

speaking, solid residence times in spray driers are shorter than those in kilns. Also, temperature profiles in spray driers are more uniform than in kilns. It is likely that both the longer residence times and the sporadic higher temperatures in a kiln would tend to cause sintering and therefore higher densities.

The third series of catalysts was chosen to determine the maximum effect of surface layering on reaction rate. The results are shown in Figure 6. The square data points represent catalysts prepared with N alumina and no acid. The larger sized particles present in the N material combined with the absence of acid would tend to hinder the penetration of solution into the alumina and enhance the surface layering effect which was shown in Figures 1 and 3. On the other hand, extensive gelling, which occurred in the smaller particles of the SB material when contacted with excess acid, resulted in a catalyst represented by the circular data points. In Figure 6 it appears that the surface layered catalysts may have caused higher sulfur removals and lower nitrogen removals. In both events the differences were minor and were only observed for low concentrations of catalytic ingredients. It also appears that on increasing these concentrations the differences between surface layered and gelled catalysts may have decreased.

The findings in this work are summarized as follows. The surface layering effect alluded to in earlier work was found actually to occur. The surface layering was found to have very little effect on sulfur and nitrogen conversion. This technique might be useful when supported catalysts of very low con-

centrations are to be prepared. Other variables such as the type of alumina monohydrate had no effect on conversion. However, the time-temperature history (spray drying vs. kiln drying) of the alumina monohydrate did alter the density and porosity of the catalyst pellets. This in turn was reflected in the reaction rate per unit weight of catalyst (Figure 5).

Acknowledgments

The authors wish to thank R. Campbell, E. C. McColgan, and V. Moore for technical assistance.

Literature Cited

- Iler, R. K., "Surface and Colloidal Science", Vol. VI, p. 1, E. Matijevic, Ed., Wiley, New York, N.Y., 1973.
- Kriz, J. F., Ternan, M., Packwood, R. H., Parsons, B. I., Preprints, Vol. 22, No. 3, p. 1013, Symposium on Refining of Synthetic Crudes, Division of Petroleum Chemistry, 174th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1977.
- McColgan, E. C., Soutar, P. S., Rethier, M. A., Parsons, B. I. "The Hydrocracking of Residual Oils and Tars. Part 5: Surface-Coated Cobalt Molybdate Catalysts for Hydro-treating"; Mines Branch Research Report R-263; Department of Energy, Mines and Resources, Ottawa, 1973.
- Merrill, W. H., Logie, R. B., Denis, J. M., "A Pilot Scale Investigation of Thermal Hydrocracking of Athabasca Bitumen", Mines Branch Research Report R-281; Department of Energy, Mines and Resources, Ottawa, 1973.
- O'Grady, M. A., Parsons, B. I., "The Hydrogenation of Alberta Bitumen over Cobalt Molybdate Catalysts", Mines Branch Research Report R-194; Department of Energy, Mines and Resources, Ottawa, 1967.
- Parsons, B. I., Ternan, M., *Proc. 6th Int. Congr. Catal.*, **2**, 1965 (1977).

Received for review October 4, 1977

Accepted February 19, 1978

Parametric and Durability Studies of NO_x Reduction with NH₃ on V₂O₅ Catalysts

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Vanadium pentoxide-alumina catalysts have been shown to be both highly effective for the selective removal of NO_x with NH₃ in simulated flue gas and resistant to SO_x during an exposure period of over 600 h. During the durability test, the nominal inlet concentrations were about 1000 ppm of NO_x, 0.5 to 1.5 mole ratio of NH₃/NO, and up to 2500 ppm of SO_x. Although variations in H₂O and CO₂ in the concentration ranges applicable to power plant exhausts did not affect catalytic activity, the excess oxygen greatly enhanced NO_x removal. This acceleration effect was most pronounced with increase in O₂ concentration below 0.5% O₂. The intrinsic rate expression developed for NO_x removal over the 15% V₂O₅-Al₂O₃ catalyst indicates strong pore diffusion effects between 200 and 400 °C.

Introduction

A preliminary study of the selective reduction of NO_x on V₂O₅ catalysts with NH₃ (Bauerle et al., 1975b; part 2 in this series) between 220 and 460 °C has shown that O₂ accelerates the reaction. In simulated flue gas containing up to 1500 ppm of SO₂, conversion of NO at 400 °C varied typically from about 70% at 20 000 h⁻¹ (STP) space velocity to 96% at 5000 h⁻¹. Conversion remained essentially constant for given flow and concentration conditions over a total exposure to SO₂ of 71 h.

