

# Characterization of Vanadium Oxide Supported on Zirconia and Modified with MoO<sub>3</sub>

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Vanadium oxides supported on zirconia and modified with MoO<sub>3</sub> were prepared by adding Zr(OH)<sub>4</sub> powder into a mixed aqueous solution of ammonium metavanadate and ammonium molybdate followed by drying and calcining at high temperatures. The characterization of prepared catalysts was performed using FTIR, Raman spectroscopy and solid-state <sup>51</sup>V NMR. In the case of a calcination temperature of 773 K, for samples containing low loading of V<sub>2</sub>O<sub>5</sub>, below 15 wt %, vanadium oxide was in a highly dispersed state, while for samples containing high loading of V<sub>2</sub>O<sub>5</sub>, equal to or above 15 wt %, vanadium oxide was well crystallized because the V<sub>2</sub>O<sub>5</sub> loading exceeded the formation of a monolayer on the surface of ZrO<sub>2</sub>. The ZrV<sub>2</sub>O<sub>7</sub> compound was formed through the reaction of V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 873 K and the compound decomposed into V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 1073 K, which were confirmed by FTIR spectroscopy and solid-state <sup>51</sup>V NMR. IR spectroscopic studies of ammonia adsorbed on V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/ZrO<sub>2</sub> showed the presence of both Lewis and Brønsted acids.

**Key Words :** Characterization, V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/ZrO<sub>2</sub>, <sup>51</sup>V NMR, FTIR, XRD

## Introduction

Vanadium oxides are widely used as catalysts in oxidation reactions, for example, the oxidation of sulfur dioxide, carbon monoxide, and hydrocarbons.<sup>1-4</sup> These systems have also been found to be effective catalysts for the oxidation of methanol to methylformate<sup>5,6</sup> and for the ammoxidation of 3-picoline.<sup>7</sup> Vanadia catalysts supported on titania-alumina mixed oxide and titania modified with alumina were found to exhibit superior activities in selective catalytic reduction of NO<sub>x</sub>.<sup>8-11</sup> 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.<sup>12-14</sup> So far, silica, titania, zirconia and alumina<sup>15-21</sup> have been commonly employed as the vanadium oxide supports.

Recently, metal oxides modified with sulfur compounds have been studied as strong solid acidic catalysts,<sup>22-24</sup> especially sulfate promoted zirconia containing iron or manganese as promoters<sup>25,26</sup> or noble metals to inhibit deactivation.<sup>27,28</sup> The high catalytic activity and small deactivation upon the addition of noble metals can be explained by both the elimination of coke by hydrogenation and hydrogenolysis,<sup>29</sup> and the formation of Brønsted acid sites from H<sub>2</sub> on the catalysts.<sup>28</sup> Recently, Zhao et al. reported zirconia-supported molybdenum oxide as an alternative material for reactions requiring strong acid sites.<sup>30</sup> Several advantages of molybdate, over sulfate, as dopant include that it does not suffer from dopant loss during thermal treatment and it undergoes significantly less deactivation during catalytic reactions.<sup>31</sup> So far, however, comparatively few studies have been reported

on binary oxide, vanadium oxide-molybdenum oxide supported on zirconia.

It is well known that the dispersion and the structural features of supported species are strongly dependent on the support. The promoting effect of a TiO<sub>2</sub> support on the oxidation of o-xylene on V<sub>2</sub>O<sub>5</sub> has been ascribed to an increase of the number of surface V=O bonds on the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts and weakening of these bonds.<sup>32</sup> In many studies concerning the mechanism of the catalytic reactions on vanadium oxide, the V=O species have been considered to play a significant role as the active sites for the reactions.<sup>33</sup> Structure and other physicochemical properties of 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 which 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 <sup>51</sup>V NMR and Fourier transform infrared (FTIR) have been utilized to characterize a series of V<sub>2</sub>O<sub>5</sub> samples supported on ZrO<sub>2</sub> and modified with MoO<sub>3</sub>.

## Experimental Section

**Catalyst Preparation.** Precipitate of Zr(OH)<sub>4</sub> was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride (Aldrich) at room temperature

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with stirring until the pH of mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected by  $\text{AgNO}_3$  solution, and was dried at room temperature for 12 h. The dried precipitate was powdered below 100 mesh.

