

## NOTE

# The Selective Catalytic Reduction of $\text{NO}_x$ with $\text{NH}_3$ over Titania Supported Rhenium Oxide Catalysts

Titania supported vanadium oxide catalysts have been demonstrated to be very efficient catalysts for the selective reduction of  $\text{NO}_x$  with  $\text{NH}_3$  and have found widespread industrial application for the control of  $\text{NO}_x$  emissions from stationary sources (1). Characterization studies have demonstrated that supported vanadium oxide catalysts consist of a two-dimensional metal oxide overlayer on the oxide support substrate (2–5). The surface vanadia overlayer consists of redox and acid sites that are critical for the efficient selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  (6–8). The titania support is superior to other oxide supports (e.g., alumina, silica, etc.) for the SCR of NO with  $\text{NH}_3$  primarily because of its ability to simultaneously enhance the redox properties of the surface vanadia species (5, 9, 10), stabilize surface acid sites in the surface vanadia overlayer (5–8), and remain resistant to corrosive gases such as  $\text{SO}_2/\text{SO}_3$  that are typically present in industrial environments (1). Consequently, there have been numerous studies investigating the SCR of NO with  $\text{NH}_3$  with other surface metal oxides on titania:  $\text{MoO}_3$  (11),  $\text{WO}_3$  (12–14),  $\text{CrO}_3$  (15),  $\text{Nb}_2\text{O}_5$  (16, 17), and  $\text{SO}_x$  (8, 18). The above supported metal oxide catalyst systems, however, have generally been less active and selective for the SCR of NO with  $\text{NH}_3$  than the efficient titania supported vanadia catalyst.

A titania supported catalyst that possesses very active redox sites (19, 20) and surface acid sites in the metal oxide overlayer (21) is the titania supported rhenium oxide system. However, there have been no SCR of NO with  $\text{NH}_3$  studies on this catalytic system to date. The redox properties of titania supported metal oxide catalysts were probed by methanol oxidation and follow the trend  $\text{Re} \sim \text{V} \gg \text{Cr} \sim \text{Mo} \gg \text{Nb}$ , W, and S (8, 19, 22, 23), which reveals that surface rhenia and vanadia species possess comparable redox activities toward methanol. The selectivities for redox products were in excess of 90% for both surface rhenia and vanadia species on titania, but formaldehyde was exclusively formed with vanadia and formaldehyde as well as methylformate (approximately 3:1 ratio) were formed with rhenia (9, 20). The distribution of surface Lewis and Brønsted acid sites for these two systems are also very similar as a function of surface coverage: the concentration of surface Lewis acid sites decreases and the concentration

of surface Brønsted acid sites increases with coverage (21, 24). The molecular structures of the surface rhenia species on titania, as well as other supports, have been extensively characterized with Raman and IR spectroscopy and consist of isolated surface  $\text{S-O-Re(=O)}_3$  species (complete absence of  $\text{Re-O-Re}$  vibrations at  $\sim 200$  and  $\sim 450 \text{ cm}^{-1}$ ), where S is the support cation (25). Two slightly different isolated surface rhenia species are observed as a function of coverage and give rise to  $\text{Re=O}$  symmetric stretches at  $1004\text{--}1006$  and  $1009\text{--}1011 \text{ cm}^{-1}$ . The isolated surface metal oxide species is unique for the titania supported rhenia system since other supported metal oxide systems typically contain a mixture of isolated and polymerized surface metal oxide species (3, 4, 19, 23, 25). For example, titania supported vanadia catalysts possess surface  $\text{VO}_4$  units that exhibit Raman bands at  $1027\text{--}1031 \text{ cm}^{-1}$  and  $920\text{--}950 \text{ cm}^{-1}$  due to terminal  $\text{V=O}$  and polymeric  $\text{V-O-V}$  functionalities, respectively (3, 4). Thus, the high redox activity, the surface acidity characteristics, and the isolated nature of the surface rhenia species on titania allow this catalyst to serve as a model system that can provide additional insight into the nature of the surface sites involved in the selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$ .

The  $\text{Re}_2\text{O}_7/\text{TiO}_2$  catalysts were prepared by the incipient-wetness impregnation of a 60–70% aqueous solution of perrhenic acid,  $\text{HReO}_4$  (Alfa), on  $\text{TiO}_2$  (Degussa P25,  $50 \text{ m}^2/\text{g}$ ). After the impregnation step, the sample was dried at room temperature overnight, followed by additional drying at 383 K overnight, and calcination at 723 K for 2 h. Characterization of the catalysts by Raman, IR, TPR, and BET were reported previously (25). The surface areas of the catalysts were not influenced by the calcination treatment. The acidity of the  $\text{Re}_2\text{O}_7/\text{TiO}_2$  catalysts were measured by pyridine adsorption using a diffuse-reflectance fourier transform infrared instrument. Only relative amounts of Lewis and Brønsted acid sites are reported. Details of the acidity measurements can be found elsewhere (8).

