Selective Catalytic Reduction of NO over Vanadia on Pillared Titanium Phosphate

Lawrence J. Czarnecki
Rayford G. Anthony
Kinetics, Catalysis, and Reaction Engineering Laboratory
Department of Chemical Engineering
Texas A&M University
College Station, TX 77843

During the last 15 years, the reduction of nitrogen oxides emissions, particularly from combustion sources, has become increasingly important. As limits have become stricter, the use of selective catalytic reduction (SCR) has become a major method of controlling nitrogen oxide emissions from stationary sources.

Selective catalytic reduction is a process in which ammonia is added to the exhaust stream where it reacts with the nitrogen oxides, produced during combustion, over a catalyst. A wide variety of different catalysts can be used, but the most effective catalyst so far is supported vanadium pentoxide (Bauerle et al., 1975; Yoshida et al., 1979; Naruse et al., 1980; Blanco et al., 1986; Wong and Nobe, 1986). Titanium dioxide has been shown to be one of the better support materials for vanadia catalysts for SCR (Takagi-Kawai et al., 1980; Inomata et al., 1982). Even though titania typically has a lower surface area than γ-alumina and silica, vanadia on titania catalysts generally exhibit higher activities. In addition, titiania-based catalysts are resistant to SO_x poisoning (Shikada et al., 1981). Research on SCR is continuing in the development of better catalysts and catalyst support media.

Pillared materials, such as pillared clays, have shown promise as support materials for catalysis (Burch, 1988). Pillared titanium phosphate is a noncrystalline material composed of titanium phosphate layers separated by aluminum structures (Clearfield and Roberts, 1988). Micropores created by the space between the layers ranges from 0.6 nm to 3.0 nm. This material showed promise as a possible support material for two reasons. First, pillared titanium phosphate has a much higher surface area, 237 m^2/g, than typical anatase titanium which is usually less than 100 m^2/g. Second, there is a possibility of a promoter effect which is present in titania-based catalysts.

Experimental Methods

The catalyst used in this study, VTAP-12C, contained 10 wt. % V_2O_5 on titanium phosphate pillared with aluminum. The support material was prepared by Bryan Roberts, a member of Prof. A. Clearfield's research group, the Department of Chemistry, Texas A&M University. The support was impregnated with a vanadyl oxalate solution, prepared from ammonium vanadate and oxalic acid, using the incipient wetness technique in a stepwise manner. The impregnated catalyst was dried at 383 K for 24 hours and then calcined at 623 K, under flowing oxygen, for 4 hours. The calcined catalyst powder was then pressed into 4-cm-diameter cakes which were crushed and sieved at 25/35 mesh.

Reactor system

The reactor used was a tubular, upflow reactor. Nitric oxide and ammonia were fed from separate cylinders containing 5,000 ppm reactant in nitrogen. The flow rates of these two gases were controlled and measured using needle valves and rotameters. Pure, dry oxygen and nitrogen flow rates were controlled with mass flowmeters. Typical feed composition was 950 ppm NO, 980 ppm NH_3, 5% O_2, and the balance nitrogen. The space velocity was usually 20,000 $cm^3/g\ cat \cdot h$ (evaluated at 0°C and 1 atm).

The entire reactor was constructed of Pyrex glass tubing. The reactor body diameter was 1.5 cm and a thermowell (of 0.64 cm OD) extended through the center of the reactor. Thermocouples were located at the front (bottom) and the center of the catalyst bed. The temperature difference between the thermocouples was never more than 2 K. The catalyst charge was 3 g. The inlet leg of the reactor was a U-shaped section of 0.64-cm-OD tubing which served as a preheating zone. The reactor was heated in a fluidized sand bath, and the temperature was controlled with a Variac.

Gas scrubbers, filled with a 4% boric acid solution, removed ammonia for analysis and prevented ammonia from entering the nitric oxide analyzer. Two scrubbers were used so that nitric oxide measurements would not be interrupted. Ammonia analysis was performed with an ammonium-ion-selective pH electrode (Orion Research Inc., Model 95-12), and nitric oxide was measured with a chemiluminescence analyzer (Thermo Electron Corp., Model 10AR).

Reactor design

Film transfer limitations were checked according to equations given by Froment and Bischoff (1979). Criteria specified by Mears (1971) were also used in order to confirm the absence of mass and heat transfer limitations. For further information on experimental details and reactor design please refer to Czarnecki (1988).

