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^{15}N NMR Study of the Adsorption of NO and NH_3 on Titania-Supported Vanadia Catalysts

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The adsorption of nitric oxide (NO) by ammonia over a series of V_2O_5/TiO_2 catalysts used for selective catalytic reduction (SCR) has been investigated by solid-state ^{15}N NMR. The chemistry and the surface acidity are found to vary dramatically as the weight loading of vanadia is increased from 0 to 10%. NO reacts over evacuated TiO_2 and V_2O_5/TiO_2 at room temperature to form nitrous oxide (N_2O). Over the V_2O_5/TiO_2 catalysts N_2 is also produced upon room temperature adsorption. The chemical shift of the terminal nitrogen of N_2O adsorbed on the catalyst is an indicator of the Lewis acid character of the surface. The Lewis acidity of the surface is found to decrease with the loading of V_2O_5 on the titania support. Ammonia adsorbs in two forms on evacuated TiO_2 and V_2O_5/TiO_2. These two forms differ in their surface mobility. The reaction of NO with NH_3 over the catalysts proceeds to a measurable degree at room temperature. N_2 is the predominant product; however, N_2O is also produced by the partial reduction of NO. Following preadsorption of ammonia, the chemical shift of the terminal nitrogen of N_2O is similar to that of samples with a high V_2O_5 loading regardless of the actual vanadia loading. This indicates that ammonia is adsorbed predominately on the Lewis acid sites of the catalyst, blocking the access of N_2O to these sites. © 1996 Academic Press, Inc.

INTRODUCTION

Nitrogen oxides (NO_x) are major pollutants emitted during many combustion processes. Among the various catalysts used for the removal of NO_x from stationary sources such as smokestacks titania-supported vanadia catalysts have proven to be the most effective (1–17). These catalysts are used commercially (1, 2) in SCR of nitrogen oxides by ammonia. Although it is generally accepted that the vanadia portion of the catalyst is essential for this reaction, the nature of the active sites and the mechanism of the reaction over the catalyst are quite controversial (1–28).

Inomata *et al.* (18) have found that the $V^{5+}{=}O$ sites are catalytically active toward the reaction of NO with NH_3 in the presence of oxygen over both bulk and supported V_2O_5. They further deduced from gas chromatography and infrared investigations that NH_4^+ acts as the active ammonia species. They proposed that the ammonium ion reacts with NO from the gas phase according to an Eley–Rideal mechanism. Gasior *et al.* (19) found this same mechanism by XPS and FT-IR measurements. Their results indicated that the SCR reaction proceeds via participation of ammonia adsorbed at Brønsted acid sites and the acidic VOH groups are the principal active sites for the SCR of NO.

On the basis of transient isotope studies, a dual-site mechanism for the reaction of NO and NH_3 in the presence of oxygen (20) has been proposed; two neighboring $V^{5+}{=}O$ groups participating as the active sites. Other results (21) indicate that ammonia oxidation and NO reduction are closely coupled over vanadium pentoxide catalysts and the sites that selectively reduce NO to N_2 are the V—O—V sites. V=O sites were found to promote direct oxidation of ammonia to NO and the formation of N_2O from NO and NH_3. Topsøe (22, 23) has suggested that the Brønsted acid sites on the vanadia–titania catalysts or the acidic V—OH groups are the principal reaction sites in SCR of NO_x. Their results also indicate that an interaction exists between the Brønsted and Lewis acid sites on the vanadia–titania surface or possibly a transformation between V—OH and V=O caused by the reagents during reduction by NH_3.

In contrast, Ramis *et al.* (24, 25) concluded that the reaction between ammonia and NO involves ammonia species coordinated to Lewis acid sites and not ammonium ions bonded to Brønsted acid centers.

