Solid-State Vanadium-51 NMR Studies of Supported V_2O_5−WO_3/TiO_2 Catalysts

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Solid-state wide-line vanadium-51 NMR spectra of supported V_2O_5−WO_3/TiO_2 catalysts were obtained under ambient conditions. A distorted tetrahedral vanadium unit is favored at low vanadia loadings in the absence of tungsten oxide. Generally, addition of tungsten oxide to low loadings of vanadia supported on titania promotes the formation of a distorted octahedral vanadium species, while a distorted tetrahedral vanadium unit is also present. A distorted octahedral vanadium unit is favored on the surface at high vanadia loadings in both the presence and absence of tungsten oxide.

Introduction

Nitrogen oxides (NO_x) are a significant source of pollution which arise from stationary and automotive exhaust. Supported vanadia catalysts have proven to be effective for the selective catalytic reduction (SCR) of nitric oxide with ammonia in the presence of oxygen: $O_2 + 4NO + 4NH_3 \rightarrow 4N_2 + 6H_2O$. In particular vanadia supported on titania has exhibited superior catalytic reactivity and selectivity compared to vanadia supported on alumina and silica.[1]

Improvements in the catalytic performance and resistance to poisoning can be made by the addition of ions to the vanadia surface layer. Previous research has suggested that the addition of promoters such as tungsten oxide significantly enhances the catalytic performance of vanadia supported on titania while maintaining a high selectivity for NO conversion to N_2.[2,3] It has been reported that V_2O_5−WO_3/TiO_2 catalysts are more resistant to poisoning by alkali metal oxides, less reactive toward the undesired oxidation of SO_2, and are active in a wider operating temperature range than V_2O_5/TiO_2 materials.[4,5] Recent work has shown that the turnover frequency, which was defined as the molecules of NO converted per vanadium oxide site per second, was a factor of 10 higher for 1 wt % V_2O_5/7 wt % WO_3/TiO_2 than 1 wt % V_2O_5/TiO_2.[3] Other work has reported similar findings.[2]

Previous work has suggested that vanadium species such as V−O−V and V−OH, V═O, polymeric and monomeric vanadium species, or a O═V−O−V═O pyrovanadate structure are intimately involved in the SCR.[6−10] A dual-site mechanism involving a Brønsted acid site and a surface V═O bond has been proposed.[11,12] A study of tungsten oxide promoted V_2O_5/TiO_2 suggested that a dual site consisting of a surface vanadia redox center and a neighboring nonreducible tungsten site are involved in the SCR.[3]

The role of the vanadia surface structure in the SCR of NO with NH_3 has motivated a number of structural studies of V_2O_5/TiO_2-based catalysts. Generally, it has been demonstrated that the vanadium local coordination environment is not influenced by the crystallographic phase of the titania support, whereas the vanadia surface coverage, the presence of surface water, and/or the presence of surface additives promote the formation of different nearest neighbor vanadium environments.[13,14,17] A Raman spectroscopy study suggested that for 1 wt % V_2O_5 loadings on TiO_2 and under ambient conditions, addition of WO_3 to the vanadia overlayer resulted in the conversion of a tetrahedrally coordinated vanadium species to an octahedrally coordinated one.[15] The presence of WO_3 in catalysts with ≥4.5 wt % V_2O_5 under similar conditions did not influence the vanadium local coordination environment. The same work also suggested that at high tungsten loadings a moderately distorted tetrahedral vanadium structure became more abundant on the surface of dehydrated V_2O_5−WO_3/TiO_2 catalysts. More recent studies concluded that the addition of tungsten oxide to the surface had little influence on the ratio of polymerized to isolated vanadium species

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on a dehydrated surface.[3,16] A ^{51}V NMR study of 3 wt % V_2O_5/10 wt % WO_3 supported on $TiO_2-Al_2O_3$ suggested that both a tetrahedrally coordinated and an octahedrally coordinated vanadium species are present under ambient and dehydrated samples conditions.[17] A systematic study of the vanadium local environment as a function of V_2O_5 and WO_3 loadings on TiO_2 was not performed. Although these previous studies have provided useful insights concerning the vanadium surface structures, the influence of tungsten oxide on the local vanadium coordination environment has not been unequivocally established to date. We have employed solid-state ^{51}V nuclear magnetic resonance (NMR) spectroscopy to elucidate the local coordination environment as a function of vanadia and WO_3 loadings on TiO_2.