The catalysts containing various vanadium oxide content and modified with  $\text{MoO}_3$  were prepared by adding  $\text{Zr}(\text{OH})_4$  powder into a mixed aqueous solution of ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) (Aldrich) and ammonium molybdate  $[(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24})(4\text{H}_2\text{O})]$  (Aldrich) followed by drying and calcining at high temperatures for 1.5 h. This series of catalysts were denoted by their weight percentage of  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  and calcination temperature. For example,  $3\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2(773)$  indicated the catalyst containing 3 wt%  $\text{V}_2\text{O}_5$  and 15 wt%  $\text{MoO}_3$  calcined at 773 K.

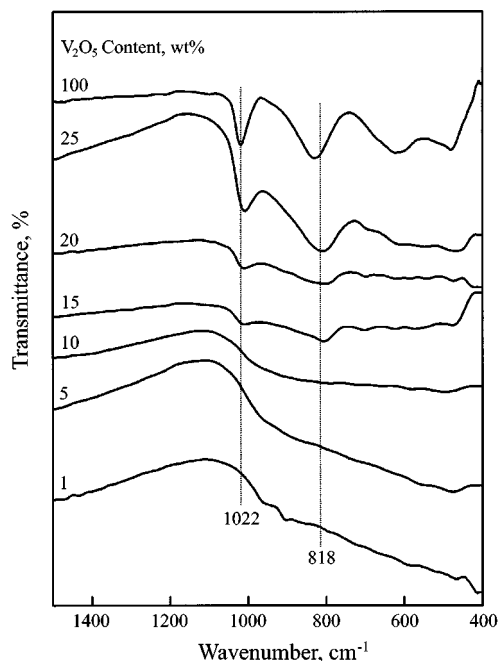
**Characterization.** FTIR absorption spectra of  $\text{V}_2\text{O}_5\text{-MoO}_3/\text{ZrO}_2$  powders were measured by KBr disk method over the range  $1200\text{-}400\text{ cm}^{-1}$ . The samples for the KBr disk method were prepared by grinding a mixture of the catalyst and KBr powders in an 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  $9\text{ mg/cm}^2$ . Before the spectra were obtained, the samples were heated under vacuum at  $673\text{-}773\text{ K}$  for 1.5 h.

The FT-Raman spectra were obtained with a Bruker model FRA 106 A spectrometer equipped with an InGaAs detector and a Nd:YAG laser source with a resolution of  $4\text{ cm}^{-1}$ . The laser beam was focussed onto an area  $0.1 \times 0.1\text{ mm}^2$  in size of the sample surface; a  $180^\circ$  scattering geometry was used.

$^{51}\text{V}$  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. An 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 varied from 400 to 4,000, depending on the concentration of vanadium. The signal was acquired from the time point 4 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  $\text{VOCl}_3$  being 0 ppm, and the higher frequency shift from the standard was positive. Practically, solid  $\text{NH}_4\text{VO}_3$  ( $-571.5\text{ ppm}$ ) was used as the second external reference.<sup>34-36</sup>

## Results and Discussion

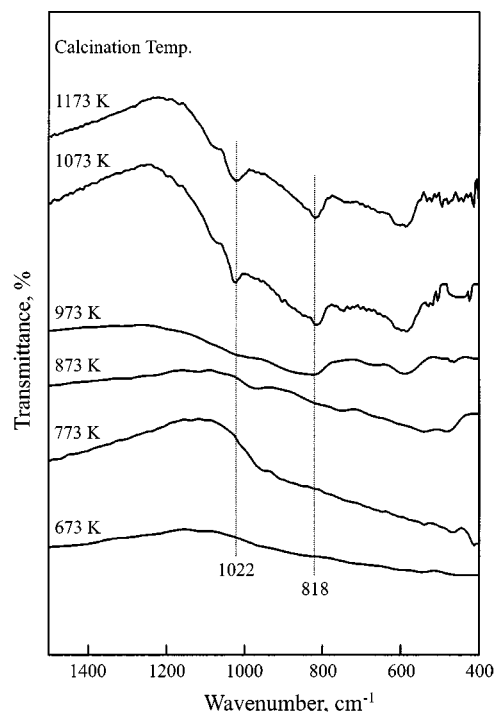
**Infrared Spectra.** Figure 1 shows IR spectra of  $\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2(773)$  catalysts with various  $\text{V}_2\text{O}_5$  contents calcined at 773 K for 1.5 h. Although with samples having less than 18 wt % of  $\text{V}_2\text{O}_5$  definite peaks were not observed, the absorption bands at  $1022$  and  $818\text{ cm}^{-1}$  appeared for  $15\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$ ,  $20\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$ ,  $25\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$  and pure  $\text{V}_2\text{O}_5$  containing high  $\text{V}_2\text{O}_5$  content. The band at  $1022\text{ cm}^{-1}$  was assigned to the V=O stretching vibration, while that at  $818\text{ cm}^{-1}$  was attributable to the coupled vibration between V=O and to V-O-V.<sup>36,37</sup> Gene-



