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Characterization of Vanadium Oxide Supported on TiO_2-ZrO_2 Catalysts by ^{51}V Solid-State NMR Spectroscopy

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Abstract: Supported vanadium oxides are being used extensively as catalysts for a variety of reactions, including partial oxidations and ammoxidations. A series of vanadium oxide supported on TiO_2-ZrO_2 was obtained by impregnating ammonium metavanadate slowly into a mixed precipitate of $Ti(OH)_4$-$Zr(OH)_4$, followed by calcining in air at high temperatures. The prepared catalysts were characterized by ^{51}V solid-state NMR. In the calcined catalysts ^{51}V NMR studies indicated the peaks corresponding to distorted tetrahedral vanadia species at low V_2O_5 contents and octahedral vanadia species at high vanadia loadings. These results illustrate the suitability of ^{51}V NMR as a unique quantitative spectroscopic tool in the structural analysis of vanadium(V) oxide catalytic materials.

INTRODUCTION

Supported vanadium oxides are being used extensively as catalysts for a variety of reactions including partial oxidations and ammoxidations.[1-5] It is well known that the dispersion and the structural features of supported species can strongly depend on the support. 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 support. Recently V_2O_5-TiO_2 mixed oxides have received considerable attention in catalysts. In particular, V_2O_5 supported on the anatase modification of TiO_2 increases the selectivity of the oxidation of o-xylene to phthalic anhydride and are very promising for the reduction of NO_x with NH_3.[6,7] Vanadia catalysts supported on titania-alumina mixed oxide and titania modified alumina were found to exhibit superior activities in selective catalytic reduction of NO_x.[8-11] The promoting effect of a TiO_2 support on the oxidation of o-xylene on V_2O_5 has been ascribed to an increase

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of the number of surface V=O bonds on the V_2O_5/TiO_2 catalysts and weakening of these bonds.[12,13] 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.[14-16]

Several important spectroscopic investigations of supported V_2O_5 catalysts has appeared in the literature. Roozeboom et al.[17] have used wet impregnation of ammonium metavanadate to deposit V_2O_5 onto several oxides(Al_2O_3, CeO_2, Cr_2O_4, SiO_2, TiO_2 and ZrO_2). From solution and solid state NMR data, the presences of tetrahedrally coordinated V ions at low coverages, of polymeric arrays consisting of VO_6 octahedra at higher loadings and of crystalline V_2O_5 in the deposit was inferred. With the V_2O_5/ZrO_2system, the information of a ZrV_2O_7 phase has been detected.[17] For the preparation of V_2O_5 deposited on TiO_2 by NH_4VO_3-oxalic acid wet impregnation, Bond et al.[18,19] have developed a structural model that involved extended V_2O_5 layers before calcination and crystallites of V_2O_5 after calcination. Wachs et al.[20] have given a survey on V_2O_5 structures created on TiO_2 at various loadings, both under hydrated and dehydrated conditions by NMR spectroscopy. Solid state NMR methods represent a novel promising approach to studying local structure. Since only the local environment of the necleus 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 of interest in the present study, in which the lack of long-range order precludes the application of standard diffraction methods.

^{51}V solid-state NMR has been used by various investigators to differentiate different kinds of vanadia species in the catalysts.[21-25] The types of vanadia species were found to depend upon the precursor used, chemical nature of the support, method of preparation and type of pretreatment, eg. evacuation of the catalysts prior to recording the spectra. In a recent paper by Le Costumer et al.[26], the pH dependence of the ^{51}V NMR spectra on impregnated aluminas in the wet, dried, and cured states has been investigated, but to date, no systematic studies of the effect of different metal oxide supports or surface coverages have been carried out yet. Went et al.[27] have compared V_2O_5 supported on SiO_2, TiO_2 and Al_2O_3 and have indicated reference vibrational data for monomeric species as well as one- and two-dimensional vanadate chains.