Srnak *et al.* (26) have concluded from their TPR/TPD experiments that both Langmuir–Hinshelwood and the Eley–Rideal mechanisms are effective for the SCR of NO_x depending on the reaction conditions. They proposed that a key step in the reaction between NO_x and NH_3 might be activation of the adsorbed NH_3 species. Recently, Dumesic *et al.* (27) also proposed an activated ammonia species formed from adsorbed ammonia. This species subsequently reacts with NO.

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Although a variety of spectroscopic techniques have been used to study the SCR of NO_x by NH_3, infrared spectroscopy is the most common (1, 2). However, solid state NMR measurements of supported vanadium oxide catalysts have significantly contributed to the understanding of the molecular structure of these catalytic systems. Eckert and co-workers (28, 29) have used ^{51}V NMR to study the local environments of two dimensional vanadium (V) oxide surface layers on titania. Went and Reimer (30) have used *in situ* proton and deuteron NMR techniques to study the adsorption and desorption of ammonia as a function of temperature on titania supported catalysts. Mastikhin *et al.* (31, 32) have probed by ^{15}N NMR the Lewis acidity of heterogeneous catalysts with N_2O and have investigated the SCR of NO over ZSM-5 zeolites (33).

In this work we report the results of ^{15}N NMR on the reaction of NO and NH_3 with NO over TiO_2 and V_2O_5/TiO_2 catalysts with various loadings of vanadia. In this initial study, the interaction of these species with the surface is examined in the absence of oxygen. We show that, in addition to N_2, N_2O is formed over both titania and vanadia–titania catalysts. The change in the chemical shift of the terminal N of N_2O on the various catalyst surfaces provides insight into the Lewis/Brønsted acidity of the catalysts through the chemical shift of the terminal nitrogen. Ammonia is found to adsorb predominantly at the Lewis acid sites on the surface.

METHODS

Catalyst Preparation

The titania support was prepared from titanium isopropoxide according to the method described by Krishna and Bell (34). The resulting catalyst was anatase with a BET surface area of 81 m^2/g. Vanadia–titania catalysts with vanadia weight loadings of 0, 1, 3, 6, and 10% were prepared using incipient-wetness impregnation. For each sample, the amount of the ammonium metavanadate (NH_4VO_3, Aldrich 99%) required to give the desired weight percent of V_2O_5 was slowly added to a mixture of a stoichiometric amount of oxalic acid and water. The oxalic acid is partially dissolved in water at room temperature and completely dissolved when heated to 343 K with vigorous stirring. The resulting deep blue solution containing the complex $(NH_4)_2[VO(C_2O_4)_2]$ was cooled to room temperature and diluted to the appropriate volume determined by the incipient-wetness point of titania, 0.7 to 1.0 ml/g. This solution was then dispersed dropwise on the titania. The resulting mixture was ground slowly and dried in N_2 flow in an oven at 373 K overnight. In order to obtain a uniform distribution for those samples with 6 and 10 wt% V_2O_5 loading, two impregnations were performed with an intermediate drying period. The oven-dried powder was pelletized to particles having diameters ranging from 125 to 250 μm (125–60 mesh). The catalyst was then calcined in a quartz tube under oxygen flow at 150 cm^3/min for 4 h at 473 K, followed by 8 h at 733 K. The catalyst was then cooled in 50 cm^3/min oxygen flow to room temperature. The oxidized samples ranged in color from pale yellow (1 wt%) to brown (10 wt%). BET surface areas ranged from 81 m^2/g (1 wt%) to 72 m^2/g (10 wt%).

Preparation of Samples for NMR Analysis

About 0.20 grams of the V_2O_5/TiO_2 or TiO_2 sample was loaded into a 5mm NMR tube and ca. 50 mg of glass wool was placed on the top of the catalyst in order to prevent the sample from drawing up during evacuation and to maintain a safe distance between the catalysts and the flame during flame sealing. The tube was then mounted on a glass vacuum system and evacuated to a pressure of less than 1×10^{-5} Torr (1 Torr = 133.3 Nm^{-2}) during heating at 373 K.