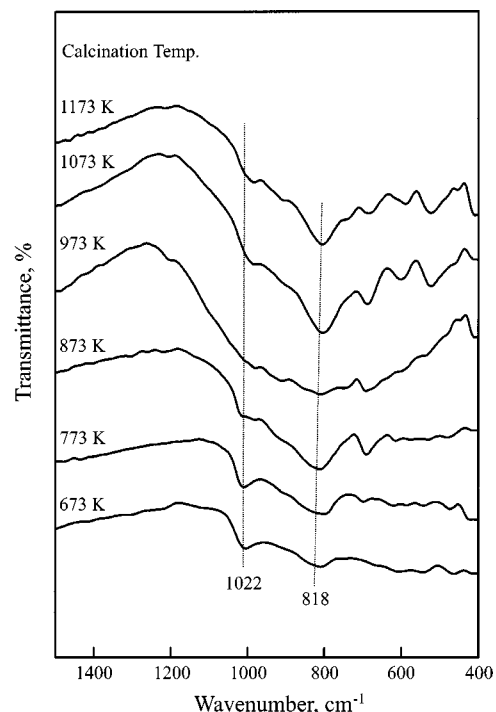
**Figure 1.** Infrared spectra of  $\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$  (773) catalysts with different  $\text{V}_2\text{O}_5$  contents.

rally, the IR band of V=O in crystalline  $\text{V}_2\text{O}_5$  showed at  $1020\text{-}1025\text{ cm}^{-1}$  and the Raman band at  $995\text{ cm}^{-1}$ .<sup>2,38</sup> The intensity of the V=O absorption gradually decreased with increasing  $\text{ZrO}_2$  content, although the band position did not change. This observation suggests that vanadium oxide below 15 wt % is in a highly dispersed state. It is reported that  $\text{V}_2\text{O}_5$  loading exceeding the formation of monolayer on the surface of  $\text{ZrO}_2$  is well crystallized and observed in the spectra of IR and solid state  $^{51}\text{V}$  NMR.<sup>34,36</sup>

It is necessary to examine the formation of crystalline  $\text{V}_2\text{O}_5$  as a function of calcination temperature. Variation of IR spectra against calcination temperature for  $3\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$  is shown in Figure 2. There were no V=O stretching bands at  $1022\text{ cm}^{-1}$  at calcination temperatures from 673 to 973 K, indicating no formation of crystalline  $\text{V}_2\text{O}_5$ . However, as shown in Figure 2, V=O stretching bands due to crystalline  $\text{V}_2\text{O}_5$  at 1073 and 1173 K appeared at  $1022\text{ cm}^{-1}$  together with lattice vibration bands of  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  below  $900\text{ cm}^{-1}$ .<sup>35,39</sup> The formation of crystalline  $\text{V}_2\text{O}_5$  at above 1073 K can be explained in terms of the decomposition of  $\text{ZrV}_2\text{O}_7$  compound which was formed through the reaction of  $\text{V}_2\text{O}_5$  and  $\text{ZrO}_2$  at  $873\text{-}973\text{ K}$ . In this study, on X-ray diffraction patterns the cubic phase of  $\text{ZrV}_2\text{O}_7$  was observed in the samples calcined at 873 K and for sample calcined at 1173 K the  $\text{ZrV}_2\text{O}_7$  phase disappeared due to the decomposition of  $\text{ZrV}_2\text{O}_7$ , leaving the  $\text{V}_2\text{O}_5$  phase and the monoclinic phase of  $\text{ZrO}_2$ . These results are in good agreement with those of  $^{51}\text{V}$  solid state NMR described later. In fact, it is known that the formation of  $\text{ZrV}_2\text{O}_7$  from  $\text{V}_2\text{O}_5$  and  $\text{ZrO}_2$  occurs at calcination temperature of 873 K and the  $\text{ZrV}_2\text{O}_7$  decomposes into  $\text{ZrO}_2$  and  $\text{V}_2\text{O}_5$  at 1073 K.<sup>34,36,40</sup> In separate experiments, variation of IR spectra against calcination temperature for  $10\text{V}_2\text{O}_5\text{-}15\text{MoO}_3/\text{ZrO}_2$  (not shown in the Figure) was similar