In this paper, we have studied that a series of vanadium oxide supported on TiO_2-ZrO_2 was obtained by impregnating ammonium metavanadate slowly into a mixed precipitate of $Ti(OH)_4$-$Zr(OH)_4$, followed by calcining in air at high temperatures. The characterization of prepared catalysts was performed using ^{51}V solid state NMR.

EXPERIMENTAL SECTION

Catalyst Preparation

The coprecipitate of $Ti(OH)_4$-$Zr(OH)_4$ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The mole ratio of titanium tetrachloride to zirconium oxychloride was 1. The coprecipitates in which chloride ion was not detected by $AgNO_3$ solution were dried at 110℃ for 12 h. The dried coprecipitates were powdered below 100 mesh by grinding. The catalysts containing various vanadium oxide contents were prepared by adding an aqueous solution of ammonium metavanadate(NH_4VO_3, Aldrich) to the $Ti(OH)_4$-$Zr(OH)_4$ powder followed by drying and calcining at high temperatures for 2 h in air. This series of catalysts are denoted by their weight percentage of V_2O_5 and calcination temperature. For example, 10-V_2O_5/TiO_2-ZrO_2(500) indicates the catalyst containing 10 wt% V_2O_5, and calcined at 500℃

Measurements

^{51}V NMR spectra were measured by a Varian Unity Inova 300 WB spectrometer with a static magnetic field strength of 7.05 T. Lamor frequency was 78.87 MHz for ^{51}V nucleus. The ordinary single pulse sequence was used, in which the pulse width was set at 3.5μs (90° pulse length), the acquisition time was 0.04 s. The spectral width was 500 kHz. The number of scans was varied from 200 to 15,000, depending on the concentration of vanadium and calcination temperature of catalysts. The signal was acquired from the time point 4 (s after the end of the pulse. The sample was static, and was measured at ambient temperature(294K). The chemical shift of spectra were expressed versus the signal of 0.6 M $NaVO_3$ solution being -574.28 ppm.

RESULT AND DISCUSSION

The ^{51}V nucleus has spin I of 7/2 and natural abundant of 99.76%. In general, three different types of interaction influence the ^{51}V NMR spectra of solid diamagnetic samples, the dipole interaction of the magnetic moment of the nucleus with moments of other nuclei, leading to broad lines, the quadrupolar interaction of the ^{51}V nucleus with the electric field gradient, which splits the lines and contributes to the shift of the central(m_1=1/2(m_1=-1/2) line and the chemical shift interaction, which changes the position of the lines and makes them asymmetric

Solid-state wide-line ^{51}V NMR spectra of V_2O_5/TiO_2-ZrO_2 catalysts calcined at 773 K are shown in Figure 1. As can be seen, several lines are observed for these samples. Line A with