For those samples exposed to NH_3, the sample was then subjected to about 50 Torr of $^{15}NH_3$ gas (Cambridge Isotopes). All adsorption processes were monitored using a capacitance manometer (MKS Instruments Inc.). When a stable pressure reading was obtained, the remaining gaseous $^{15}NH_3$ was pumped out. For reaction studies, approximately 40 Torr of ^{15}NO (Cambridge Isotopes) was introduced and allowed to react with the preadsorbed NH_3. The sample was then sealed while the tube was immersed in liquid nitrogen. Within our detection limits no other nitrogen oxides were present in the starting gases.

NMR Methods

^{15}N NMR measurements were carried out at 36.47 MHz on a Chemagnetic CMX-360 spectrometer, equipped with a double-resonance probe. Standard phase cycling and quadrature detection were employed. The 90° pulse width was 10 μs corresponding to a B_1 field of 25 kHz for ^{15}N with a repetition time of 10 s. The same pulse width was used for CP experiments with a contact time of 3 ms. The number of signal accumulations ranged from 1000 to 2000. To avoid baseline distortions due to electronic probe recovery, the first 20 μs of all free induction decays were removed prior to Fourier transformation. All chemical shifts were referenced to external ammonium nitrate ($^{15}NH_4NO_3$) and are reported to an accuracy of ± 1 ppm.

RESULTS

^{15}N NMR spectra of NO over V_2O_5/TiO_2 catalysts with V_2O_5 weight loadings ranging from 0 to 10 wt.% are shown in Fig. 1. We observe three resonances for each of the catalyst samples. By comparison of the shifts to those reported in the literature (31, 35), we can assign unambiguously the most deshielded peak at 286 ppm appearing in

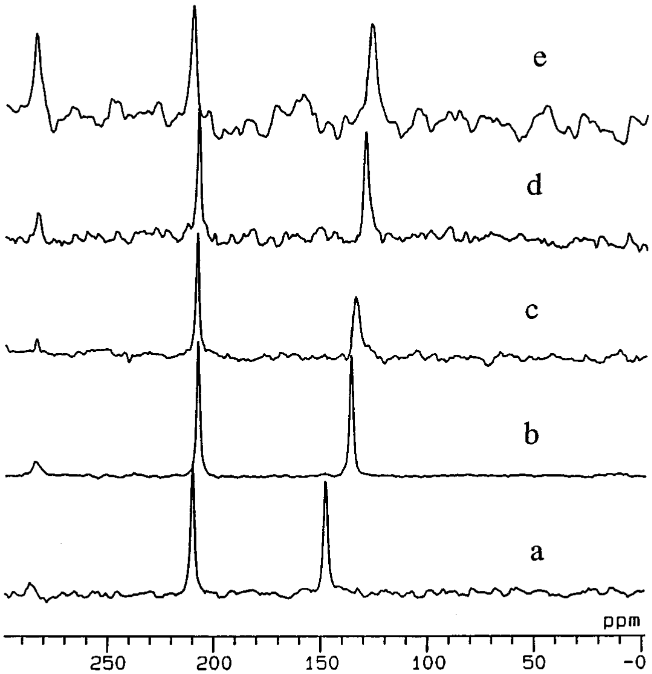

FIG. 1. ^{15}N NMR spectra of NO adsorbed on TiO_2 and V_2O_5/TiO_2 catalysts: (a) 0%, (b) 1%, (c) 3%, (d) 6%, (e) 10%.

all spectra to N_2, and the peaks at 212 ppm and 149 ppm in Fig. 1a to the central and terminal nitrogens of N_2O, respectively. The chemical shift of the central nitrogen remains nearly constant for all samples, changing by at most ±3 ppm. The chemical shift of the resonance assigned to the terminal nitrogen, however, changes with the nature of the support. Based upon the size of the NMR signals in Fig. 1 and their comparison to a standard sample we estimate that about 20 ± 5% of the NO is observable as either N_2 or N_2O following room temperature adsorption over all samples except the 10% V_2O_5/TiO_2, which converts approximately 15 ± 5%.