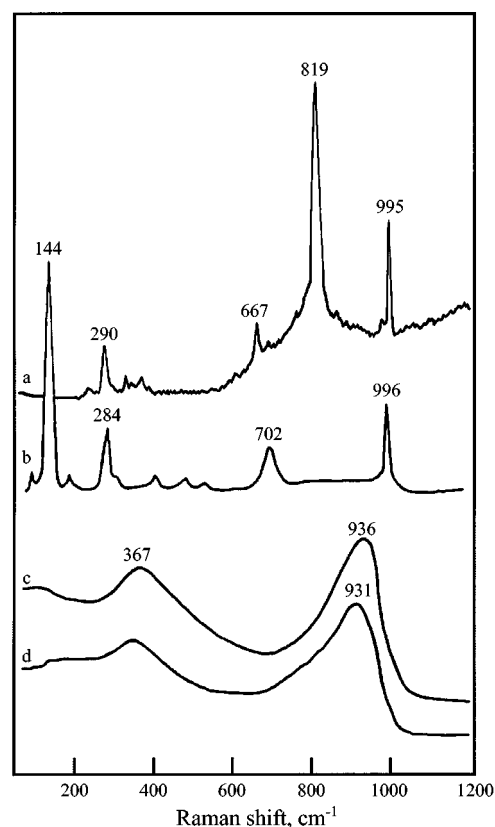
**Figure 2.** Infrared spectra of  $3V_2O_5$ - $15MoO_3/ZrO_2$  catalysts calcined at different temperatures.



**Figure 3.** Infrared spectra of  $20V_2O_5$ - $15MoO_3/ZrO_2$  catalysts calcined at different temperatures.

to that for  $3V_2O_5$ - $15MoO_3/ZrO_2$  as shown in Figure 2.

Figure 3 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



**Figure 4.** Raman spectra of (a)  $MoO_3$ , (b)  $V_2O_5$ , (c)  $10V_2O_5$ - $15MoO_3/ZrO_2(773)$ , and (d)  $15V_2O_5$ - $15MoO_3/ZrO_2(773)$ .

stretching band was observed at  $1022\text{ cm}^{-1}$ . This is because a  $V_2O_5$  loading exceeding the formation of monolayer on the surface of  $ZrO_2$  is well crystallized.<sup>34</sup> However, at 973 K all  $V_2O_5$  reacted with  $ZrO_2$  and changed into  $ZrV_2O_7$  so that V=O stretching at  $1022\text{ cm}^{-1}$  disappeared completely, as shown in Figure 3.

At a calcination temperature of 1073 K, some of the  $ZrV_2O_7$  decomposed into  $V_2O_5$  and  $ZrO_2$  and then V=O stretching band due to the crystalline  $V_2O_5$  was again observed at  $1022\text{ cm}^{-1}$ . These are in good agreement with those of  $^{51}V$  solid-state NMR described later

**Raman spectra.** Raman spectroscopy is a valuable tool for the characterization of dispersed metal oxides and detects vibrational modes surface and bulk structures. In order to analyze the nature of the surface species, laser Raman measurements of bulk  $MoO_3$ , bulk  $V_2O_5$  and  $V_2O_5$ - $15MoO_3/ZrO_2$  samples calcined at 773 K and with different vanadium oxide loadings were made. Figure 4 shows Raman spectra of four samples under ambient condition. Bulk  $MoO_3$ , obtained by calcining ammonium molybdate at 773 K, shows the main bands in good agreement with data previously reported.<sup>41,42</sup> The major vibrational modes of  $MoO_3$  [Figure 4(a)] are located at 995, 819, 667 and  $290\text{ cm}^{-1}$ , and have been assigned to the Mo=O stretching mode, the Mo-O-Mo asymmetric stretching mode, the Mo-O-Mo symmetric stretching mode, and the M=O bending mode, respectively.<sup>41,42</sup>

We will discuss the Raman spectrum of the bulk  $V_2O_5$ , obtained by calcining ammonium metavanadate at 773 K,