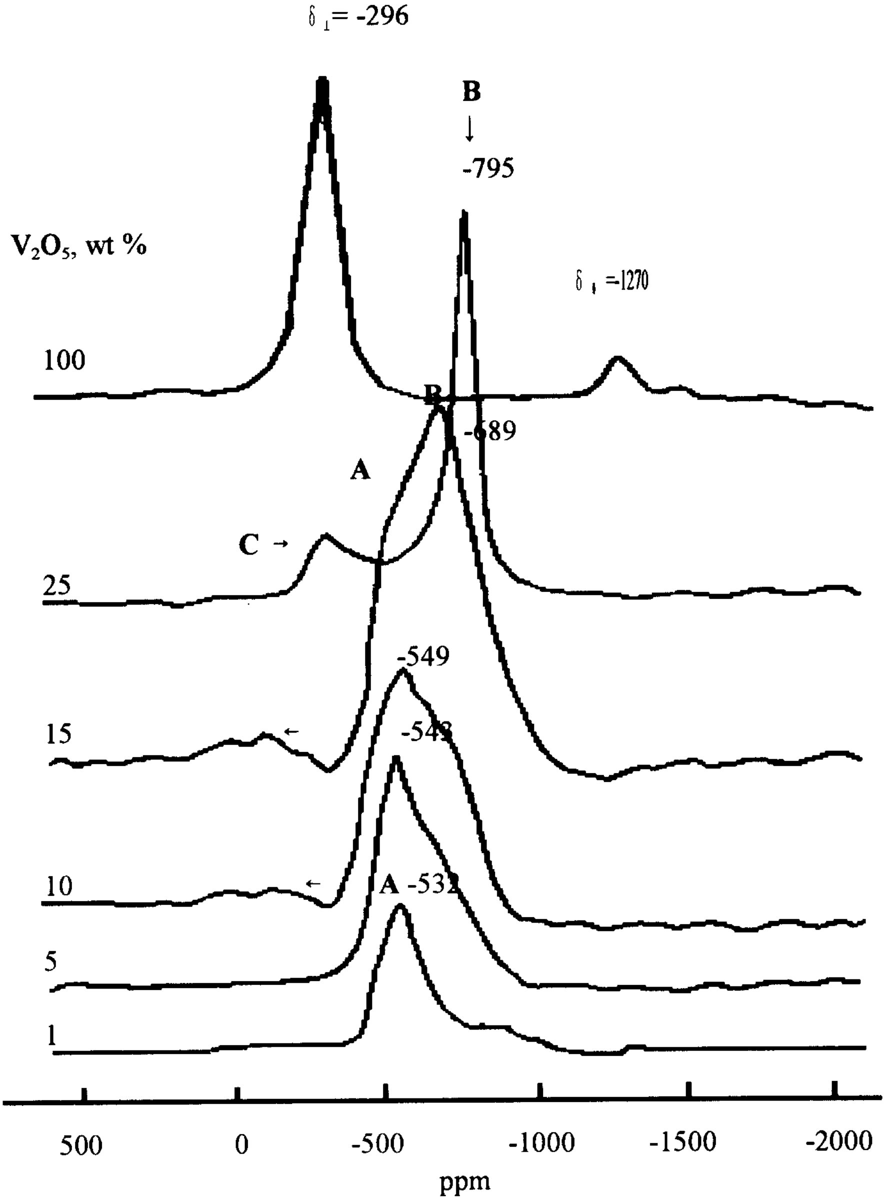

Fig. 1. Solid-state ^{51}V NMR spectra of V_2O_5/TiO_2-ZrO_2 clatalysts calcined at 773 K as a function of vanadia content.

the peak at – 532 to – 560 ppm prevails at small V contents. The increase of V content results in the appearance of line B with a peak in the range from – 670 to – 689 ppm, and line C with (= - 296 ppm, (= - 1270 ppm. The latter line is dominant in the spectra of the samples with a large V content. Line A is observed at low V concentration, while line C appears at large V concentrations. Lines A and B can be attributed to tetrahedral vanadia complexes, while lines C is from V atoms in a distorted octahedral environment.[29,30] The bonding geometry in V_2O_5 is typically described as square-pyramidal, consisting of four equatorial V-O bonds of similar length and one very short axial V-O bond (1.58 Å). Alternatively, the environment cold be described as 6-coordinate, if the very long (2.79 Å) second axial V-O distance is included.[31,32] This coordination is reflected in a near-axially symmetric chemical shift tensor with maximized shielding along the axial direction. The wide-line ^{51}V spectrum of V_2O_5 shown in Figure 1 was obtained on vanadium oxide prepared in microcrystalline form on a TiO_2-ZrO_2 surface. It differs from the V_2O_5 spectra previously published in the literature[29] by the absence of first-order quadrupolar satellites, which usually overlap with the chemical shift anisotropy powder pattern of the central transition. Presumably, the disorder present in this sample results in a spread of quadrupole coupling constants that renders these satellites unobservable, hence enabling the observation of a cleaner spectrum. 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 coverage, while in the case of ($-Al_2O_3$ a tetrahedral surface vanadium species is the favored. As shown in Figure 1, at low vanadium loading on TiO_2-ZrO_2 a tetrahedral vanadium species is exclusively dominant compared with a octahedral coordination of vanadium oxide, while at higher surface coverage vanadium oxide becomes increasingly octahedral-coordinated. In general it is known that low surface coverage favor a tetrahedral coordination of vanadium oxide, while at higher surface coverage vanadium oxide becomes increasingly octahedral coordinated. Increasing the V_2O_5 content on the TiO_2-ZrO_2 surface changes the shape of the spectrum to a rather intense and sharp peak because at high V contents are observed octahedral vanadia.