Results and Discussion

The temperature effect on reactant conversion measured initially provided an operating temperature range and information on the reaction stoichiometry. The conversions of NO from 373 K to 613 K are shown in Figure 1. At any given temperature, variations in NO conversion was less than 3%. At temperatures greater than 373 K, NO conversion increased as temperature increased. At a temperature of 517 K, the NO conversion over VTAP-12C was 45%. Nonimpregnated pillared titanium phosphate support showed no catalytic activity.

No nitrogen dioxide formation was observed during the nitric oxide-ammonia reaction study nor in studies without ammonia present in the feed gas. It is therefore unlikely that nitric oxide was oxidized during the reaction. Oxidation of ammonia is possible, but this usually occurs at temperatures greater than 570 K (Bauerle et al., 1978).

Reaction rate constants were determined for the first-order rate equation

$$r_{NO} = kP^{1}_{NO} P^{0}_{NH} \qquad (1)$$

Several authors have used this simple equation which is based on proposed reaction mechanisms (Inomata et al., 1980; Wong and Nobe, 1984).

The role of oxygen is not evident in this equation. Other studies on the nitric oxide-ammonia reaction have mentioned that an excess of oxygen (usually greater than 0.5%) has no additional effect on nitric oxide conversions. At these oxygen concentrations, the rate of nitric oxide reduction is not influenced by slight variations in oxygen concentration. This suggests a zeroth-order dependence on oxygen, and, for simplicity, the contribution of oxygen to the reaction rate is nested in the rate constant. The reaction was found to be dependent strongly on oxygen. When oxygen was excluded from the reactant feed mixture, the NO conversion over VTAP-12C at 530 K decreased from 58% to 10% within 45 minutes.

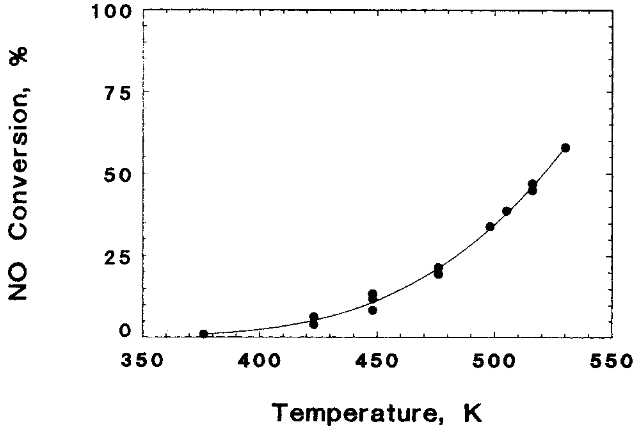

Figure 1. Activity of VTAP-12C.
Reaction conditions: 950 ppm NO, 980 ppm NH_3, 5% O_2, SV = 20,000 h^{-1}, 1 atm.

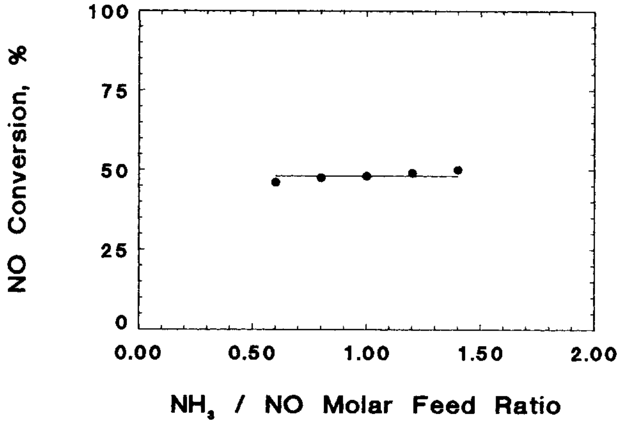

Figure 2. Effect of reactant feed ratio on NO conversion.
Reaction conditions: 950 ppm NO, 517 K, SV = 20,000 h^{-1}, 1 atm.

Based on the assumption that ammonia is strongly adsorbed on the catalyst surface, the reaction rate is independent of the ammonia concentration. This conclusion yields a zeroth-order rate dependence on ammonia. As shown in Figure 2, varying the ammonia-nitric oxide molar feed ratio from 0.6 to 1.4 had only a slight effect on NO conversion.