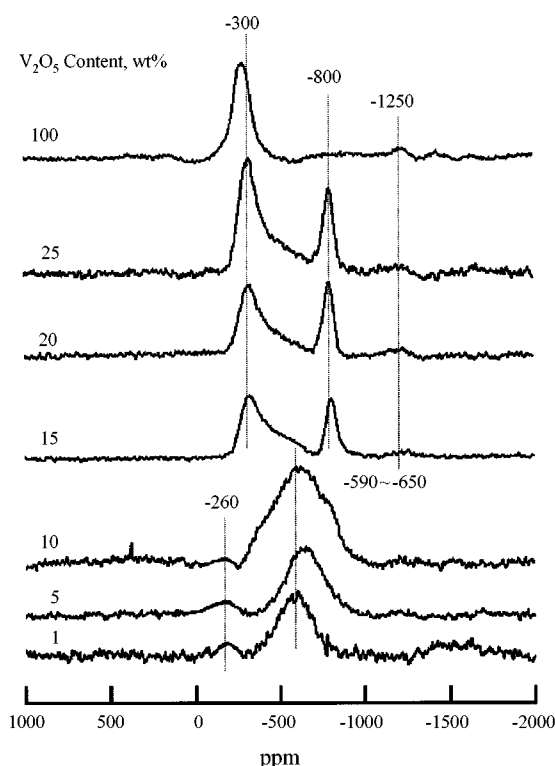
which is shown in Figure 4(b). The spectrum displayed bands at 144, 196, 284, 304, 406, 484, 528, 702 and 996  $\text{cm}^{-1}$ , all of which are characteristic of crystalline  $\text{V}_2\text{O}_5$ .<sup>43</sup> The 996  $\text{cm}^{-1}$  band is assigned to the vibration of the short vanadium oxygen bond normally regarded as a  $\text{V}=\text{O}$  species.<sup>43</sup> However, as shown in Figure 4(c), for 10 $\text{V}_2\text{O}_5$ -15 $\text{MoO}_3$ / $\text{ZrO}_2$  (773) no bands corresponding to  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  crystallites appear, indicating that  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  are in a highly dispersed state. As described in IR spectra, the catalysts at vanadia loadings below 15 wt% gave no absorption bands due to crystalline  $\text{V}_2\text{O}_5$ . However, as shown in Figure 4(d), for 15 $\text{V}_2\text{O}_5$ -15 $\text{MoO}_3$ / $\text{ZrO}_2$ (773) containing 15%  $\text{V}_2\text{O}_5$  the bands due to  $\text{V}_2\text{O}_5$  crystalline were observed, showing good agreement with the results of IR spectra.

The molecular structure of the supported molybdenum oxide species depends on the loading. Several authors observed that the nature of surface molybdenum species on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  depends on the amount of  $\text{MoO}_3$ . Raman bands between 910 and 980  $\text{cm}^{-1}$  are usually attributed to the  $\text{Mo}=\text{O}$  vibration of Mo species in either octahedral or tetrahedral environment.<sup>44</sup> Generally, monomolybdate or tetrahedral molybdenum oxygen species have been assigned for low  $\text{MoO}_3$  loading samples,<sup>42,44,45</sup> and two-dimensional poly-molybdates or octahedral molybdenum-oxygen species with characteristic band around 950-980  $\text{cm}^{-1}$ , for high  $\text{MoO}_3$  loading samples.<sup>42,44,45</sup> The frequency of Raman feature (1000-940  $\text{cm}^{-1}$ ), the maximum of which shifts slightly upwards on increasing vanadium content, is assigned to the  $\text{V}=\text{O}$  stretching mode vanadyl species in a hydrated form.<sup>9,46</sup> Therefore, the broad band observed in the 950-1000  $\text{cm}^{-1}$  region in Figure 4(c and d) will be interpreted as an overlap of three characteristic bands (two molybdenum oxide species and one vanadyl species).

For 10 $\text{V}_2\text{O}_5$ -15 $\text{MoO}_3$ / $\text{ZrO}_2$ (773) and 15 $\text{V}_2\text{O}_5$ -15 $\text{MoO}_3$ / $\text{ZrO}_2$ (773) in Figure 4(c and d), most of zirconia is amorphous to x-ray diffraction, showing tiny amount of tetragonal phase zirconia. The Raman spectrum of amorphous zirconia is characterized by a very weak and broad band at 550-600  $\text{cm}^{-1}$ .<sup>47</sup> Tetragonal zirconia is expected to yield a spectrum consisting of Raman bands in the region of 150-640  $\text{cm}^{-1}$ .<sup>36,48</sup> Therefore the very broad band around 367  $\text{cm}^{-1}$  is interpreted as an overlap of amorphous and tetragonal phase zirconia.