Ammonia was adsorbed on both TiO_2 and V_2O_5/TiO_2 catalysts at room temperature. The saturation adsorption levels of NH_3 on the catalysts were about 380 μmol of NH_3 per gram of catalyst. The loading of NH_3 on TiO_2 did not differ significantly from that on the V_2O_5/TiO_2 catalysts.

The ^{15}N NMR spectra of NH_3 adsorbed on 3% V_2O_5/TiO_2 at room temperature are shown in Fig. 2. Spectra 2a and 2b were obtained using single pulse and cross polarization experiments, respectively. The single pulse experiment shows one resonance at −9 ppm. This peak is much broader than those observed for N_2O. In the cross-polarization experiment a second broader peak is apparent, centered at 7 ppm. There are, thus, two different adsorption sites or adsorbed forms of NH_3. No drastic differences were observed for NH_3 adsorbed on the other V_2O_5/TiO_2 catalysts.

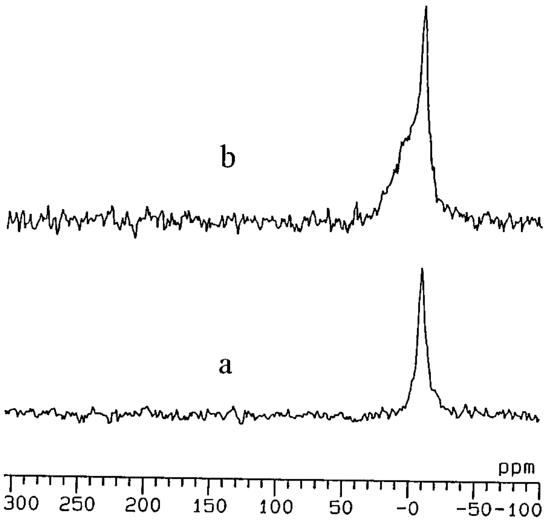

FIG. 2. ^{15}N NMR spectra of NH_3 adsorbed on $V_2O_5(3\%)/TiO_2$ catalysts at room temperature: (a) single pulse, (b) cross-polarization.

V_2O_5/TiO_2 catalysts, previously dosed with NH_3, were exposed to 40 Torr of NO. Only a small pressure drop is observed during reaction, corresponding to 10 μmol gas/gram of catalysts. The color of the samples, however, changes dramatically from yellow to a whitish-gray. The ^{15}N NMR spectra of representative samples are shown in Fig. 3. Figure 3a is a sample of TiO_2 and no significant

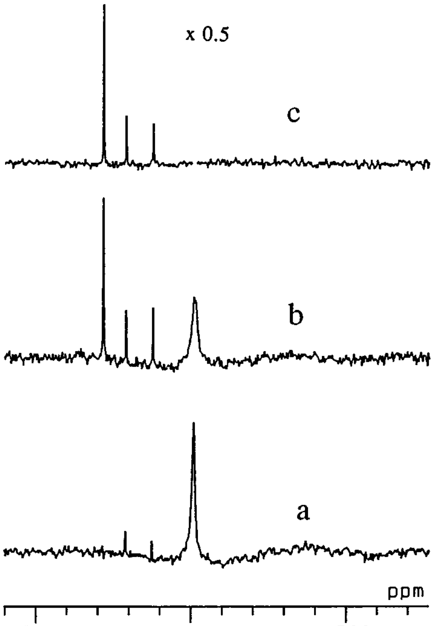

FIG. 3. ^{15}N NMR spectra of NO and NH_3 over TiO_2 and V_2O_5/TiO_2 catalysts: (a) TiO_2, (b) $V_2O_5(6\%)/TiO_2$ at room temperature 12 h after NO induction, (c) after heating at 373 K for 2 h.

amount of N_2 is observed. The two resonances in Fig. 3a correspond to the central nitrogen (211 ppm) and the terminal nitrogen (125 ppm) of N_2O. Figure 3b shows a sample of 6% V_2O_5/TiO_2. An intense peak due to N_2 is observed, as well as small resonances due to N_2O. When the sample is held at 373 K the peak at −9 ppm due to NH_3 nearly disappears, while the intensity of the peak for N_2 increases (Fig. 3c).