In a continuous-flow reactor, the behavior of a first-order reaction follows the equation

$$-\log_e (1 - x) = kWP^{o}_{NO}/F^{o}_{NO} \qquad (2)$$

The fit of this rate equation to the experimental data is represented in Figure 3.

Activation energies and reaction rate constants were calcu-

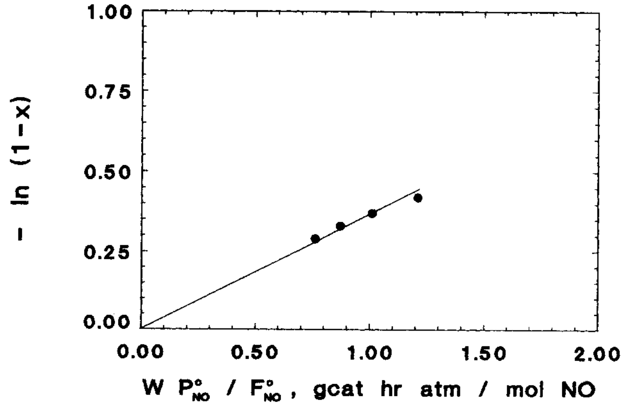

Figure 3. First-order rate determination.
Reaction conditions: 950 ppm NO, 980 ppm NH_3, 5% O_2, 498 K.

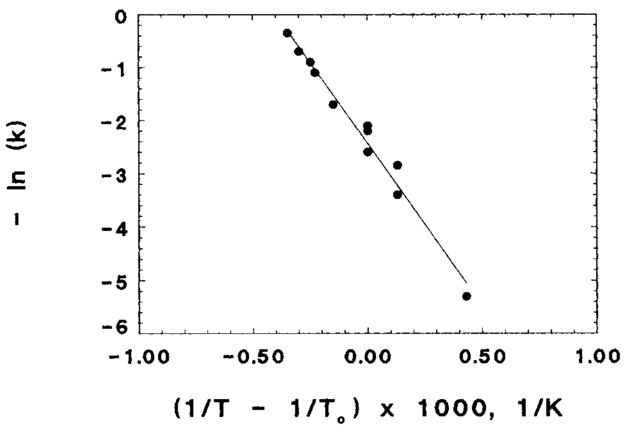

Figure 4. Reaction rate constant parameters.

Reaction conditions: 950 ppm NO, 980 ppm NH_3, 5% O_2, SV = 20,000 h^{-1}, 1 atm.

lated using Eq. 2 and the modified Arrhenius equation

$$k = k^o \exp\left[-E_a/R(1/T - 1/T_o)\right] \qquad (3)$$

where T_o equals 450 K. The linearized form of Eq. 3 is shown graphically in Figure 4. Effectiveness factors were 0.98 to 1.0 as determined by using the Weisz-Prater (1954) criterion and the random pore model (Wakao and Smith, 1962). Therefore, resistance to intraparticle diffusion was negligible, and the measured rate constants were equal to the intrinsic rate constants. The rate constants at 450 K and the activation energies for this work and for vanadia on aluminum and on titania are reported in Table 1.

The rate of NO reduction was found to be much lower than the intrinsic rates measured by Wong and Nobe (1986) on alumina and titania supported vanadia catalysts. The metal-support interaction observed on titania-supported catalysts probably did not occur with the pillared titanium phosphate support. The lower reaction rate may be due to the large amount of phosphate which could act as an inhibitor. Hodnett and Delmon (1984) have shown that vanadium-phosphate catalysts with an excess amount of phosphorous exhibit a stabilized V^{+4} state. If the same effect occurred on the experimental catalyst, the oxidation rate of the redox mechanism, such as that proposed by Inomata et al. (1980), would be reduced. This would reflect in an overall lower reaction rate, if this became the rate-limiting step.

Table 1. Reaction Rate Constant Parameters

Catalyst	Rate	k_o* (10^4) @ 450 K	E_a** kJ/mol
VTAP-12C	Intrinsic	0.264	51.5
V_2O_5-Al_2O_3*	Intrinsic	2.9	61.9
V_2O_5-TiO_2**	Intrinsic	7.8	54.0

*mol NO/gcat s atm
**Wong and Nobe (1986)

Notation

E_a = activation energy
F_{NO} = molar NO flow rate
k = reaction rate constant
P = pressure
P_i = partial pressure component i
R = gas constant
r = reaction rate
T = temperature
W = mass catalyst
x = conversion

Literature Cited

Bauerle, G. L., S. C. Wu, and K. Nobe, "Reduction of Nitric Oxide with Ammonia on Noble Metal Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 123 (1975).