The SCR of NO with  $\text{NH}_3$  was measured using a reactant gas mixture of  $\text{O}_2$  (2%), NO (500 ppm),  $\text{NH}_3$  (550 ppm), and balance He (supplied by UCAR–Union Carbide) fed through four mass controllers (Hi-Tec MFC 201). Analysis of the reactants and products were performed by a mass

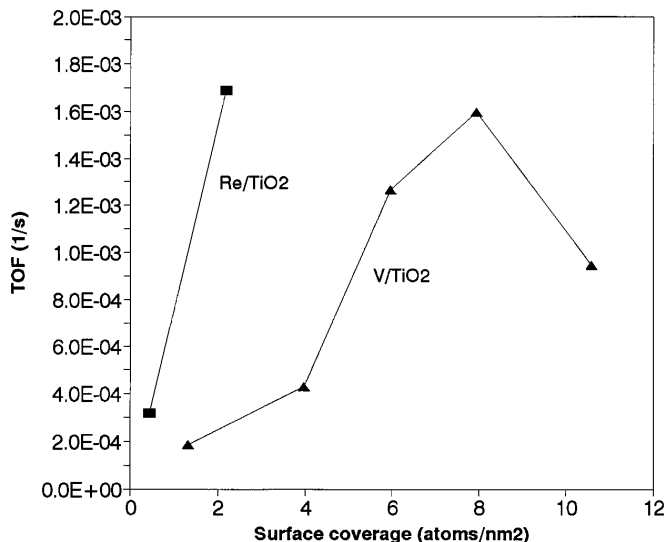


FIG. 1. TOF ( $s^{-1}$ ) for  $Re_2O_7/TiO_2$  and  $V_2O_5/TiO_2$  catalysts as a function of surface coverage (atoms/nm<sup>2</sup>) at 473 K.

spectrometer. The total amount of rhenium oxide in the reactor was kept the same for both runs, which reveals that the specific reactivity, or turnover frequencies, TOF (NO converted per Re atom per s), of the surface rhenium oxide species significantly increases with surface coverage. Additional details of the SCR of NO reactor and analysis can be found elsewhere (8).

The TOF for the SCR of NO with  $NH_3$  at 473 K are compared as a function of surface coverage for the titania supported rhenia and vanadia catalysts (8) in Fig. 1. At low surface coverages, both titania supported metal oxide catalysts exhibit comparable TOF; at intermediate surface coverages, the titania supported rhenia catalyst is much more active than the titania supported vanadia catalyst. The titania supported rhenia catalyst system, however, was not as selective for  $N_2$  formation as the titania supported vanadia catalyst system. The corresponding titania supported vanadia catalysts possessing similar surface coverages yielded essentially 100% selectivities for  $N_2$  formation at 473 (8), while the titania supported rhenia catalysts gave rise to  $\sim 70$  and  $\sim 55\%$  selectivities for the 1 and 4.9%  $Re_2O_7/TiO_2$  catalysts, respectively. The titania supported rhenia catalyst system did exhibit selectivities approaching  $\sim 100\%$   $N_2$  formation at lower temperatures. Thus, the surface rhenia species on titania are more active than the surface vanadia species on titania for the selective reduction of NO with  $NH_3$ , but are not as selective for  $N_2$  formation at elevated temperatures.

The surface acidity characteristics of the titania supported rhenia and vanadia catalysts were probed with pyridine adsorption and are presented in Table 1 (8, 21). The  $TiO_2$  support possesses only surface Lewis acid sites and

TABLE 1  
Acidity of Titania, Rhenia/Titania, and Vanadia/Titania Catalysts

| Catalyst             | Relative no. of Lewis acid sites (arbitrary units) | Relative no. of Brønsted acid sites (arbitrary units) |
|----------------------|--|---|
| $TiO_2$              | 0.2  | —   |
| 4.9% $Re_2O_7/TiO_2$ | 0.02   | 0.03  |
| 7% $V_2O_5/TiO_2$    | 0.02   | 0.01  |

the addition of surface rhenium oxide as well as surface vanadium oxide species decreases the number of surface Lewis acid sites and introduces surface Brønsted acid sites. A similar trend was observed for titania supported vanadia catalysts by Miyata *et al.* (24) and is a typical pattern observed for many supported metal oxide catalysts (26). The number of surface Brønsted acid sites appears somewhat greater for the rhenia system than the vanadia system.