Evacuation of the samples at 523 K and 10^{-5} Torr for 2 h results in a change in the spectra (Figure .2). For the evacuated samples of the position of the peak is shifted compared to nonevacuated samples. They can be attributed to surface tetrahedral vanadia complexes which do not contain water molecules or OH groups in their first coordination sphere, since evacuation does not change the position of their peaks. Figure 2 can be attributed to surface tetrahedral complexes containing one or more OH groups or water molecules in their coordination sphere, since evacuation does not change the position of their peaks. This is indicated by the change of the peak position for the nonevacuation and evacuation samples. The decrease of the intensity of Figure 2 on evacuation compared to that of Figure 1, indicates that dehydration at 523 K results in transformation of the main part of surface tetrahedral complexes to V_2O_5. Note that the surface species observed for the V_2O_5/TiO_2-ZrO_2 system are different from those observed for V_2O_5/TiO_2 catalysts. Thus, the influence of ZrO_2 on the types of surface V species is quite strong. The observed chemical shift are give in Table 1.

It is necessary to examine the effect of calcination temperature on the surface vanadium oxide structure. The spectra of 10-V_2O_5/TiO_2-ZrO_2 containing lower vanadium oxide content and calcined at various temperatures are shown in Figure 3. The shape of the spectrum is very different depending on the calcination temperature. For the sample calcined at 673 K, a peak at -294 ppm due to the crystalline V_2O_5 and an intense peak at -568 ppm attributable to V atoms in tetrahedral environment are observed. For the samples calcined at lower temperature (673-773K), two peaks at about -260 ppm and -568 ~ -660 ppm due to the octahedral and tetrahedral vanadium-oxygen structures are shown, indicating the monolayer dispersion of V_2O_5 on the TiO_2-ZrO_2 surface.[29,30] However, for the samples calcined at 873 K, in addition to the above two peaks a sharp peak at -796 ppm due to crystalline TiV_2O_7 appeared, indicating the formation of a new compound from V_2O_5 and TiO_2 at high calcination temperature. This observation is in accordance with the ^{51}V NMR studies of Blasco et al..[33] They noticed that more acidic supports result in the formation of polymeric octahedral coordinated vanadia because they observed only peaks corresponding to octahedral coordinated vanadia species. At higher temperature, for sample calcined at 873K-1073K only a peak at -799 ppm due to the TiV_2O_7 phase appeared, saying that most of V_2O_5 on the surface of TiO_2-ZrO_2 was consumed to form the TiV_2O_7 compound. However, at 1173 K of calcination temperature we can observe only the peaks of crystalline V_2O_5 at –302 ppm and about –1300 ppm, indicating the decomposition of TiV_2O_7. As shown in Figure 3, the peak intensity of TiV_2O_7 increased with increase in calcination temperature, consuming the content of crystalline V_2O_5. The spectra of 25-V_2O_5/TiO_2-ZrO_2 calcined at various temperatures ate shown in Figure 4. Unlike, 10-V_2O_5/TiO_2-ZrO_2 catalysts in Fiures 3, for 25-V_2O_5/TiO_2-ZrO_2 calcined even at lower temperatures(673-773 K) a sharp peak due to crystalline V_2O_5 appeared at –300 ppm together with peaks at –650 ppm and –790 ppm due to the tetrahedral surface species. However, for sample calcined at 873 K, in addition to a peak at –300 ppm due to crystalline V_2O_5 a sharp peak at –790 ppm due to TiV_2O_7 compound appeared.