The work of other investigations on the reduction of nitric oxide with ammonia has been reviewed in part 1 (Bauerle et al., 1975a) of this series. This paper (part 3) reports on a more

thorough examination of V₂O₅ catalysts to determine the optimum concentration of V₂O₅ on alumina carrier for a series of laboratory-prepared catalysts and the effect of SO_x on catalytic activity over an extended period of operation. In addition, parametric studies have been conducted in order to develop an intrinsic rate expression for the removal of NO_x with NH₃ on V₂O₅ catalysts from flue gas of stationary sources.

Experimental Section

Reactor System. V₂O₅ catalyst optimization, parametric, and durability studies in the presence of SO_x were conducted with a tubular, upflow reactor operating under isothermal

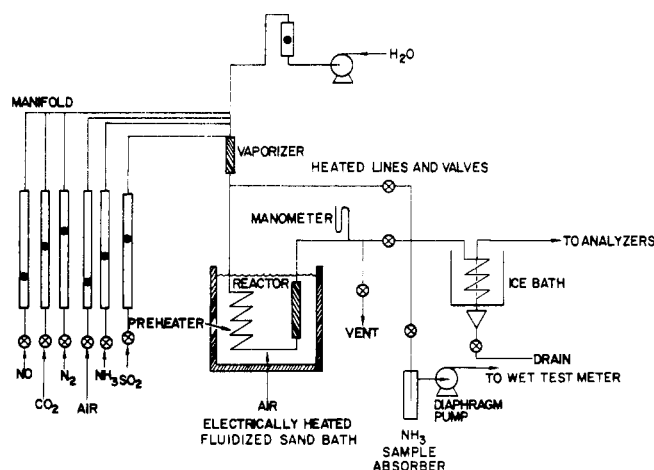


Figure 1. Catalyst test apparatus.

conditions. Figure 1 shows a schematic diagram of the reactor and associated equipment and instrumentation.

The reactor, as well as tubular preheater, was maintained at preselected temperatures in an air-flow, fluidized sand bath heater. A back-pressure valve on the reactor outlet was adjusted to maintain constant pressure (≈ 1.05 atm) in the system at all temperatures and to compensate for changes in pressure drop across the reactor bed when switching from inlet to outlet modes.

Nitrogen, carbon dioxide, and nitric oxide gases were mixed in a glass manifold after passing through needle valves and rotameters. The flow rate of nitric oxide was measured accurately with a soap-bubble flowmeter.

Oxygen was added to the gas stream, upstream of the vaporizer-mixer unit by appropriate injection of air. Ammonia and water were also introduced at this point. The ammonia feed was supplied from an anhydrous liquid NH_3 tank using a rotameter for coarse flow adjustment. Water was injected in liquid form using a small rotary pump. The vaporizer-mixer unit was a stainless steel tube (1.6 cm diameter, 25 cm long) filled with 0.32-cm glass beads. The tube was lagged with a heating tape and insulated to maintain a temperature of at least 350°C . The SO_2 injection point was immediately upstream of this unit.

The reactor was made of stainless steel tubing with end fittings containing stainless steel screen disks to retain the catalyst. Two reactor sizes were employed; the standard size, used in most of the tests, was constructed of 1.6-cm o.d. tubing to contain 14 mL of catalyst. The second reactor was constructed of 2.5-cm tubing and had an internal volume of 28 mL.

Gas Analyses. Inlet and outlet analyses of NO were obtained with a Beckman nondispersive infrared analyzer. The NO_2 was routinely analyzed with a Beckman flow colorimeter. Nitrous oxide (N_2O) was determined with a Perkin-Elmer Model 990 gas chromatograph with a 1.8 m, 0.32 cm diameter column of Poropak Q operating at room temperature. The temperature was varied periodically during analyses of outlet gases in the presence of SO_x to check for the production of H_2S and COS (surface dissociation of NH_3 was considered to be a possible source of H_2 , which with H_2O and CO_2 , through the water gas shift, could produce CO). In view of the overall oxidizing nature of the test atmosphere, the presence of either species was considered unlikely; neither was detected in any instance.

Ammonia was analyzed by two methods. In the absence of SO_x , a wet titration method was employed. A measured volume of gas was passed through an absorber containing 4% boric acid in water. The absorber contents were titrated with

Table I. List of Catalysts Tested

Prepared catalyst	Carrier ^a	Commercial catalysts
10% V_2O_5	Filtrol 86	10% V_2O_5 Harshaw V-0601 T
15% V_2O_5	Filtrol 86	1/8 (Al_2O_3 carrier)
20% V_2O_5	Filtrol 86	
25% V_2O_5	Filtrol 86	Girdler Südchemie G101,
15% V_2O_5	Alcoa H-151-8	$\text{V}_2\text{O}_5\text{-K}_2\text{O-SiO}_2$ ($\text{V}_2\text{O}_5/\text{K}_2\text{O}$ = 1/2.7)
15% V_2O_5	Alcoa F-1-1/4-8	
15% V_2O_5	Aeroban	

^a Alumina.

