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# Influence of Water on the Reactivity of Vanadia/Titania for Catalytic Reduction of $NO_x$

The increasing global concern in the recent years over air pollution problems caused by $NO_x$ emission has brought forth extensive research on $NO_x$ reduction. The most important current process used to remove $NO_x$ from flue gas is the selective catalytic reduction (SCR) of $NO_x$ by $NH_3$. Titania-based vanadia catalysts (*1*) are most often used today, due to their SCR activity and resistance to $SO_2$ poisoning (*2, 3*). Numerous studies on this and similar catalyst systems have been reported in the literature in the last few years, as reviewed recently (*1*). Many of these studies have been aimed at understanding the surface properties and reactivity of these catalysts under industrial $DeNO_x$ reaction conditions. However, most of these studies have been carried out in the absence of water, which is usually present in flue gas. Thus, there is a need to study the effects of water on the catalyst itself and on the catalyst activity and selectivity. Accordingly, we report the results of catalytic activity and *in situ* FTIR studies, which have been carried out on a vanadia/titania catalyst with and without water in the feed gas, as well as some results from vacuum temperature-programmed desorption studies.

Vanadia/titania catalysts with different vanadia loadings were used in the catalytic activity and FTIR studies. We report here the results on a 6% vanadia/titania catalyst that was prepared by impregnating $TiO_2$ in the anatase form (90 $m^2/g$) with an oxalic acid solution of ammonium metavanadate followed by drying and calcination for 1 h at 673 K. The ground catalyst sample of 170 mg was then pressed into a self-supporting wafer and mounted into a quartz *in situ* IR cell/reactor for combined activity and *in situ* IR experiments. These studies were carried out at atmospheric pressure by combining a gas feed system to the *in situ* IR cell/reactor and a mass spectrometer (Balzers QMG420). This arrangement, described in detail previously (*4*), allowed simultaneous measurements of the surface adsorbed species and the concentration of the reactants and products. The gas feed system allowed gas mixing and water dosing capabilities and provided feed gas of the desired composition and flow rate. The gas mixture used in the present study consisted of 340 ppm NO, 500 ppm $NH_3$, 8% $O_2$ (1.7% $H_2O$ in the case of wet feed gas), and balance Ar. The IR spectra were recorded on a Digilab FTS80 FTIR spectrometer with an MCT (Mercury–Cadmium–Telluride) detector at a spectral resolution of 4 $cm^{-1}$. The mass spectrometer data were quantitatively analyzed using the fragmentation patterns determined experimentally from calibration gases. Water was calibrated by passing a known amount of water vapor mixed with Ar through the mass spectrometer.

The apparatus used for temperature-programmed desorption studies, as described elsewhere (*5*), consisted of a high-capacity ion pump and titanium sublimation pump combination connected to an ultra-high-vacuum stainless-steel chamber via a poppet valve. A mass spectrometer, Auger electron spectrometer, Ar sputtering gun, ionization gauge, and gas dosers were connected to a gas delivery system. Desorption spectra were obtained at a heating rate of typically 20 K/s.

The samples for the TPD studies consisted of about four monolayers of vanadia on a 100- to 200-nm rutile surface deposited on a 0.25-mm-thick plate of tungsten. Car-

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bon contaminants were removed by heat treatment (at ~1000 K) in the UHV chamber in oxygen at a pressure of $10^{-5}$–$10^{-7}$ Torr. Surface cleanliness was confirmed with AES and the crystalline structure was checked by X-ray diffraction. The temperature was measured by a thermocouple spot-welded to the back of the sample. Before each TPD experiment, where the adsorption temperature was about 100 K, the sample was oxidized in $10^{-5}$–$10^{-7}$ Torr of $O_2$ at 650 K for 30 min. It should be noted that since the higher SCR activity reported for anatase vs rutile-supported vanadia (see, e.g., Ref. (*1*)) is mainly attributed to a higher active surface area for the former catalyst (*6–8*), the essential surface chemistry of the active sites is expected to be similar.

Reaction kinetic studies were conducted in a glass tube plug flow reactor. The concentration of NO was measured with a ThermoElectron Model 10 chemiluminescent analyzer, whereas the $N_2O$ concentration was analyzed on a gas chromatograph using a Porapak Q column. The feed gas used in the present experiments consisted of 500 ppm $NO_x$, 535 ppm $NH_3$, 1000 ppm $SO_2$, 4.6% $O_2$ (5% $H_2O$ in the case of wet feed gas), and balance $N_2$.