Consequently at 973-1073 K of calcination temperature only a peak due to the TiV_2O_7 phase appeared at –790 ppm. At 1173 K of calcination temperature a peak of crystalline of V_2O_5 at –290 ppm due to the decomposition of TiV_2O_7 was again observed.

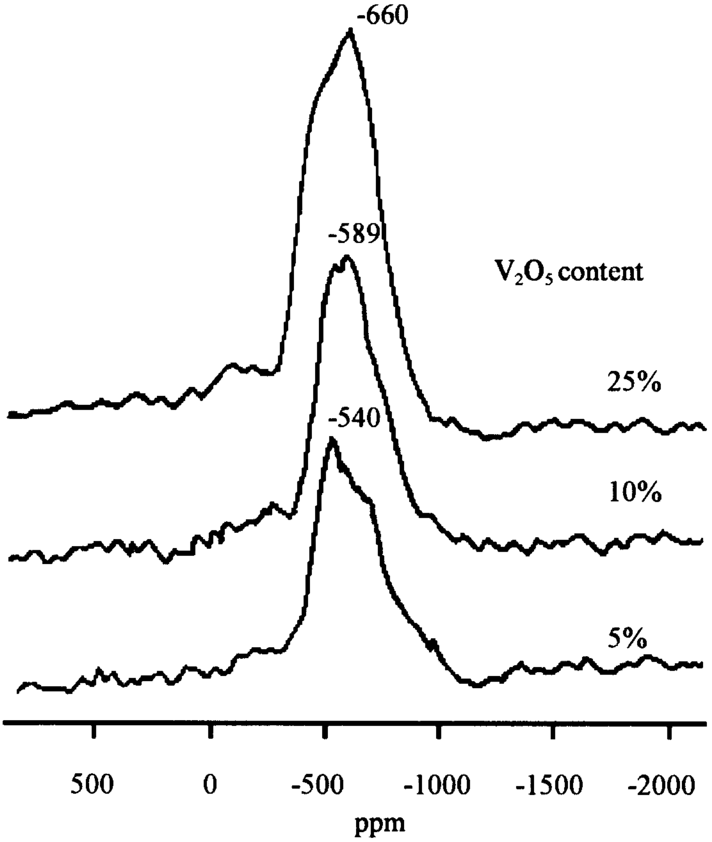

Fig. 2. Solid-state ^{51}V NMR of V_2O_5/TiO_2-ZrO_2 samples as a function of vanadia content after evacuation at 523 K, 2 h and 10^{-5} Torr

Table 1. ^{51}V NMR peaks of calcined and evacuated the catalysts

Catalysts	δ *, ppm	δ **, ppm
5-V_2O_5/TiO_2-ZrO_2	-549	-540
10-V_2O_5/TiO_2-ZrO_2	-600	-589
25-V_2O_5/TiO_2-ZrO_2	-680	-660