DISCUSSION

The room temperature adsorption of NO on all evacuated catalysts shows resonances for only N_2 and N_2O (Fig. 1). At room temperature ^{15}NO is paramagnetic and, therefore, NMR inactive. The resonance for the terminal nitrogen of N_2O is strongly dependent upon the support. This provides strong evidence that the bonding of N_2O to the surface involves a strong contribution from the N side. This result does not, however, rule out any contribution from the O side to the surface bonding of the molecule on the time scale of the NMR experiment. The change in shift with the nature of the catalyst surface may be attributed to the varying acidic character as one incorporates increasing amounts of V_2O_5 onto the TiO_2 surface. It has been reported (31, 32) that interaction of N_2O with Lewis acid sites results in a downfield shift of the terminal nitrogen of N_2O, while interaction with Brønsted acid sites has little effect on the shift. In Fig. 1a, the terminal nitrogen has a chemical shift of 149 ppm, in agreement with the predominantly Lewis acid nature of anatase TiO_2. As the loading of V_2O_5 increases, the shift gradually moves upfield, eventually reaching 125 ppm for 10% V_2O_5 loadings. From this result it appears that the Lewis acidity of the surface is decreasing with increased V_2O_5 loading. A slight increase in linewidths with V_2O_5 loading is also noted in Fig. 1. This increase is presumably due to decreased mobility of the adsorbed N_2O since both the terminal and central resonance are broadened. In addition room temperature ESR spectra of these unreduced catalysts revealed no paramagnetic species.

Although the intensity of the peak due to N_2 increases with V_2O_5 loading, the selectivity of the catalyst to N_2 is still very low without coadsorption of NH_3. All catalysts show a rather low ratio of N_2 production relative to N_2O.

Ramis *et al.* (24, 25) have reported that N_2O is formed upon NO adsorption on pure titania, but not on evacuated V_2O_5/TiO_2 surfaces. They argued that Ti^{3+} ions were the reaction centers and that these exist only on the evacuated titania surface, not on the evacuated vanadia–titania surface. Our data show clearly that N_2O is formed not only on the pure titania surface, but also on the various vanadia–titania surfaces. The presence of Ti^{3+} ions on the surface of TiO_2 and other oxides is well known (36). V_2O_5 and TiO_2 are both *n*-type semiconductor oxides, and as such, they lose oxygen upon heating with an accompanying reduction of some Ti^{4+} to Ti^{3+} or V^{5+} to V^{4+}. V^{4+} centers are good candidates for the reaction center. The formation of N_2O under our experimental conditions is likely to involve a mechanism similar to that of NO photodecomposition (37, 38), involving reduced metal ions:

$$2Ti^{3+} + 2NO \rightarrow 2\,Ti^{4+} + O^{2-} + N_2O$$

or

$$2V^{4+} + 2NO \rightarrow 2\,V^{5+} + O^{2-} + N_2O.$$

Our preliminary ESR results show that all of the evacuated V_2O_5/TiO_2 catalysts give rise to V^{4+} centers.