The catalytic activity results from the laboratory plug flow reactor on a 6% vanadia/titania catalyst showing the effects of water are summarized in Fig. 1, where the rate of $NO_x$ reduction (mol/h/g) and the $N_2O$ concentration are plotted against the reaction temperature. It can be seen that, in the presence of water, the $NO_x$ conversion is slightly lower than in the dry feed gas at reaction temperatures lower than 663 K. Furthermore, while the catalytic activity reaches a maximum at 630 K in the dry gas, the activity seems to approach first a maximum value at higher temperatures in the wet feed gas. It is also seen that the formation of $N_2O$ is negligible under the wet reaction condition as compared to that under the dry condition, where a $N_2O/NO_x$ ratio between 0.04 to 0.2 is found in the temperature range of 593 and 673 K. Unlike NO, the $N_2O$ could not be reduced by $NH_3$ under similar experimental conditions.

Temperature-programmed desorption spectra for $NH_3$ and $H_2O$ from the vanadia/titania surface are shown in Fig. 2. It can be seen that the rate of $NH_3$ desorption shows maxima at temperatures of 170 and 340 K, whereas $H_2O$ desorbs at 200 and 275 K. Desorption activation energies can be estimated from these peak temperatures, assuming a standard value of $10^{13}$ $s^{-1}$ for the preexponential factor. The high-temperature state of ammonia is found to adsorb more strongly (105 kJ/mol) than the high-temperature state of water (71 kJ/mol). The difference in the heats of adsorption between $NH_3$ and water is 33 kJ/mol, and this leads to a factor of about $10^3$ in the ratio between the corresponding adsorption equilibrium constants at 573 K. Temperature-programmed desorption studies of $N_2O$ from the vanadia/titania sample showed a peak temperature near 150 K. Thus, $N_2O$ is adsorbed more weakly than either $NH_3$ or $H_2O$ on vanadia/titania.

Figure 3 shows IR spectra of the catalyst (with the background spectrum of the sample in Ar flow at the same temperature subtracted) during the SCR reaction at 573 K in the wet feed gas mixture (with 1.7% water) versus that in the dry gas mixture. The spectra show mainly the absorption bands due to N–H stretching vibrational modes in the high-frequency region and the corresponding N–H deformation modes in the lower-frequency region. In the high-frequency region, broadbands at 3019 and 2808 $cm^{-1}$ are due to the stretching vibration of $NH_4^+$, whereas the bands at 3364 and 3334 $cm^{-1}$ are attributed to the stretching vibrational frequencies of the coordinated $NH_3$ (*9, 10*). The corresponding deformation band for $NH_4^+$ species appears at 1419 $cm^{-1}$, whereas those for the coordinated $NH_3$ are observed at 1606 and 1237 $cm^{-1}$. The spectra also show negative band area in the high-frequency region, with an isolated negative band at 3640 $cm^{-1}$. This behavior reflects the disappearance of surface hydroxyl

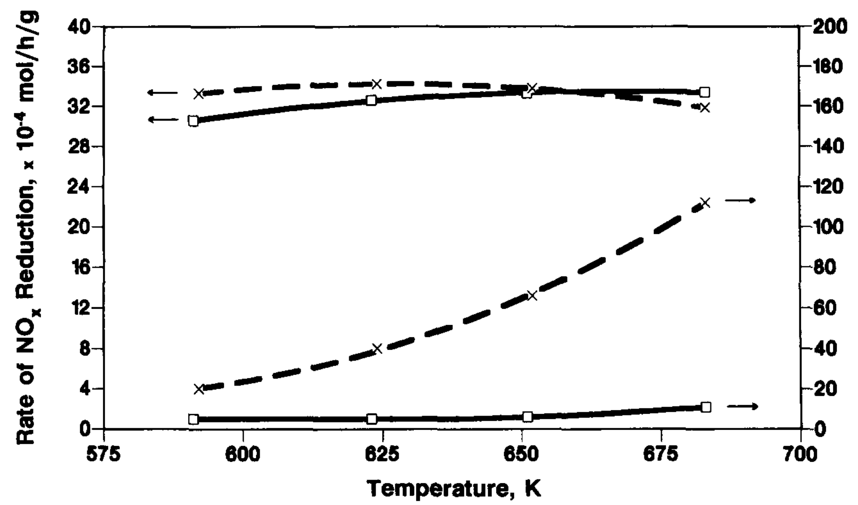

FIG. 1. Rate of $NO_x$ reduction and $N_2O$ concentration on the 6% vanadia/titania versus reaction temperature. The solid and stippled curves are obtained in the wet and dry feed gas, respectively.