Bauerle, G. L., S. C. Wu, and K. Nobe, "Parametric and Durability Studies of NO_x Reaction with NH_3 on V_2O_5 Catalysts," *ibid.*, **17**, 117 (1978).

Blanco, J., J. F. Garcia de la Banda, P. Avila, and F. Melo, "Selective Reduction of Nitric Oxide on Nickel Oxide—Copper Oxide Supported Catalysts," *J. Phys. Chem.*, **90**, 4789 (1986).

Burch, R., "Pillared Clays," *Cat. Today*, **2** (1988).

Clearfield, A., and B. D. Roberts, "Pillaring of Layered Zirconium and Titanium Phosphates," *Inorg. Chem.*, **27**, 3237 (1988).

Czarnecki, L. J., "Selective Reduction of Nitric Oxide With Ammonia Over Vanadia on Pillared Titanium Phosphate," MS Thesis, Texas A&M Univ., College Station (1988).

Froment, G. F., and K. B. Bischoff, *Chemical Reactor Analysis and Design*, 150, Wiley, New York (1979).

Hodnett, B. K., and B. Delmon, "Influence of the Phosphorus/Vanadium Ratio on the Solid State Chemistry and Redox Properties of Vanadium Phosphate-Based Catalyst," *J. Cat.*, **88**, 43 (1984).

Inomata, M., A. Miyamoto, and Y. Murakami, "Mechanism of the Reaction of NO and NH_3 on Vanadium Oxide Catalyst in the Presence of Oxygen Under the Dilute Gas Condition," *ibid.*, **62**, 140 (1980).

Inomata, M., A. Miyamoto, T. Ui, K. Kobayashi, and Y. Murakami, "Activities of V_2O_5/TiO_2 and V_2O_5/Al_2O_3 Catalysts for the Reaction of NO and NH_3 in the Presence of O_2," *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 424 (1982).

Mears, D. E., "Tests for Transport Limitations in Experimental Catalytic Reactors," *ibid.*, **10**, 541 (1971).

Naruse, Y., T. Ogasawara, T. Hata, and H. Kishitaka, "Properties and Performances of Various Iron Oxide Catalysts for NO Reduction with NH_3," *ibid.*, **19**, 57 (1980).

Shikada, T., K. Fujimoto, T. Kunugi, H. Tominaga, S. Kaneko, and Y. Kubo, "Reduction of Nitric Oxide with Ammonia on Vanadium Oxide Catalysts Supported on Homogeneously Precipitated Silica-Titania," *ibid.*, **20**, 91 (1981).

Takagi-Kawai, M., M. Soma, T. Onishi, and K. Tamaru, "The Adsorption and the Reaction of NH_3 and NO_x on Supported V_2O_5 Catalysts: Effect of Supporting Materials," *Can. J. Chem.*, **58**, 2132 (1980).

Wakao, N., and J. M. Smith, "Diffusion in Catalyst Pellets," *Chem. Eng. Sci.*, **17**, 826 (1962).

Weisz, P. B., and C. D. Prater, "Interpretation of Measurements in Experimental Catalysts," *Adv. Cat.*, **6**, 163 (1954).

Wong, W. C., and K. Nobe, "Kinetics of NO Reduction with NH_3 on "Chemical Mixed" and Impregnated V_2O_5-TiO_2 Catalysts," *Ind. Eng. Chem. Prod. Res. Dev.*, **23**, 564 (1986).

Wong, W. C., and K. Nobe, "Reduction of Nitric Oxide with Ammonia on Al_2O_3- and TiO_2-Supported Metal Oxide Catalysts," *ibid.*, **25**, 179 (1986).

Yoshida, S., A. Ueda, and K. Tarama, "Surface Oxygen Species as Active Species in the Reduction of Nitrogen Oxide by Ammonia over Copper Vanadate," *ibid.*, **18**, 283 (1979).

Manuscript received Feb. 16, 1989, and revision received Feb. 20, 1990.