The high redox activity of the titania supported rhenia catalyst system initially found for the methanol oxidation reaction was also found for the SCR reaction in the current investigation. Ammonia oxidation over supported metal oxide catalysts has been shown to follow the same trend as methanol oxidation (27). The redox potential of methanol, however, is significantly greater than that of ammonia since methanol oxidation over vanadia–titania catalysts exhibits a TOF that is much higher than the TOF for ammonia oxidation (28). In the present investigation, methanol oxidation is used to probe the *relative* redox properties among the various catalysts. In general, the relative order of activities for both reactions follows the same trend with the specific surface metal oxide species on titania:  $Re \sim V \gg Cr \sim Mo \gg Nb, W, \text{ and } S$  (10–19, 22, 23). The selectivity pattern for methanol oxidation also appears to correlate with the selectivities of the SCR of NO to  $N_2$  formation since only titania supported vanadia catalysts gave rise to the exclusive formation of formaldehyde, whereas the other active titania supported metal oxide catalysts (Re, Cr, and Mo) also yield significant quantities of methylformate (9, 20, 29, 30). The titania supported niobium oxide, tungsten oxide, and sulfate catalysts were essentially inactive for either methanol oxidation and the SCR of NO with  $NH_3$  reactions at low temperatures, which reflects the low redox potentials of these catalytic systems (8–18, 22, 23). Thus, the methanol oxidation redox probe reaction appears to provide useful information about the redox properties of SCR of NO with  $NH_3$  catalysts.

The titania supported rhenia and vanadia catalytic systems behaved very similarly as a function of surface coverage during methanol oxidation (19) and the SCR reactions

(see Fig. 1). Both catalytic systems exhibited a constant TOF as a function of surface coverage during methanol oxidation (19) and an increase in TOF as a function of surface coverage during the selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$ . The constant TOF of the methanol oxidation reaction with surface coverage reflects the single site requirement of this unimolecular redox reaction (9, 31). The increase in TOF of the SCR of NO with  $\text{NH}_3$  with surface coverage suggests that more than one site may be required for this bimolecular reaction (6, 8). Increasing the surface coverage of the metal oxides on titania increases the number of Re–Re or V–V neighbors as well as the number of surface brønsted acid sites. It has been proposed that the SCR reaction requires a dual site containing a surface redox site and an adjacent surface acid site to proceed most efficiently (6, 8). The current acidity and TOF of the SCR of NO with  $\text{NH}_3$  measurements are consistent with this model since the number of brønsted acid sites increases with surface coverage and is somewhat greater for the rhenia system than the vanadia system at high coverages (see Table 1).

The specific molecular structure of the surface metal oxide species does not appear to affect the increase in the TOF trend with surface coverage. For the titania supported rhenia system, two isolated surface rhenia species are present as a function of surface coverage, corresponding to  $\text{Re}=\text{O}$  symmetric stretches at 1004–1006 and 1009–1011  $\text{cm}^{-1}$ , and the ratio of the higher frequency species to the lower frequency species increases with surface coverage (25). It has been proposed that the slight difference between the two surface rhenia species may be due to distortions brought about by the presence of a proton on the Re–O support bond of the higher frequency rhenia species (26). For the titania supported vanadia system, both polymerized and isolated surface vanadia species are present and the ratio of polymerized to isolated surface vanadia species increases with surface coverage (3, 4). Thus, the increase in the TOF for the SCR of NO with  $\text{NH}_3$  is not related to the extent of polymerization of the surface metal oxide species with coverage since both the titania supported rhenia catalysts, possessing only isolated surface metal oxide species, and the titania supported vanadia catalysts, possessing both isolated and polymerized surface metal oxide species, exhibit the same increase in the TOF trend with surface coverage.

In summary, the titania supported rhenia catalyst system is very active for the selective catalytic reduction of  $\text{NO}_x$  with  $\text{NH}_3$  and its TOF is comparable to the commercial titania supported vanadia catalyst. However, the selectivity toward  $\text{N}_2$  formation for the titania supported rhenia catalysts is lower than that for the titania supported vanadia catalysts. Both the redox potential, probed with methanol, oxidation, and the surface acidity properties, probed with pyridine adsorption, vary in a similar fashion with surface

coverage for the two supported catalyst systems. The increase in the TOF of the SCR of NO with  $\text{NH}_3$  with surface metal oxide coverage is consistent with a dual site mechanism requiring one surface redox site and an adjacent surface acid site. The specific molecular structure of the surface metal oxide site, isolated or polymerized, does not appear to influence the TOF for the SCR of NO with  $\text{NH}_3$ .