* : catalysts calcined at 673 K for 2 h in air condition

** : catalysts evacuated at 523 K for 2h, 10^{-5}Torr

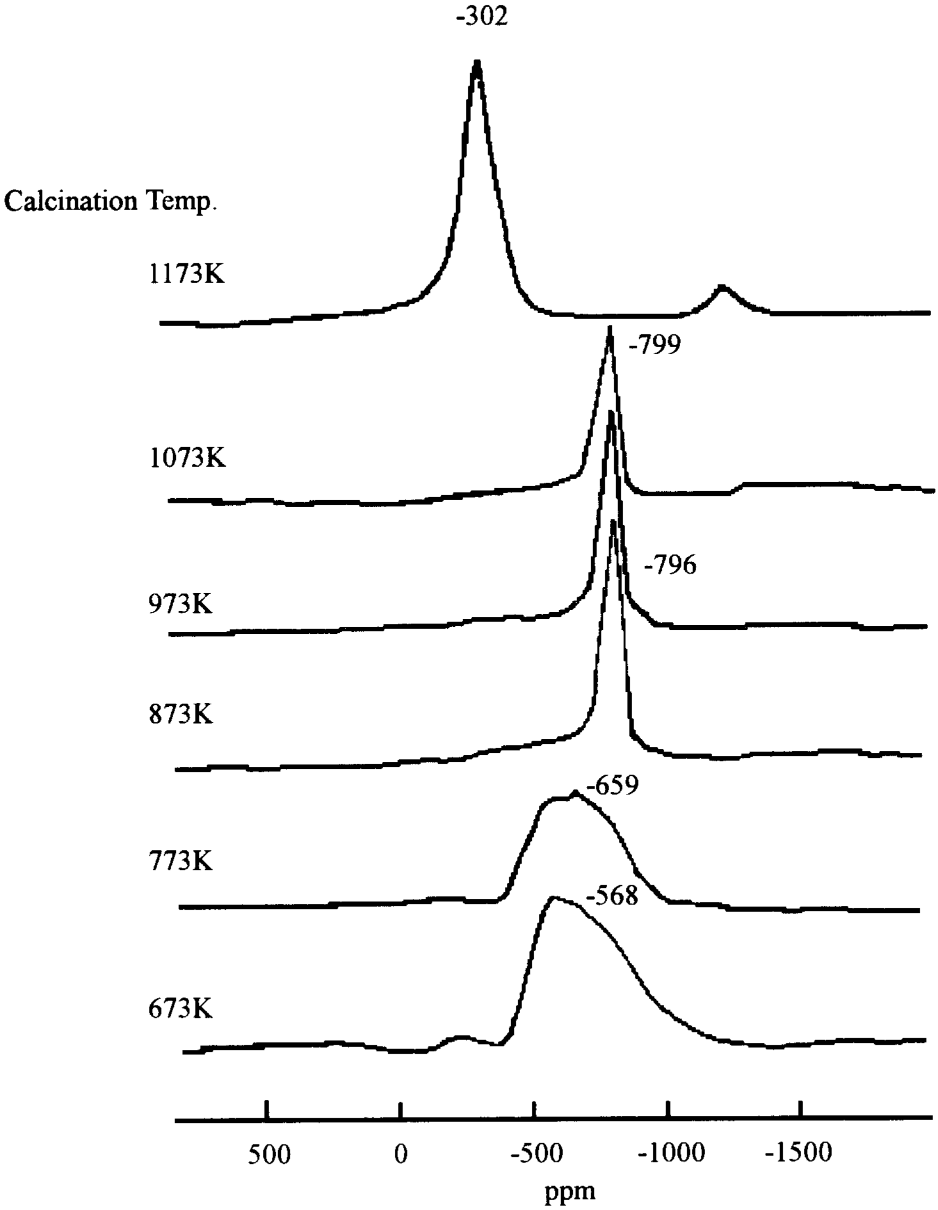

Fig. 3. Solid-state ^{51}V NMR spectra of 10-V_2O_5/TiO_2-ZrO_2 calcined at different temperature.