**Solid-State  $^{51}\text{V}$  NMR Spectra.** Solid-state NMR methods represent a promising approach to vanadium oxide catalytic materials. The solid state  $^{51}\text{V}$  NMR spectra of  $\text{V}_2\text{O}_5$ - $\text{MoO}_3$ / $\text{ZrO}_2$  catalysts calcined at 773 K followed by exposure to air are shown in Figure 5. There are three types of signals in the spectra of catalysts with varying intensities depending on  $\text{V}_2\text{O}_5$  content. At low loadings up to 10 wt%  $\text{V}_2\text{O}_5$  a shoulder at about -260 ppm and an 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.<sup>49,50</sup>

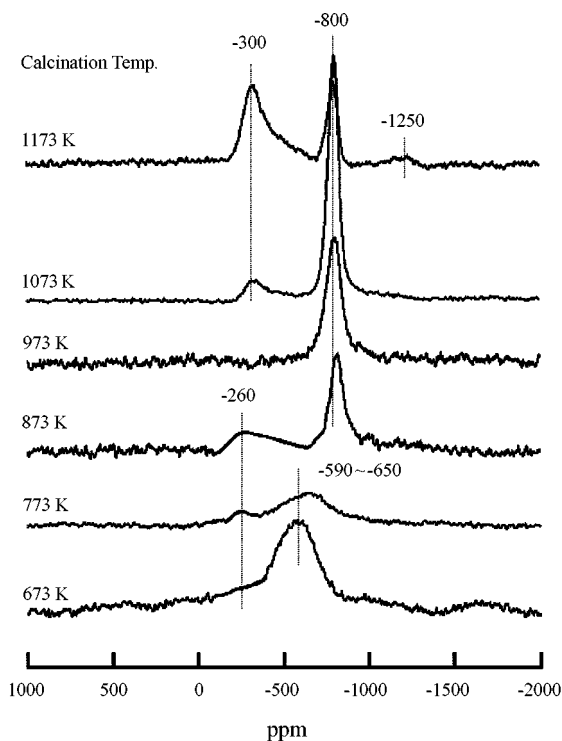
However, the surface vanadium oxide structure is remarkably dependent on the metal oxide support material. Vanadium



**Figure 5.** Solid-state  $^{51}\text{V}$  NMR spectra of  $\text{V}_2\text{O}_5$ -15 $\text{MoO}_3$ / $\text{ZrO}_2$  (773) catalysts with different  $\text{V}_2\text{O}_5$  contents.

oxide on  $\text{TiO}_2$  (anatase) displays the highest tendency to be 6-coordinated at low surface coverages, while in the case of  $\gamma$ - $\text{Al}_2\text{O}_3$  a tetrahedral surface vanadium species is favored<sup>50</sup>. As shown in Figure 5, at a low vanadium loading on zirconia 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, while at higher surface coverages vanadium oxide becomes increasingly octahedral-coordinated.

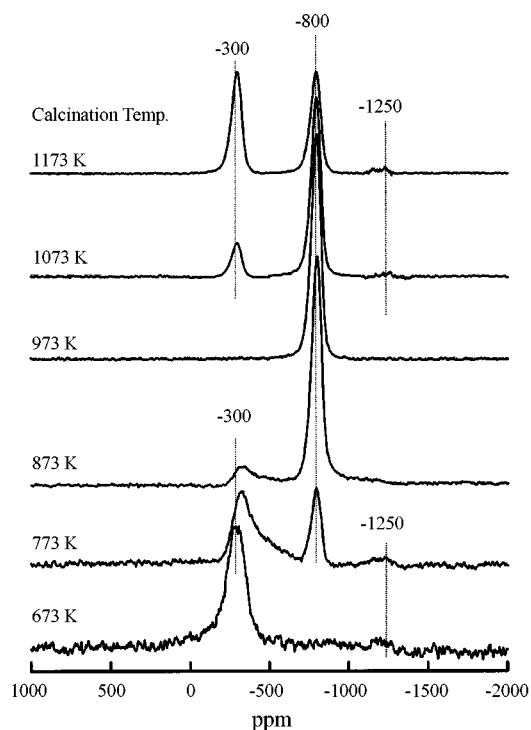
Increasing the  $\text{V}_2\text{O}_5$  content on the zirconia surface changes the shape of the spectrum to a rather intense and sharp peak at about -300 ppm and a broad low-intensity peak at about -1250 ppm, which are due to the crystalline  $\text{V}_2\text{O}_5$  of square pyramid coordination.<sup>49</sup> These observations of crystalline  $\text{V}_2\text{O}_5$  for samples containing high  $\text{V}_2\text{O}_5$  content, above 10 wt%, are in good agreement with the results of the IR spectra in Figure 1. Namely, this is because  $\text{V}_2\text{O}_5$  loading exceeding the formation of monolayer on the surface of zirconia is well crystallized.<sup>34,36</sup> Moreover, the increase in  $\text{V}_2\text{O}_5$  content resulted in the appearance of an additional signal with a peak at -800 ppm. The intensity of the signal increased with an increase in  $\text{V}_2\text{O}_5$  loading. Different peak positions normally indicate the differences of the spectral parameters and are observed due to different local environments of vanadium nuclei.<sup>49-53</sup> Thus species at -500~-650 ppm and -800 ppm can be attributed to two types of tetrahedral vanadium complexes with different oxygen environments. Namely, the signals at -500~-650 ppm can be attributed to the surface vanadium complexes containing OH groups or water molecules in their coordination sphere,<sup>50</sup>