0.04 N HCl using bromocresol green as an indicator. Since sulfite and sulfate interfere with the HCl titration, the NH_3 analyses of the absorber when SO_2 is used were performed with an Orion specific ion electrode.

Sulfur dioxide was determined indirectly by measuring separately sulfur trioxide and total oxides of sulfur. For the former, a known volume of gas was absorbed in a train of bubblers containing 80% isopropyl alcohol in water. An aliquot of the solution was titrated with 0.01 N BaClO_4 using a thorin indicator. The precipitate formed remains colloidal in the high concentration of nonaqueous solvent. Thorin, which adsorbs on the precipitate, undergoes a color change from yellow to pink in excess Ba^{2+} . Sulfur dioxide, carbon dioxide, and ammonia do not interfere with the titration which is specific for SO_4^{2-} (Seidman, 1958). Oxidation of sulfite (SO_3^{2-} from dissolved SO_2) is avoided by maintaining the absorbent at ice temperatures until titration.

Total oxides of sulfur were determined by passing a known volume of gas through bubblers containing basic 1.5% H_2O_2 (equi-volume mixture of 0.2 N NaOH and 3% H_2O_2). Any SO_2 absorbed in the bubbler was oxidized by H_2O_2 to SO_4^{2-} . The contents of the bubbler was acidified to prevent formation of $\text{Ba}(\text{OH})_2$ in the ensuing titration, boiled to drive off CO_2 , passed through a cation exchange resin to remove interfering sodium, and then titrated as above. The sulfur dioxide concentration was calculated as the difference between total oxides of sulfur and SO_3 .

Catalysts. Dry carrier pellets were impregnated with an aqueous solution of ammonium metavanadate and oxalic acid (2:1 molar ratio of NH_4VO_3 to $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). Because of solubility limitations a large amount of water was necessary for preparing catalysts with 10% or more V_2O_5 (final, dried form) preventing absorption of the solution in a single step. Excess liquor was decanted from the pellets which were then partially dried. The remaining solution was then absorbed by the pellets. The pellets were dried at 160°C and then calcined in flowing air at 500°C to decompose the vanadate and the organic acid. No other activation procedure was employed before the catalysts were tested.

Filtrol Grade 86 Al_2O_3 pellets (3.2 mm diameter, 4.8 mm length) were used as carrier material in the study of the effect of V_2O_5 loading on catalyst activity. The optimum loading thus found was also applied to Aeroban spheres (American Cyanamid, 4.8 mm spheres of $\text{Al}_2\text{O}_3\text{-SiO}_2$) for comparison of activity with the Filtrol support.

Compositions of the catalysts prepared are given in Table I. Also listed in the table are two commercial catalysts which were tested for comparison with the prepared catalysts.

Procedure. Optimization of laboratory-prepared catalyst composition was based on performance with a test gas mixture containing various NH_3 concentrations. This mixture, the "standard flue gas", was also used in most of the durability tests. The standard flue gas contained 12% CO_2 , 5% H_2O , 3% O_2 , and 1000 ppm (parts per million by volume) NO in N_2 .

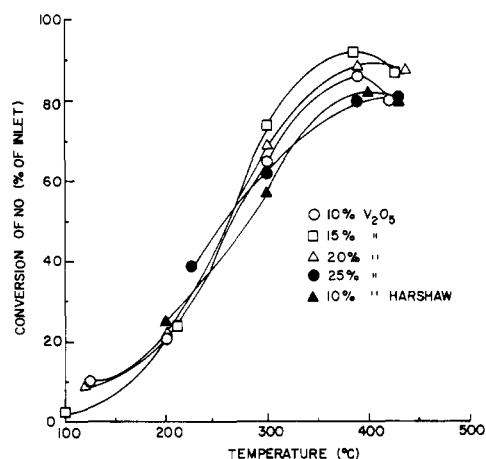


Figure 2. Reduction of NO (1000 ppm) with NH_3 (1100 ppm) on $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$ catalysts in simulated flue gas (s.v. = 20 000 h^{-1}).

Ammonia was either 650–750 ppm (670 ppm is stoichiometric) or 1000–1100 ppm. With the 14-mL reactor, the normal total gas flow rate was 280 L (STP)/h providing a space velocity of 20 000 h^{-1} . A second reactor of 28 mL volume provided a space velocity of 10 000 h^{-1} at the normal flow rate.