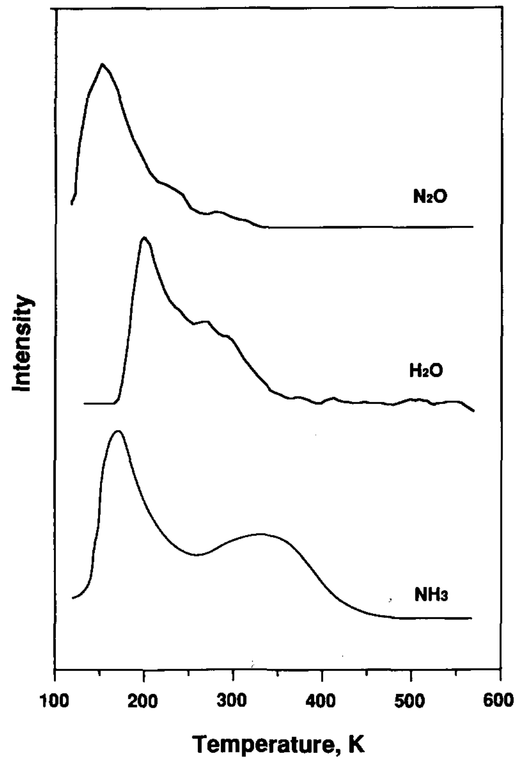

FIG. 2. Vacuum temperature-programmed desorption spectra of $N_2O$, $H_2O$, and $NH_3$ from vanadia/titania at heating rates 20, 23, and 7 K/s, respectively.

groups on the surface (*10*). A comparison of the two spectra recorded during reaction in the dry gas mixture (Fig. 3a) and in the feed gas containing water (Fig. 3b) shows a significant enhancement by water in the ammonia absorption band intensity. The difference spectrum (Fig. 3c) between the two spectra further indicates that the major spectral difference caused by the presence of water is an increase in the concentration

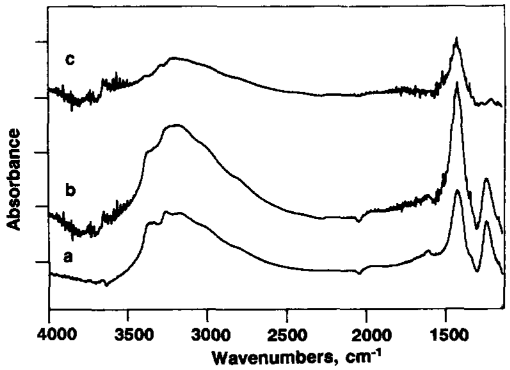

FIG. 3. *In situ* FTIR spectra of the 6% vanadia/titania during $NO_x$ reduction reaction at 573 K under (a) dry, and (b) wet conditions (background spectrum of the sample prior to reaction subtracted). (c) Difference spectrum between (b) and (c).

of surface $NH_4^+$ species. Thus, this result shows that water apparently hydroxylates the surface forming Brønsted acid sites. There is no evidence of water blocking the Brønsted acid sites, as also observed before (*10*). This result is consistent with the above TPD findings that ammonia is adsorbed more strongly than water on the vanadia/titania surface.