Solid-State Wide-Line Vanadium-51 NMR Spectroscopy. Although Raman and infrared (IR) spectroscopies have provided useful information concerning the structure of V_2O_5/TiO_2-based materials, these spectroscopies are not site specific and suffer from the inability to distinguish among the promoter oxide, vanadia, and titania. Solid-state NMR spectroscopy is highly ideal for examining the structure of supported vanadia materials for it is element specific and does not require the long range ordering of atoms as do diffraction methods. It is thereby, in principle, able to provide highly useful information about the immediate vanadium coordination environment in supported amorphous vanadia materials.

More specifically, solid-state ^{51}V NMR is ideal for the ^{51}V nucleus is 99.76% naturally abundant and has a high receptivity and a short spin−lattice relaxation delay. Field-dependent studies of supported vanadia catalyst samples and crystalline model compounds have demonstrated that the chemical shift anisotropy (CSA) dominates the central transition of the ^{51}V ($I = {}^{7}/_{2}$) resonance in diamagnetic solids at field strengths of 7 T or higher.[14,18−20]

Experimental Section

Catalyst Preparation and Characterization. Supported vanadium oxide on TiO_2 (Degussa P-25, 99.5% purity) materials were prepared by the incipient wetness impregnation method with an aqueous solution of NH_4VO_3 (Aldrich Chemical Co., 99.99% purity) The appropriate amount of NH_4VO_3 was dissolved in deionized water and slowly added dropwise to the titania. The impregnated samples were then dried at ∼120 °C for ∼12 h and calcined at 450 °C for 2 h. Incorporation of tungsten oxide into the vanadia layer was made by first dissolving an appropriate amount of ammonium metatungstate hydrate (Aldrich, 99.999% purity) in deionized water. The aqueous solution was then added dropwise to the appropriate V_2O_5/TiO_2 sample, thoroughly ground and mixed, and dried at ∼120 °C for ∼12 h. The samples were calcined at 450 °C for 2 h. Previous work has shown that this method incorporates tungsten oxide into the supported vanadia layer and that the order of impregnation does not influence the average local vanadium environment.[15]

X-ray powder diffraction (Scintag X1 powder diffractometer) results of the $V_2O_5-WO_3/TiO_2$ catalysts indicate that the TiO_2 support consists of both anatase and rutile phases of TiO_2. Extraneous diffraction peaks corresponding to crystalline precursor materials or other crystalline impurities were not observed.

Solid-State NMR. Solid-state ^{51}V NMR experiments were performed on a Chemagnetics CMX 300 spectrometer operating at 79.176401 MHz. Samples were packed in quartz ampules under ambient conditions. Spectra were subsequently acquired in the ambient. Previous solid-state ^{51}V NMR work has demonstrated that the single-pulse method with pulse lengths of 1 μs or less provides better relative signal quantitation than a quadrupolar echo sequence.[13] Therefore, wide-line spectra were acquired with a single pulse of 1 μs and recycle delays of 0.5−1 s. Nutation NMR of liquid $VOCl_3$ was performed. A 90° liquid pulse of 4 μs was determined. The 90° pulse length for $I = {}^{7}/_{2}$ corresponding to selective excitation of the central transition was therefore used (i.e., 1 μs). Possible saturation effects were verified by running a representative sample at 5- and 0.5-s recycle delays. Saturation effects were not observed. All measurements were executed with a 0.5-μs dwell time and an 8-μs preacquisition delay. Typically about 6 000 to 32 000 scans were acquired. All shifts are presented relative to liquid $VOCl_3$.