With introduction of SO_2 , inlet and outlet NH_3 analyses were performed with the Orion probe. Outlet and inlet analyses were routinely performed using as a criterion for steady-state, constant concentrations of NO, N_2O , NO_2 , and NH_3 for at least 30 min.

Results and Discussion

Negligible conversion of NO to N_2 or N_2O was obtained in the empty reactor and feed system. A small amount of NO_2 was formed in the NO_2 analyzer unit which had a 15 min residence time at the sampling flow rate employed. The inlet and outlet concentrations of NO have been corrected to include the small NO_2 concentrations observed.

Catalyst activity was determined in a simulated flue gas stream containing 12% CO_2 , 5% H_2O , 3% O_2 , and 1000 ppm of NO with approximately 700 ppm or 1100 ppm of NH_3 (balance N_2). The 700 ppm of NH_3 concentration represents a near stoichiometric amount for conversion of NO to N_2 . The 1100 ppm of NH_3 represents a 65% excess of NH_3 . Temperature was varied from 100 to about 450 °C with each catalyst. Flow rates were maintained at 280 L (STP)/h to provide a space velocity of 20 000 h^{-1} (STP).

Figure 2 shows conversion of NO as a function of temperature for 1100 ppm of NH_3 . Also included are data for commercial Harshaw V_2O_5 catalyst V-060IT 1/8 (10% V_2O_5 on Al_2O_3 , $\frac{1}{8} \times \frac{1}{8}$ in. cylinders). In general, the laboratory-prepared catalysts appear to be superior to the Harshaw catalyst between 250 and 400 °C with the 15% catalyst the most active above 250 °C. Figure 3 shows that at 300 and 400 °C, the optimum composition occurs at about 15% V_2O_5 . The decreased activity of the 25% catalyst may be due to excessive loading of V_2O_5 in the catalyst pores causing a decrease in surface area. Measured surface areas of the 15 and 25% V_2O_5 catalysts were 198 and 154 m^2/g , respectively, which lend some support to the hypotheses.

Nitrous oxide was not produced on any of the V_2O_5 catalysts. NH_3 consumption, in general, was less than 65% in excess of the theoretical amount required to achieve total reduction of NO to N_2 up to the temperature of maximum NO conversion on each catalyst. Above this temperature, NH_3 usage increased sharply and, at about 420 °C, reached values more than double that required for the conversion of NO. This result suggests that some of the NH_3 , which reacted at higher temperatures, was oxidized directly to NO.

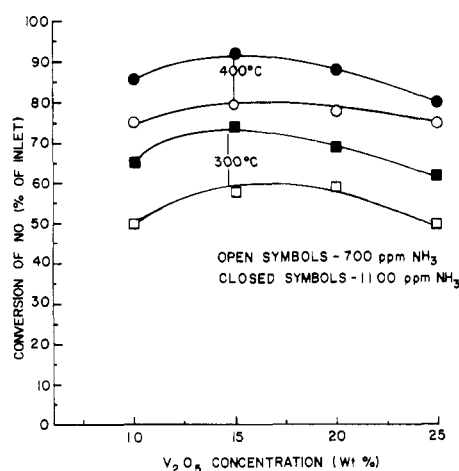


Figure 3. Influence of V_2O_5 concentration on catalyst activity in simulated flue gas (s.v. = 20 000 h^{-1}).

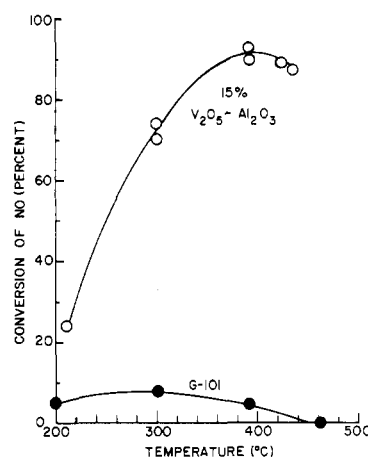


Figure 4. Comparison of 15% $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$ and commercial $\text{V}_2\text{O}_5\text{-K}_2\text{O-SiO}_2$ catalysts; 1000 ppm of NO and 1100 ppm of NH_3 in simulated flue gas (s.v. = 20 000 h^{-1}).

The 15% loading found optimum with Filtrol Al_2O_3 was impregnated on Aeroban ZW-1470 carrier ($\text{Al}_2\text{O}_3\text{-SiO}_2$, American Cyanamid) to compare activity with catalysts using the Filtrol Al_2O_3 carrier. The results indicate that, for a feed gas containing 1000 ppm of NO and excess NH_3 , there was little difference between the two catalysts while with stoichiometric NH_3 the Filtrol-supported catalyst appeared to be slightly more active.

