}_2 \), a sharp peak at -800 ppm for 25-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) calcined at 1073 K is due to the crystalline \( \text{V}_3\text{Ti}_6\text{O}_{17} \) phase. At the calcination temperature of 1173 K a sharp peak of crystalline \( \text{V}_2\text{O}_5 \) at -300 ppm due to the decomposition of \( \text{V}_3\text{Ti}_6\text{O}_{17} \) was again observed.

**Acidic Properties.** Infrared spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish Brönsted acid sites from Lewis acid sites.\(^{22,37}\) Figure 7 shows the IR spectra of ammonia adsorbed on 10-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) calcined at 973 K and evacuated at 673 K for 1 h. For 10-\( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) the bands at 1454 cm\(^{-1}\) are the characteristic peaks of ammonium ion, which are formed on the Brönsted acid sites and the bands at 1620 cm\(^{-1}\) are contributed by ammonia coordinately bonded to Lewis acid sites,\(^{22,37}\) indicating the presence of both Brönsted and Lewis acid sites. Other samples having different vanadium content also showed the presence of both Lewis and Brönsted acids. Therefore, these \( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) samples can be used as catalysts for Lewis or Brönsted acid catalysis.

**Conclusions**

This paper shows that a combination of FTIR and \( ^{51}\text{V} \) solid-state NMR can be used to perform the characterization of \( \text{V}_2\text{O}_5 \) catalysts supported on \( \text{TiO}_2-\text{ZrO}_2 \). On the basis of results of FTIR and solid state \( ^{51}\text{V} \) NMR, at low calcination temperature of 773 K up to 15 wt% of vanadium oxide was well dispersed on the surface of \( \text{TiO}_2-\text{ZrO}_2 \). However, high \( \text{V}_2\text{O}_5 \) loading (equal to or above 25 wt%) exceeding the formation of monolayer on the surface of \( \text{TiO}_2-\text{ZrO}_2 \) was well crystallized. The \( \text{ZrV}_2\text{O}_7 \) compound was formed through the reaction of \( \text{V}_2\text{O}_5 \) and \( \text{ZrO}_2 \) at 773-973 K, whereas the \( \text{V}_3\text{Ti}_6\text{O}_{17} \) compound was formed through the reaction of \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \) at 973-1073 K. The \( \text{V}_3\text{Ti}_6\text{O}_{17} \) decomposed to \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \) at 1173 K, which were confirmed by FTIR and \( ^{51}\text{V} \) NMR. Infrared spectroscopic studies of ammonia adsorbed on \( \text{V}_2\text{O}_5/\text{TiO}_2-\text{ZrO}_2 \) catalysts showed the presence of both Lewis and Brönsted acids.

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