Results

The ^{51}V wide-line NMR spectra for the catalyst samples studied are presented in Figures 1−3. The nominally 1 wt % V_2O_5/TiO_2 sample (Figure 1a) shows a resonance with a maximum at −475 ± 10 ppm and a shoulder at approximately −300 ± 10 ppm. Addition of tungsten oxide to the vanadia surface to produce 1 wt % V_2O_5/3.5 wt % WO_3/TiO_2 produces a change in the corresponding ^{51}V spectrum. Two maxima are observed at −475 ± 10 ppm and −300 ± 10 ppm (Figure 1b). The spectrum of 1 wt % V_2O_5/7 wt % WO_3/TiO_2 (Figure 1c) is dominated by a nearly axial chemical shift powder pattern with the nearly degenerate perpendicular components of the chemical shift tensor, $\delta_{\perp}$, at −300 ± 10 ppm and the parallel component at approximately −1100 ppm. However, it is somewhat difficult to clearly discern the $\delta_{||}$ component from the baseline.

Figure 2 displays wide-line ^{51}V NMR spectra of catalyst samples with nominal 2 wt % V_2O_5 loadings and 0−7 wt % WO_3 loadings. The 2 wt % V_2O_5/TiO_2 sample shows maxima at −300 ± 10 ppm and −475 ± 10 ppm. A maximum at −300 ± 10 ppm with a shoulder at −475 ± 10 ppm is observed for 2 wt % V_2O_5/3.5 wt % WO_3/TiO_2, while a maximum at about −290 ± 10 ppm with a shoulder at roughly −475 ± 10 ppm is found for 2 wt % V_2O_5/7 wt % WO_3/TiO_2. It appears that an almost axial chemical shift powder pattern, with $\delta_{\perp}$ at approximately −290 to −300 and $\delta_{||}$ possibly at about −1100 ppm, dominates the spectra of 2 wt % V_2O_5/7 wt % WO_3/TiO_2 and, to a lesser extent, 2 wt % V_2O_5/3.5 wt % WO_3/TiO_2.

The spectra of high vanadia loadings are shown in Figure 3. The ^{51}V line shape for each of these samples is dominated by an almost axially symmetric shift tensor pattern with the nearly perpendicular components at −300 ± 10 ppm, while the parallel component appears to occur between −900 to −1100 ppm. However, it is difficult to clearly identify this component. The spectra of 4 wt % V_2O_5/TiO_2 and 4 wt % V_2O_5/3.5 wt % WO_3/TiO_2 each exhibit a shoulder at about −460 ± 10 ppm, while a shoulder is not detected for 4 wt % V_2O_5/7 wt % WO_3/TiO_2.

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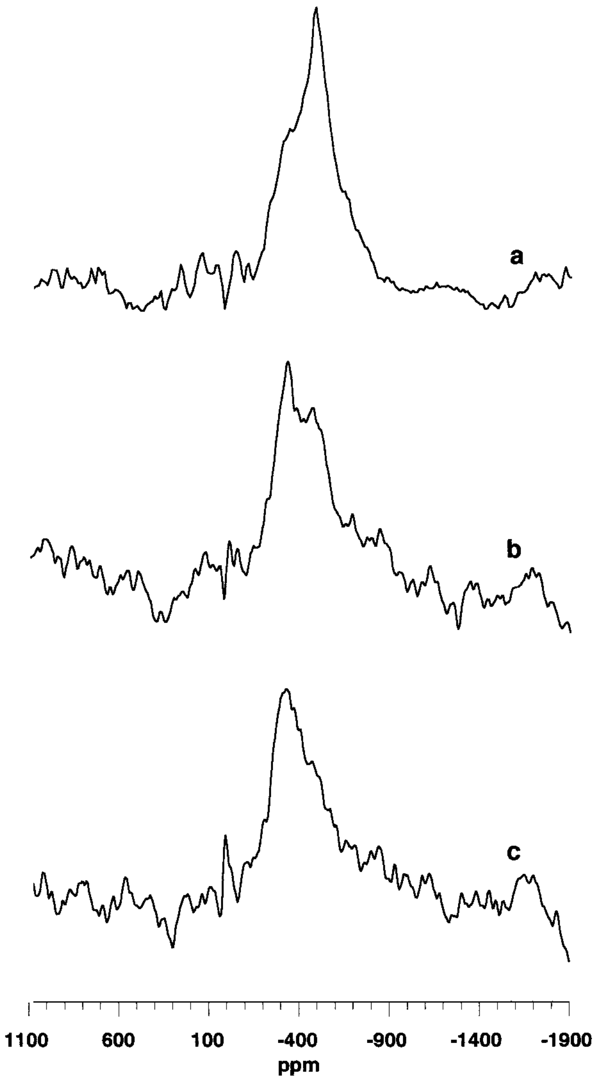