A commercial vanadia catalyst (Girdler-Sudchemie type G-101) specifically developed for SO_2 oxidation in contact sulfuric acid plants was also tested for comparison with the other V_2O_5 catalysts. This catalyst was particularly attractive because of its very high physical strength (37 lb), as reported by the manufacturer. Information provided by the manufacturer indicates a silica carrier impregnated with vanadium and potassium salts ($\text{V}_2\text{O}_5\text{:K}_2\text{O}$ ratio of about 1/2.7). Although previous work in this laboratory has shown that even small concentrations of alkali metals in V_2O_5 catalysts decreased the catalytic activity for reduction of NO with NH_3 , it was of interest to determine the activity of this commercial catalyst containing K_2O . Figure 4 shows that the G-101 catalyst has practically no activity for NO conversion in simulated flue gas containing 12% CO_2 , 5% H_2O , and 3% O_2 . Above 380 °C, effluent gas analysis, in fact, showed considerable NH_3 oxidation with O_2 to NO and N_2 . The present results combined with previous observation of alkali metal poisoning indicate that commercial sulfuric acid catalysts containing alkali metal

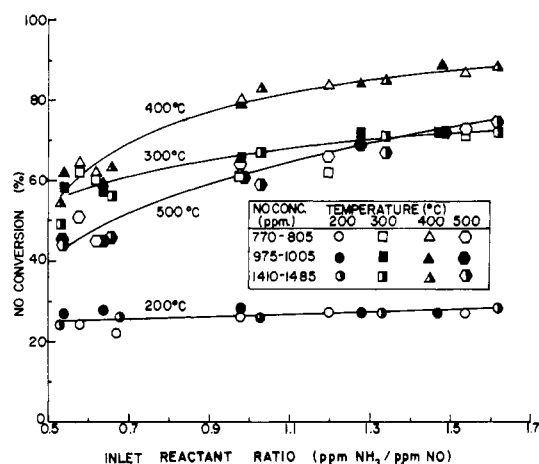


Figure 5. Removal of NO with NH_3 on V_2O_5 at high NO concentrations in simulated flue gas (s.v. = 20 000 h^{-1}).

promoters will probably not be effective for NO_x reduction with NH_3 .

Since the results of the above studies indicate that the 15% V_2O_5 Filtrol Grade 86 alumina was the most active catalyst tested, this catalyst was selected for further study in both the parametric test program and SO_x durability studies.

Parametric Studies. The experimental approach in the parametric tests was first to use the standard simulated flue gas mixture (12% CO_2 , 5% H_2O , 3% O_2) varying the NO concentration from 250 to 1500 ppm and NH_3 concentration between about 0.5 to 1.5 times the stoichiometric requirement for each NO concentration. Then, at the temperature of maximum conversion with each NO/ NH_3 ratio, the CO_2 and H_2O concentrations were perturbed from the standard flue gas concentrations over an expected range of operating conditions (e.g., from about 8% to 15% CO_2 and from about 3% to 18% H_2O). Additional tests were also conducted with gas containing neither CO_2 nor H_2O for use as reference base. The effects of changes in the O_2 concentration were investigated at NO concentrations of 750 ppm and 1000 ppm with at least two concentration levels of NH_3 (approximately stoichiometric and 1.5 times stoichiometric) and oxygen concentrations varying from 0 to 5%. In these tests, temperatures were varied from 280 to 500 °C.

The influence of the NH_3/NO ratio on the conversion of NO in the standard flue gas mixture is shown in Figure 5 for NO concentrations of 770 to 1485 ppm. The absolute NO concentration, at a given temperature, does not influence strongly the rate of NO conversion; instead, the reactant ratio and temperature determines the conversion of NO. This observation was made in the earlier studies with Pt, V_2O_5 , and Fe-Cr catalysts (Bauerle et al., 1975a,b).

The effect of water vapor on NO reduction in simulated flue gas is shown in Figure 6a. Conversion of from 885 to 1030 ppm of NO was not affected by varying H_2O concentrations at either stoichiometric or excess NH_3 . Figure 6b shows that CO_2 has only a slight effect on NO conversion. The small effect on NO conversion over practical CO_2 concentrations between 5 and 16% can be considered to be negligible.

Oxygen strongly affects NO conversion below 0.5% O_2 , as shown in Figure 7 for 1000 ppm of NO. Similar results were obtained for NO concentrations of 709–890 ppm and 490–600 ppm. Reduction of NO is enhanced by O_2 up to the temperatures of maximum conversion (400 °C) for all NO levels. At 500 °C, there were several cases in which enhancement was not observed: for intermediate NO levels enhancement occurs with excess NH_3 but not with stoichiometric NH_3 ; at low concentrations of NO, enhancement did not occur with either stoichiometric or excess NH_3 .