**Figure 6.** Solid-state  $^{51}V$  NMR spectra of  $3V_2O_5$ - $15MoO_3/ZrO_2$  catalysts calcined at different temperatures.

because the evacuation treatment decreases the intensities remarkably. On the other hand, the signal at  $-800$  ppm is due to the surface tetrahedral vanadium complex which does not contain OH groups or adsorbed water molecules.

It is necessary to examine the effect of calcination temperature on the surface of the vanadium oxide structure. The spectra of  $3V_2O_5$ - $15MoO_3/ZrO_2$  containing a lower vanadium oxide content and calcined at various temperatures are shown in Figure 6. The shape of the spectrum is very different depending on the calcination temperature. For both samples calcined at lower temperatures ( $673$ - $773$  K), two peaks at about  $-260$  ppm and  $-500$  ~  $-650$  ppm due to the octahedral and tetrahedral vanadium-oxygen structures are shown, indicating the monolayer dispersion of  $V_2O_5$  on the  $ZrO_2$  surface. These results are in good agreement with the results of the IR spectra in Figure 2. However, for samples calcined at  $873$  K, in addition to the above two peaks, a peak at  $-800$  ppm due to crystalline  $ZrV_2O_7$  appeared, indicating the formation of a new compound from  $V_2O_5$  and  $ZrO_2$  at a high calcination temperature. For samples calcined at  $873$ - $1073$  K, X-ray diffraction patterns of  $ZrV_2O_7$  were observed. Roozeboom *et al.* reported the formation of  $ZrV_2O_7$  from  $V_2O_5$  and  $ZrO_2$  at a calcination temperature of  $873$  K.<sup>40</sup> At a calcination temperature of  $973$  K only a peak at  $-800$  ppm due to the  $ZrV_2O_7$  phase appeared, saying that most of the  $V_2O_5$  on the surface of zirconia was consumed to form the  $ZrV_2O_7$  compound. However, at a calcination temperature of  $1073$ - $1173$  K we can observe only a sharp peak of crystalline  $V_2O_5$  at  $-300$  and about  $-1250$  ppm, indicating the decomposition of  $ZrV_2O_7$ . These results are in good agree-



**Figure 7.** Solid-state  $^{51}V$  NMR spectra of  $20V_2O_5$ - $15MoO_3/ZrO_2$  catalysts calcined at different temperatures.

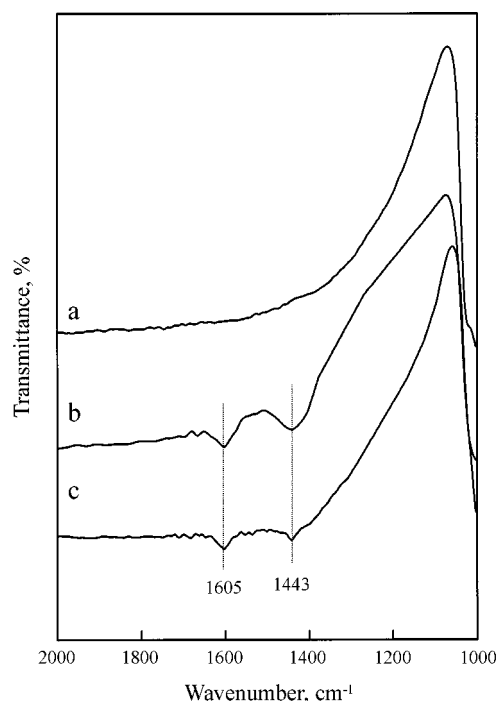
ment with those of IR spectra in Figure 2.