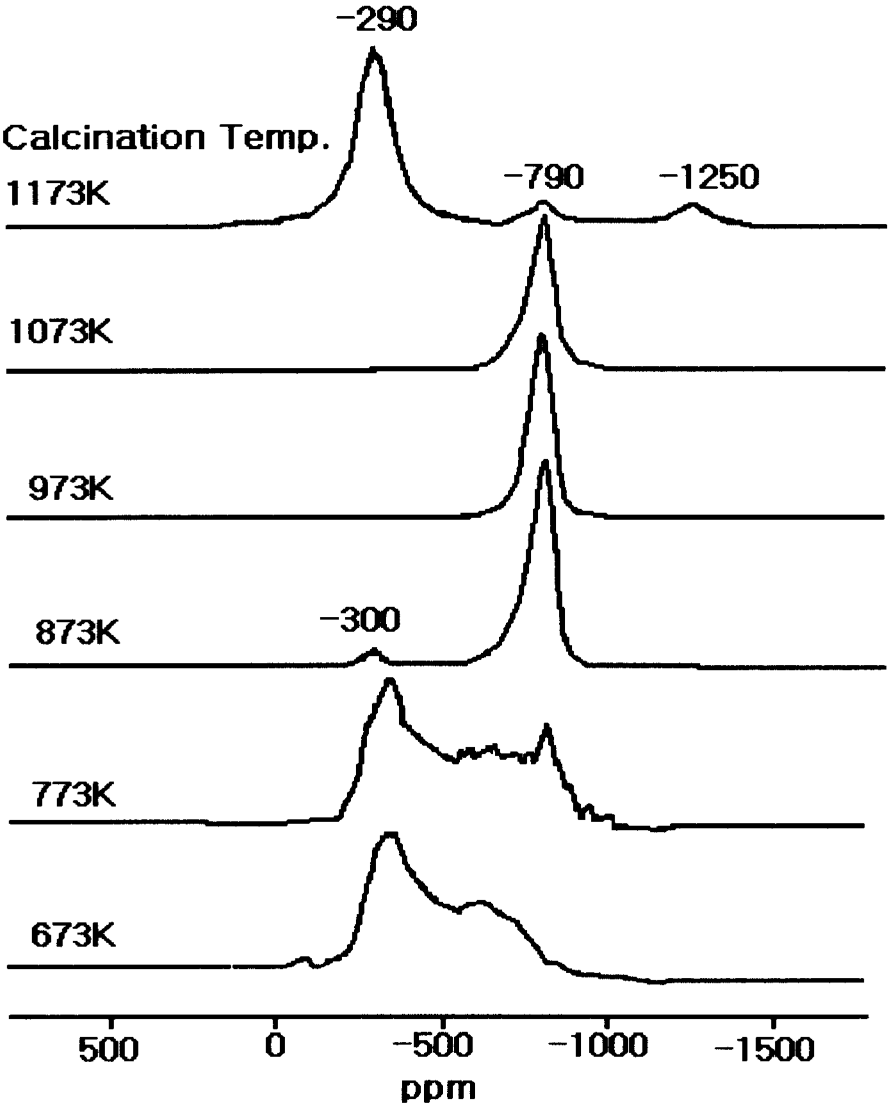

Fig. 4. Solid-state ^{51}V NMR spectra of 25-V_2O_5/TiO_2-ZrO_2 calcined at different temperature.

CONCLUSIONS

This paper has shown that ^{51}V solid-state NMR, can be used to perform the characterization of V_2O_5/TiO_2-ZrO_2 prepared by drying a mixed solution of ammonium metavanadate and $Ti(OH)_4$-$Zr(OH)_4$ and calcining in air. The interaction between vanadium oxide and titania-zirconia influences the physicochemical properties of prepared catalysts with calcination temperature. On the basis of the ^{51}V solid state NMR results, at low calcination temperature of 773 K vanadium oxide up to 10 w% was well dispersed on the surface of catalyst. A spreading of supported V_2O_5 at higher temperatures on TiO_2-ZrO_2 concluded from ^{51}V NMR experiments on V_2O_5/TiO_2-ZrO_2. Dehydration is accompanied by a decreased in coordination number from six to four, at higher V_2O_5 contents. In agreement with the proposed interpretation, three-fold (Line A, Line B and Line C)coordinated species observed at low V_2O_5 loadings do not undergo thermally induced changes.

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