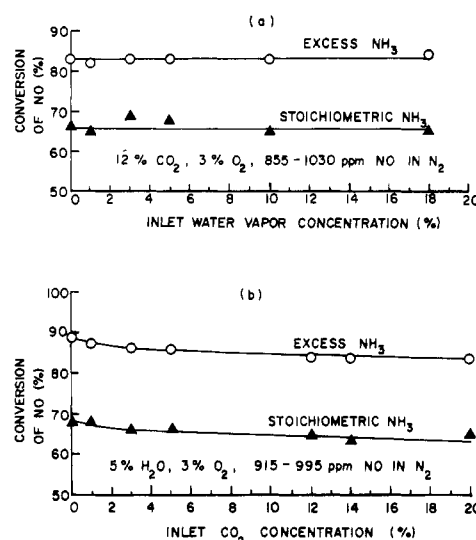


Figure 6. Effect of water vapor (a) and CO_2 (b) on NO reduction on V_2O_5 in simulated flue gas at 400 °C (s.v. = 20 000 h^{-1}).

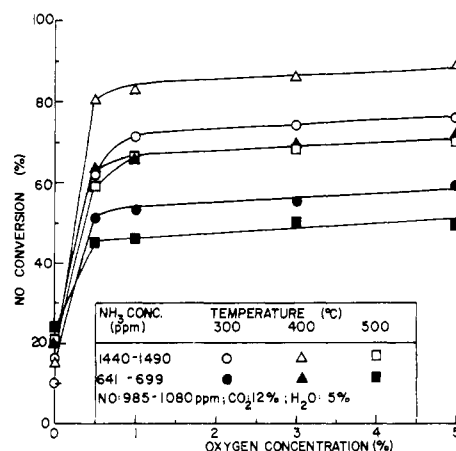


Figure 7. Effect of O_2 concentration on NO reduction on V_2O_5 in simulated flue gas; 1080 ppm of NO (s.v. = 20 000 h^{-1}).

Development of Rate Expression. The parametric data for the 15% V_2O_5 catalyst were correlated assuming a power-law rate expression of the form

$$\text{rate} = Ae^{-E/RT} p_{\text{NO}}^n p_{\text{NH}_3}^m p_{\text{O}_2}^q \quad (\text{mol of NO/h-g of cat.}) \quad (1)$$

Only the data for temperatures below the maximum conversion point ($\leq 400^\circ\text{C}$) were examined in detail.

Since CO_2 and H_2O had negligible effects on the rate of reduction of NO, reaction orders for these species in the rate expression are zero. The slight increase in conversion of NO with increasing O_2 concentration above 0.5% indicated that a power-law reaction order for O_2 would be finite but quite small.

Correlation was accomplished by minimization of the sum of squares of the difference between experimental and calculated rate constants, as determined by combining eq 1 with the plug-flow mass balance, eq 2, for successive estimations of the values of n , m , and q .

$$W/F = \int_0^x \frac{dx}{r} \quad (2)$$

where W = weight of catalyst, g, F = inlet flow rate of NO, mol/h, x = conversion, and r = reaction rate, mol/g of cat.-h.

The best-fit values of n , m , and q and the resultant corre-

Table II. Experimental and Calculated Conversion of NO on V₂O₅-Al₂O₃ Based on Intrinsic Rate Expression^a

Temp, C	Inlet partial pressures			Conversion		η
	P^0_{NO} , (atm $\times 10^6$)	$P^0_{\text{NH}_3}$, (atm $\times 10^6$)	$P^0_{\text{O}_2}$, (atm $\times 10^2$)	Exptl, %	Calcd, %	
20 000 h ⁻¹						
205	285	315	3	39	40	0.14
200	980	957	3	28	31	0.19
200	1485	1981	3	27	30	0.20
300	805	501	3	61	56	0.07
300	995	1468	3	65	59	0.07
300	1475	1981	3	61	58	0.07
400	770	921	3	84	84	0.02
400	980	1259	3	84	83	0.03
400	1485	2400	3	78	80	0.03
300	595	385	0.5	55	57	0.07
300	570	385	1	58	58	0.07
300	500	385	3	63	62	0.06
300	490	385	5	63	63	0.06
300	990	1491	0.5	62	59	0.06
300	1075	641	0.5	51	51	0.08
300	1050	1445	1	63	59	0.06
300	1000	652	3	55	55	0.08
300	980	652	5	59	56	0.07
400	990	1442	1	83	82	0.03
400	990	1442	5	89	84	0.02
400	1060	676	0.5	71	73	0.04
10 000 h ⁻¹						
300	980	689	3	71	71	0.10
400	970	1189	3	91	94	0.02
400	1020	1445	3	90	94	0.02

^a Simulated flue gas contains also 12% CO₂, 5% H₂O in N₂.

lation constants, A and E , as used in eq 1, provide the global rate expression

$$\text{rate} = 14.8e^{-3650/RT} P_{\text{NO}}^{0.5} P_{\text{NH}_3}^{0.4} P_{\text{O}_2}^{0.05} \quad (\text{mol of NO/g of cat.} \cdot \text{h}) \quad (3)$$

The global rate parameters were used as a first approximation of the appropriate values in the intrinsic rate equation.