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## REFERENCES

1. Bosch, H., and Janssen, F., *Catal. Today* **2**, 369 (1987).
2. Eckert, H., and Wachs, I. E., *J. Phys. Chem.* **93**, 6796 (1989).
3. Vuurman, M. A., Wachs, I. E., and Hirt, A. M., *J. Phys. Chem.* **95**, 9928 (1991).
4. Went, G., Leu, L.-J., and Bell, A. T., *J. Catal.* **134**, 479 (1992).
5. Deo, G., Wachs, I. E., and Haber, J., *Crit. Rev. Surf. Chem.* **4**, 141 (1994).
6. Topsoe, N.-Y., Topsoe, H., and Dumesic, J. A., *J. Catal.* **151**, 226 (1995).
7. Ramis, G., Busca, G., Bregani, F., and Forzatti, P., *Appl. Catal.* **64**, 259 (1990).
8. Deo, G., Jehng, J.-M., Kim, D. S., Wachs, I. E., Vuurman, M. A., and Andreini, A., in "Environment Catalysis" (G. Centi *et al.*, Eds.), p. 207. SCI Pub., Rome, 1995; Wachs, I. E., Deo, G., Andreini, A., Vuurman, M., de Boer, M., and Amiridis, M., submitted for publication.
9. Deo, G., and Wachs, I. E., *J. Catal.* **146**, 323 (1994).
10. Nickl, J., Dutoit, D., Baiker, A., Scharf, U., and Wokaun, A., *Ber. Bunsenges. Phys. Chem.* **97**, 217 (1993).
11. Hattori, H., Tanabe, K., Tanaka, K., and Okazaki, S., *Proc. Climax Molybdenum Conf.* 188 (1979); Okazaki, S., Kumasaka, M., Yoshida, J., Kosaka, K., and Tanabe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 301 (1981).
12. Lietti, L., Svachula, J., Forzatti, P., Busca, G., Ramis, G., and Bregani, F., *Catal. Today* **17**, 131 (1993).
13. Hilbrig, F., Schmelz, H., and Knozinger, H., in "New Frontiers in Catalysis, Proceedings, 10th International Congress on Catalysis" (L. Guzzi, F. Solymosi, and P. Tetenyi, Eds.), p. 1351. Akadémiai Kaidó, Budapest, 1993.
14. Morikawa, S., Takahashi, K., Mogi, J., and Kurita, S., *Bull. Chem. Soc. Jpn.* **55**, 2254 (1982).
15. Engwiler, J., Nickl, J., Baiker, A., Schlapfer, C. W., and von Zelewsky, A., *J. Catal.* **145**, 141 (1994).
16. Vikulov, K. V., Andreini, A., Poels, E. K., and Blied, A., *Catal. Lett.* **25**, 49 (1994).
17. Weng, R.-Y., and Lee, J.-F., *Appl. Catal.* **105**, 41 (1993).
18. Chen, J. P., and Yang, R. T., *J. Catal.* **139**, 277 (1993).
19. Wachs, I. E., Deo, G., Kim, D. S., Vuurman, M. A., and Hu, H., *J. Mol. Catal.* **83**, 443 (1993).
20. Kim, D. S., and Wachs, I. E., *J. Catal.* **141**, 419 (1993).
21. Amiridis, M., Deo, G., and Wachs, I. E., unpublished data.
22. Deo, G., and Wachs, I. E., *J. Catal.* **146**, 335 (1994).
23. Jehng, J.-M., and Wachs, I. E., *Catal. Today* **8**, 37 (1990).
24. Miyata, H., Fujii, K., and Ono, T., *J. Chem. Soc., Faraday Trans. 1* **84**, 3121 (1988).
25. Vuurman, M. A., Stufkens, D. J., Oskam, A., and Wachs, I. E., *J. Mol. Catal.* **76**, 263 (1992); Wang, L., and Hall, W. K., *J. Catal.* **82**, 177 (1983).
26. Turek, A. M., Wachs, I. E., and DeCanio, E., *J. Phys. Chem.* **96**, 5000 (1992).

27. de Boer, M., Ph.D. Thesis, University of Utrecht, The Netherlands, 1992.  
28. Charue, S., and Wachs, I. E., unpublished results.  
29. Kim, D. S., and Wachs, I. E., *J. Catal.* **142**, 166 (1993).  
30. Hu, H., and Wachs, I. E., *J. Phys. Chem.* **99**, 10911 (1994).  
31. Weber, R. S., *J. Phys. Chem.* **98**, 2999 (1994).

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