The spectra of  $20V_2O_5$ - $15MoO_3/ZrO_2$  containing a higher vanadium oxide content than monolayer loading and calcined at various temperatures are shown in Figure 7. 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 a peak 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. As shown in Figure 7, the peak intensity of  $ZrV_2O_7$  increased with an increase in calcination temperature, consuming the content of crystalline  $V_2O_5$ . Consequently, at a calcination temperature of  $973$  K only a peak due to the  $ZrV_2O_7$  phase appeared at  $-800$  ppm. At a calcination temperature of  $1073$  K, a sharp peak of crystalline  $V_2O_5$  at  $-300$  ppm due to the decomposition of  $ZrV_2O_7$  was again observed. However, unlike  $3V_2O_5$ - $15MoO_3/ZrO_2$ , for  $20V_2O_5$ - $15MoO_3/ZrO_2$ , the  $ZrV_2O_7$  compound was not decomposed completely at  $1073$  K, leaving some  $ZrV_2O_7$ . It seems likely that it is very difficult for all  $ZrV_2O_7$  to decompose for  $1.5$  h because a large amount of  $ZrV_2O_7$  was formed in the case of  $20V_2O_5$ - $15MoO_3/ZrO_2$ .

**Surface Properties.** The specific surface areas of some samples calcined at  $673$  and  $773$  K for  $1.5$  h are listed in Table 1. The presence of vanadium oxide and molybdenum oxide influences the surface area in comparison with the pure  $ZrO_2$ . Specific surface areas of  $V_2O_5$ - $MoO_3/ZrO_2$  samples are larger than that of pure  $ZrO_2$  calcined at the same temperature. It seems likely that the interaction between

**Table 1.** Specific surface areas of some V<sub>2</sub>O<sub>5</sub>-15MoO<sub>3</sub>/ZrO<sub>2</sub> samples calcined at 673 K and 773 K

Catalysts	Surface area (m <sup>2</sup> /g, 673 K)	Surface area (m <sup>2</sup> /g, 773 K)
ZrO <sub>2</sub>	185	122
1V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	219.9	218.6
3V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	236.2	221.4
5V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	223.8	216.8
10V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	207.9	165.6
15V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	170.1	148.6
20V <sub>2</sub> O <sub>5</sub> -15MoO <sub>3</sub> /ZrO <sub>2</sub>	164.5	147.1

**Figure 8.** Infrared spectra of NH<sub>3</sub> adsorbed on 15V<sub>2</sub>O<sub>5</sub>-15MoO<sub>3</sub>/ZrO<sub>2</sub> (773). (a) background of 15V<sub>2</sub>O<sub>5</sub>-15MoO<sub>3</sub>/ZrO<sub>2</sub> evacuated at 673 K for 1 h, (b) NH<sub>3</sub> (20 torr) adsorbed on sample a, (c) sample b evacuated at 503 K for 0.5 h.

vanadium oxide (or molybdenum oxide) and ZrO<sub>2</sub> protects catalysts from sintering.<sup>34</sup>

Infrared spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish between Brönsted and Lewis acid sites.<sup>23,54,55</sup> Figure 8 shows the IR spectra of ammonia adsorbed on 15V<sub>2</sub>O<sub>5</sub>-15MoO<sub>3</sub>/ZrO<sub>2</sub> calcined at 773 K and evacuated at 673 K for 1 h. For 15V<sub>2</sub>O<sub>5</sub>-15MoO<sub>3</sub>/ZrO<sub>2</sub> the bands at 1443 are the characteristic peaks of ammonium ion, which are formed on the Brönsted acid sites and the absorption peaks at 1605 cm<sup>-1</sup> are contributed by ammonia coordinately bonded to Lewis acid sites,<sup>22,54</sup> 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 V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/ZrO<sub>2</sub> samples can be used as catalysts for Lewis or Brönsted acid catalysis.

## Conclusions

On the basis of the results of FTIR, Raman spectroscopy, solid-state <sup>51</sup>V NMR and XRD, at a low calcination temperature of 773 K, it has been found that vanadium oxide up to 10 wt% was well dispersed on the surface of zirconia. However, when the V<sub>2</sub>O<sub>5</sub> loading exceeded 15 wt% (the amount equal to cover by monolayer on the surface of zirconia), the V<sub>2</sub>O<sub>5</sub> existed in well crystallized state. The ZrV<sub>2</sub>O<sub>7</sub> compound was formed by the reaction of V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 873 K and it decomposed into V<sub>2</sub>O<sub>5</sub> and ZrO<sub>2</sub> at 1073 K; these results were observed in FTIR spectra and solid-state <sup>51</sup>V NMR. Infrared spectroscopic studies of ammonia adsorbed on V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/ZrO<sub>2</sub> catalysts showed the presence of both Lewis and Brönsted acids.

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