Figure 1. Solid-state ^{51}V NMR spectra of (a) 1 wt % V_2O_5/TiO_2, (b) 1 wt % V_2O_5/3.5 wt % WO_3/TiO_2, and (c) 1 wt % V_2O_5/7 wt % WO_3/TiO_2 obtained under ambient conditions. Nominal compositions are reported.

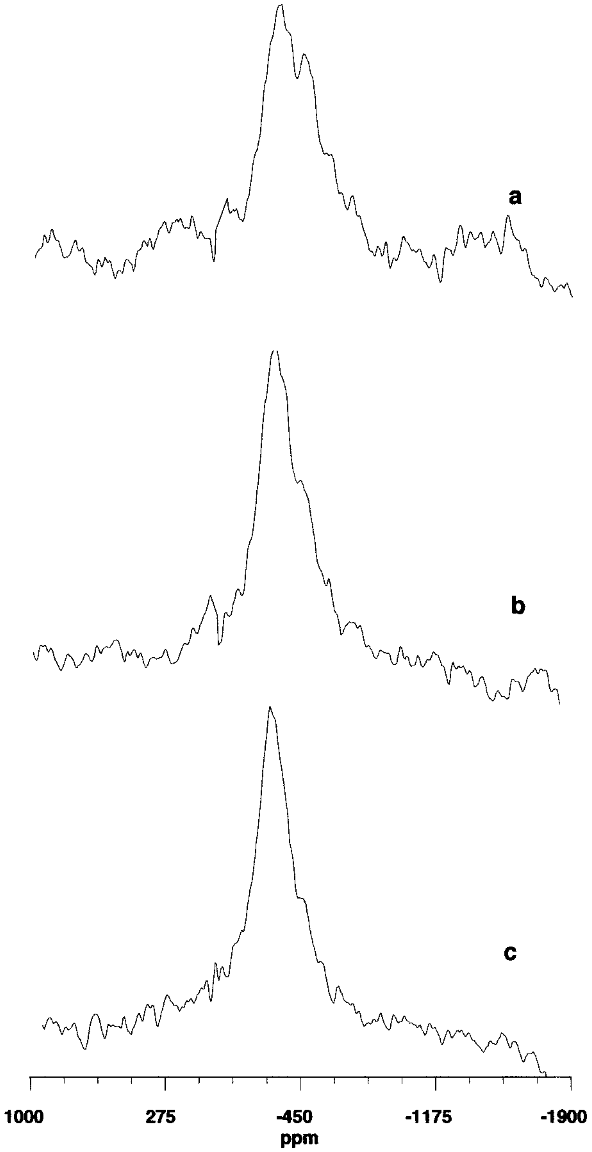

Figure 2. Solid-state ^{51}V NMR spectra of (a) 2 wt % V_2O_5/TiO_2, (b) 2 wt % V_2O_5/3.5 wt % WO_3/TiO_2, and (c) 2 wt % V_2O_5/7 wt % WO_3/TiO_2 obtained under ambient conditions. Nominal compositions are reported.