It is of interest that the apparent reaction orders for NO and NH₃ in the global rate expression are in agreement with values determined by Kudo et al. (1974) for zirconium-doped lanthanum copper oxide (0.5 reaction order for both reactants). It can be shown that as the sum of the reaction orders in a power law rate expression approaches unity the conversion becomes a function of the reactant ratio which is in accord with the relationship between conversion and reactant ratio shown in Figure 5.

To determine the intrinsic rate expression, a computer program was employed which determines, in a step-by-step manner from reactor inlet to outlet, the surface concentrations of reactants and surface temperatures based on mass and heat transfer correlations, and the effectiveness factor, η (defined below) which parameterizes internal diffusion effects. By assuming an intrinsic rate expression, the degree of conversion of NO is calculated throughout the catalyst bed. The rate at any point (i) in the catalyst bed is determined by

$$r_i = \eta k_s P_{\text{NO}}^n P_{\text{NH}_3}^m P_{\text{O}_2}^q \quad (4)$$

where k_s is the intrinsic rate constant and the partial pressures are those at the catalyst surface, as determined in the calculations of bulk diffusion effects. Calculated conversion at the reactor outlet is compared with the experimental value, and the process is repeated with modified forms of the assumed intrinsic rate expression until agreement is obtained. Near-unity values of η indicate that pore diffusion effects are negligible. For convenience, as mentioned above, the calculation procedure begins by assuming that the intrinsic rate parameters are those determined from the correlation of the global

rates (i.e., initially assuming negligible mass transfer resistances).

The intrinsic rate expression that best describes the data up to 400 °C is

$$\text{rate} = 2.05 \times 10^3 e^{-9650/RT} P_{\text{NO}}^{0.30} P_{\text{NH}_3}^{0.22} P_{\text{O}_2}^{0.05} \quad (\text{mol of NO/g of cat.} \cdot \text{h}) \quad (5)$$

Table II, which compares some typical calculated and experimental values of conversion for 20 000 and 10 000 h⁻¹ space velocity, shows that a good representation of the rate of removal of NO_x is given by eq 5. The low η values indicate that internal diffusion effects are significant with the V₂O₅-Al₂O₃ catalyst even at the lowest temperatures employed.

The final form of the intrinsic rate expression can be utilized for the determination of global rates of reaction at a larger scale of operation (assuming catalyst surface activity is unchanged) by calculating surface concentrations and temperatures and effectiveness factors for the desired conditions. Complete details of the computer program have been given by Caretto (1969).

Durability Studies in Presence of SO_x. Table III gives a brief summary of the results of the SO_x exposure studies with the 15% V₂O₅-Al₂O₃ catalyst. Although there was some oxidation of SO₂ to SO₃ in the feed system, the amount of SO₃ formed in the reactor at 400 °C was not appreciable. There was reasonable agreement, within experimental error, between inlet and outlet total SO_x concentrations, indicating (based on these results only), that formation of solids in the system was either negligible or had reached steady-state levels.

It was of interest to determine if operation at lower temperatures would lead to significant catalyst poisoning or salt deposition (e.g., sulfites and sulfates). Several runs were performed at temperatures as low as 250 °C in the presence and absence of SO₂. These tests were conducted between 204 and 252 h exposure. Typical results are also given in Table III. The concentration data are representative of those determined near the end of each test period. As observed at 400 °C,

Table III. Typical Durability Test Results. V₂O₅ Catalyst in the Presence of SO_x^a