A closer examination of the V═O overtone band region (2000–2060 $cm^{-1}$) shows that both the V═O overtone band intensity and frequency are slightly lower for the sample in the wet gas mixture. The decrease in the band frequency is likely due to a weakening of the V═O bond associated with surface hydroxylation, as suggested earlier (*10, 11*) and also evidenced above in the increase of Brønsted acid sites. Furthermore, the IR spectra also revealed traces of $N_2O$, as reflected by the appearance of a weak absorption band at 2224 $cm^{-1}$ (discernible upon expansion of the absorbance scale), adsorbed on the catalyst surface under the dry gas reaction conditions. No such band could be detected when water was present in the reaction gas. This result indicates that water inhibits the reduction of NO to $N_2O$ on the vanadia/titania catalyst surface, which is in agreement with the behavior observed in the separate reactor studies discussed above. Since the TPD studies indicated that water adsorbs more strongly than $N_2O$ on vanadia/titania, fewer sites should be available for $N_2O$ adsorption in the presence of water; therefore, the role of water appears to be the inhibition of $N_2O$ formation in contrast to the enhancement of $N_2O$ consumption by readsorption and subsequent reaction. This idea is confirmed by the observation from the present kinetic investigation, where $N_2O$ is found not to be reduced by $NH_3$ under typical $NO_x$ reduction conditions.

From the analysis of the concentration of the reactants and products, a lower $NO_x$ conversion is found at 573 K for the feed gas containing water. The observation that a higher surface concentration of $NH_4^+$ showed a lower activity for SCR suggests that the adsorption of $NH_3$ on the surface cannot be the rate-limiting step in the reaction mechanism. It has been suggested in the literature (*12*) that the reaction of nitric oxide with adsorbed ammonia is a critical step in the SCR reaction. The fact that the catalytic activity decreased in the presence of water, despite the increase in the extent of ammonia adsorption on Brønsted acid sites, indicates that this slow step must be affected by water. A possible explanation for the influence of water on the catalytic activity and selectivity may be proposed by analogy with the dehydrogenation and dehydration of formic acid on oxides (*13*), where both reaction temperature and water vapor can affect the selectivity. Thus, in the SCR reaction, a reactive intermediate such as $NH_xNO$, formed from reaction between nitric oxide and surface adsorbed ammonia can either dehydrogenate or dehydrate to form $N_2O$ or $N_2$, respectively, depending on the extent of surface hydroxylation by water. This behavior is depicted in the following:

$$N_2O \underset{\text{dehydrogenation}}{\overset{\text{dry}}{\rightleftharpoons}} NH_xNO \underset{\text{dehydration}}{\overset{\text{wet}}{\rightleftharpoons}} N_2$$

In summary, water is found to adsorb on the surface more weakly than ammonia and it does not inhibit the adsorption of ammonia on the vanadia surface under SCR reaction conditions. Furthermore, water hydroxylates the surface leading to more Brønsted acid sites, which interact with ammonia. In addition, water appears to inhibit slightly the overall catalytic activity for SCR at temperatures lower than 663 K, while preventing the formation of $N_2O$. The latter effect seems to be associated with the surface hydroxylation by water, which promotes dehydration leading to the formation of $N_2$. The important catalytic implications of these findings are that the adsorption of ammonia cannot be a rate-limiting step in the SCR reaction and that water inhibits $N_2O$ formation on the surface.

## REFERENCES

*1.* Bosch, H., and Janssen, F., *Catal. Today* **2,** 369 (1988).

2. Reh, L., *Petrochem.* **39,** 182 (1986).
3. Morikawa, S., Yoshida, H., Takahashi, K., and Kurita, S., *Chem. Lett.,* 251 (1981).
4. Topsøe, N., and Topsøe, H., *Catal. Today* **9,** 77 (1991).
5. Raupp, G. B., and Dumesic, J. A., *J. Catal.* **95,** 587 (1985).
6. Inomata, M., Mori, K., Miyamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **87,** 754 (1983).
7. Pearson, I. M., Ryu, H., Wong, W. C., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **22,** 381 (1983).
8. Murakami, Y., Inomata, M., Mori, K., Ui, T., Suzuki, K., Miyamoto, A., and Hattori, T., *in* "Preparation of Catalysts III" (G. Poncelet, P. Grange, and P. A. Jacobs, Eds.), p. 531. Elsevier, Amsterdam, 1983.
9. Busca, G., *Langmuir* **2,** 577 (1986).
10. Topsøe, N., *J. Catal.* **128,** 499 (1991).
11. Schraml-Marth, M., Wokaun, A., and Baiker, A., *J. Catal.* **124,** 86 (1990).
12. Inomata, M., Miyamoto, A., and Murakami, Y., *J. Catal.* **62,** 140 (1980).
13. Mars, P., Scholten, J. J. F., and Zwietering, P., "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 14, p. 35. Academic Press, New York, 1963.

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