Discussion

As seen in Figures 1a, 2a, and 3a, the ^{51}V NMR wide-line spectra of V_2O_5/TiO_2 catalysts change as a function of vanadia loading under ambient conditions. Generally, the shape of each resonance and the maxima are consistent with those previous reported for V_2O_5/TiO_2.[13,14,21] All samples exhibit a maximum or shoulder at about -475 ppm and a component likely due to an almost axially symmetric shift tensor with $\delta_\perp = -300$ ppm. The maximum at approximately -475 ppm observed for 1 wt % V_2O_5/TiO_2 is most consistent with that assigned to a distorted tetrahedral vanadium unit in vanadia supported catalysts and crystalline model compounds, while the shoulder at about -300 ppm is assigned to the $\delta_\perp$ component of the almost axially symmetric chemical shift tensor arising from a distorted octahedral species.[13,14,21] The greater intensity of the -300 ppm component relative to the -475 ppm component, suggests that a greater concentration of a distorted octahedral vanadium species relative to a distorted tetrahedral vanadium unit exists on 2 wt % V_2O_5/TiO_2. At the highest vanadia loading studied, the line shape is dominated by a nearly axially symmetric shift tensor which suggests the presence of a distorted octahedral vanadium unit on the surface with perhaps a relatively minor concentration of a distorted tetrahedral species which is indicated by the shoulder at -475 ppm. The presence of a distorted tetrahedral vanadium unit at low vanadia loadings and the formation of a distorted octahedral vanadium species at higher coverages under ambient conditions are consistent with previously reported work.[13,14,21]

Addition of tungsten oxide markedly affects the vanadia wide-line spectra of samples with nominal compositions of 1 wt % V_2O_5. Addition of tungsten oxide to the vanadia overlayer results in a greater concentration of a distorted octahedral vanadium species and a smaller concentration of a distorted tetrahedral vanadium unit on the surface. This is suggested by the increased intensity of the $\delta_\perp$ component at about -300 ppm with a concomitant decrease in the intensity of the

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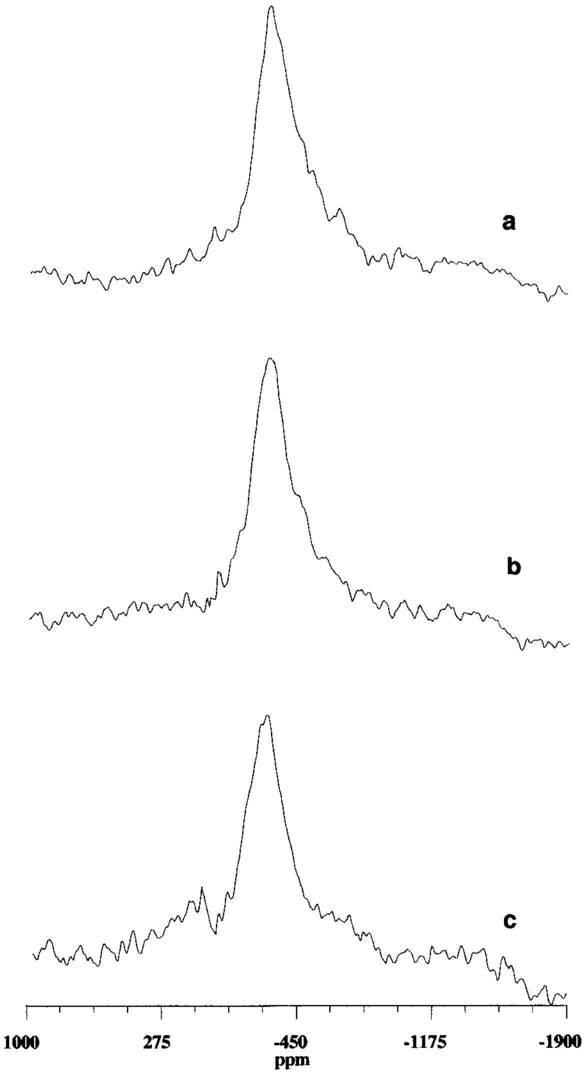