The adsorption of NH_3 on the evacuated catalysts shows primarily a single resonance at −9 ppm (Fig. 2). The line width of this peak indicates that NH_3 is rather strongly anchored to the surface and has restricted mobility. It is, however, by no means rigid. The single pulse NMR experiment reveals all of the NH_3 on the surface, while the cross-polarization experiment emphasizes the more rigidly held adsorbates. In the cross-polarization experiment a second form of ammonia is clearly evident. This second species has a slightly different chemical shift (+7 ppm) and a greater line width. All catalysts showed two adsorbed forms of NH_3 by ^{15}N NMR. There are, thus, two different adsorption sites or adsorbed forms of NH_3 on all of the catalysts. No drastic differences in shifts or linewidths were observed for the various catalysts. We rule out, therefore, the possiblity that these two lines represent ammonia adsorbed at Brønsted and Lewis acid sites, since the proportion of these sites should change dramatically between catalysts. It is possible that these two forms correspond to the active and inactive forms of ammonia proposed by Dumesic *et al.* (27). The species having the greater line width is more strongly held to the surface. This species differs more from physisorbed NH_3 than the narrow line in both shift and line width. This makes it the more likely candidate for the active form. Further work is necessary to confirm this hypothesis.

On these evacuated surfaces, TiO_2 adsorbs roughly the same amount of NH_3 as V_2O_5/TiO_2. This is in contrast to the report (39) that a significantly lower amount of NH_3 is adsorbed on evacuated TiO_2 than on the supported catalysts.

While several authors (5, 40) have reported the formation of N_2O due to the direct oxidation of NH_3 at higher temperature over these catalysts, we found no evidence of N_2O following heating of these samples loaded only with NH_3 to 423 K.

When NO was exposed to TiO_2 predosed with NH_3 (Fig. 3a) only two resonances corresponding to N_2O are observed. Thus at room temperature TiO_2 is catalytically inactive for the SCR of NO by NH_3. This observation is consistent with reports in the literature (2). It is interesting to note that the chemical shift of the terminal nitrogen over the TiO_2 catalyst has shifted upfield by over 20 ppm relative to its position in the absence of the preadsorbed NH_3. Because the greater downfield shift observed for the terminal nitrogen on TiO_2 not dosed with NH_3 is due to interaction of N_2O with Lewis sites, these sites must not be available on TiO_2 that has been dosed with NH_3. NH_3 must, therefore, preferentially adsorb on the Lewis sites of the titania surface.

NO reacts with preadsorbed NH_3 on 6% V_2O_5/TiO_2 at room temperature (Fig. 3b), giving an intense peak from N_2. This peak grows with time and a concurrent decrease in the intensity of the ammonia resonance is observed. At higher temperatures this occurs far more rapidly (Fig. 3c). N_2O is also observed over all V_2O_5/TiO_2 catalysts. The origin of the N_2O in these coadsorption experiments will be the subject of a later paper. The chemical shift of the terminal nitrogen of N_2O is always close to that of the samples with 6% vanadia loading. Thus, ammonia prefers to adsorb predominately on the Lewis sites of the V_2O_5/TiO_2 catalysts. Intermediates such as NH_2NO, have been reported (41) during this reaction at between 573 K and 673 K. Our ^{15}N NMR experiments do not reveal the presence of such species at room temperature, however, they may exist in quantities too small for observation by ^{15}N NMR, or their lifetimes may be too short for observation on the NMR timescale.

As mentioned previously, the V_2O_5/TiO_2 catalysts undergo a color change from yellow to white grey during SCR. This color change is reversible by exposure of the catalyst to O_2 or air. It appears that in the absence of O_2, surface vanadium atoms are undergoing a reduction during SCR. We are investigating this further by ESR.

CONCLUSIONS

Exposure of evacuated TiO_2 and V_2O_5/TiO_2 catalysts to NO results in the production of N_2O. N_2 is also formed in significant amounts over the vanadia-containing catalysts, but not over TiO_2. The ^{15}N chemical shift observed for the terminal nitrogen of N_2O suggests that the Lewis acidity of the V_2O_5/TiO_2 surfaces decreases with the loading of vanadia.

NH_3 adsorbs readily on both TiO_2 and V_2O_5/TiO_2. Two forms of NH_3 are revealed by ^{15}N NMR upon adsorption of ammonia. These two types differ in their mobilities, one being more strongly held to the surface. NH_3 adsorbs preferentially at Lewis acid sites, preventing N_2O adsorption at those sites.

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