Figure 3. Solid-state ^{51}V NMR spectra of (a) 4 wt % V_2O_5/TiO_2, (b) 4 wt % V_2O_5/3.5 wt % WO_3/TiO_2, and (c) 4 wt % V_2O_5/7 wt % WO_3/TiO_2 obtained under ambient conditions. Nominal compositions are reported.

resonance at approximately −475 ppm for 1 wt % V_2O_5/3.5-wt % WO_3/TiO_2 (Figure 1b). The nearly axially symmetric shift tensor line shape and the shoulder at −475 ppm suggests that a distorted octahedral vanadium unit is the predominant vanadium structure on 1 wt % V_2O_5/7 wt % WO_3/TiO_2, while a distorted tetrahedral vanadium species is present but at a significantly smaller concentration.

The local vanadium environment found on the 2 wt % V_2O_5 series of samples is also modified by addition of tungsten oxide to the vanadia overlayer as indicated by the change in line shape (Figure 2). The maxima at approximately −300 ppm and −475 ppm observed for 2 wt % V_2O_5/TiO_2 (Figure 2a) suggest that both a distorted octahedrally coordinated vanadium unit and a distorted tetrahedrally coordinated vanadium species are present on the surface. The 2 wt % V_2O_5/3.5 wt % WO_3/TiO_2 contains a much larger concentration of a distorted octahedral vanadium unit which is suggested by the relatively strong intensity of the $\delta_\perp$ component at −300 ppm relative to the shoulder at approximately −475 ppm. For 2 wt % V_2O_5/7 wt % WO_3/TiO_2, the surface consists primarily of a distorted octahedral vanadium unit with a relatively small concentration of a distorted tetrahedral vanadium species as indicated by the strong $\delta_\perp$ component of the nearly axial shift tensor at −290 ppm and the relatively weak shoulder at −475 ppm (Figure 2c).

The ^{51}V resonance for each of the highest vanadia loadings examined is dominated by an almost axially symmetric shift tensor which suggests that the surface primarily consists of a distorted octahedral vanadium site (Figure 3). For 2 wt % V_2O_5/TiO_2 and 4 wt % V_2O_5/3.5 wt % WO_3/TiO_2 , a shoulder at about −460 ppm suggests that a distorted tetrahedral vanadium unit is also present on the surface, but in a smaller concentration than the distorted octahedral species.

Previous work has suggested that surface acidity influences the vanadium coordination environment.[22] In particular, addition of tungsten oxide increases the surface acidity under ambient conditions. This increase is proposed to favor octahedrally coordinated vanadium. Our results are consistent with this previous work.

Conclusions

Under ambient conditions, addition of tungsten oxide to vanadia supported on titania promotes the formation of a distorted octahedral vanadium species. At lower vanadia loadings a distorted tetrahedrally coordinated vanadium unit is also present on the surface with a distorted octahedral species in tungsten oxide promoted samples. A distorted octahedral vanadium unit is prevalent on the surface at high vanadia loadings in both the presence and absence of tungsten oxide.

Previous work on dehydrated samples has demonstrated that surface water influences the vanadium coordination environment.[14,16] At catalytic reaction temperatures of 200−500 °C the surface will become dehydrated and the vanadium coordination environment will then be modified. In situ measurements under catalytic reaction conditions should prove useful in elucidating the vanadium environment in vanadia supported on titania-based catalysts and will be one focus of our future efforts.

Vanadium-51 magic-angle spinning (MAS) NMR spectra may provide additional information concerning the local vanadium environment. Our current ^{51}V MAS NMR results suggest the presence of one vanadium site in the catalysts with the highest vanadium contents. Additional work in our laboratory is being performed.

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