Accumulated time, h	Temp, °C	Inlet gas concn, ppm				Outlet gas concn, ppm				Conv. of NO, %
		NO _x	NH ₃	SO ₂	SO ₃	NO _x	NH ₃	SO ₂	SO ₃	
Reference	400	1050	1160	0	0	145	372	0	0	86
8	400	1180	1160	703	0	105	—	—	—	91
15	400	1060	1089	1035	0	130	—	—	—	88
25	400	1090	1065	1489	0	105	—	1425	113	90
40	400	1060	1114	1982	90	175	—	—	—	83
47	400	1140	1065	1000	71	90	—	—	—	92
112	400	1060	1090	1034	0	130	86	—	—	88
145	400	1125	1113	2583	0	150	152	2414	52	84
Reference	400	1050	1574	0	0	85	508	0	0	92
172	400	1050	858	974	61	195	60	1073	52	81
205	400	1070	747	1086	0	120	30	1088	26	89
Reference	255	880	862	0	0	410	404	0	0	53
221	250	955	859	1188	0	440	153	702	528	54
232	250	980	859	1188	0	400	—	—	—	59
236	300	870	845	1024	0	130	140	575	539	85
238	255	1075	858	1100	0	500	28	567	507	53
244	300	1085	858	1100	0	295	—	—	—	73
272	350	840	858	1100	0	90	—	—	—	89
Reference	355	890	768	0	0	170	27	0	0	81
313	400	715	1225	875	31	80	318	890	42	89
480	400	1065	706	583	52	130	93	554	42	88
599	400	940	884	595	219	50	319	658	219	95
628	400	1180	1780	553	93	70	671	407	188	94
648	400	1005	710	0	0	215	—	0	0	79

^a Simulated flue gas contains 12% CO₂, 3% O₂, 5% H₂O in N₂; 20 000 h⁻¹ space velocity.

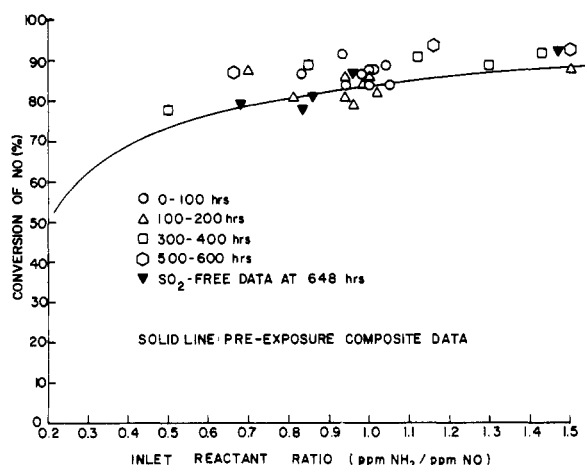
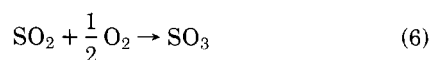


Figure 8. Conversion of NO on V₂O₅ catalyst during SO_x exposure test in simulated flue gas (1000 ppm of NO) at 400 °C (s.v. = 20 000 h⁻¹).

NO_x conversion at lower temperatures was not significantly altered by the presence of SO_x. The results at 250 °C were surprising in that the anticipated formation of sulfites and sulfates was expected to "poison" the V₂O₅ catalyst as observed for the platinum catalyst in the earlier study (Bauerle et al., 1975a).

At the lower temperatures (≤350 °C), there was significant oxidation of SO₂ to SO₃ on V₂O₅, but it is not certain whether oxidation was catalytic or homogeneous. Formation of SO₃ is thermodynamically favored over the entire temperature range examined. For the reaction



the equilibrium constant increases approximately by two orders of magnitude when temperature is decreased from 400 (K = 600) to 250 °C (K = 85 000). The failure to observe the presence of significant SO₃ at the reactor inlet when the

mixer-vaporizer temperature was reduced to 250 °C (data not shown) suggests that the oxidation may be catalyzed on the V₂O₅ below 400 °C.

Immediately after introduction of SO₂, NO_x conversion decreased (10% or less). Recovery of the initial activity appeared to be a function of temperature; at 250 °C recovery required from 2 to 5 h while at 400 °C recovery occurred in a matter of minutes. The data in Table III are steady-state results for each test period. Additional data other than NO_x conversion were not obtained during the recovery period. The observed induction period for the recovery of activity suggests that formation of salts somewhere in the test system may have occurred initially, depleting the NH₃ supply. Subsequently, a steady-state salt level was attained in accord with the satisfactory balances between steady-state inlet and outlet SO_x.

Figure 8 shows that throughout the SO_x exposure period the conversion of NO_x was consistent with pre-exposure data (the solid line is representative of pre-exposure data). Also shown in the figure are several data points obtained in the absence of SO_x after 648 h of exposure to SO_x. No change in activity is evident. The results of this study indicate that V₂O₅ is a highly effective, durable, and sulfur-resistant catalyst for controlling nitrogen oxide emissions from stationary sources.

Literature Cited

- Bauerle, G. L., Wu, S. C., Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 123 (1975a).
- Bauerle, G. L., Wu, S. C., Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.*, **14**, 268 (1975b).
- Caretto, L. S., Nobe, K., *AIChE J.*, **15**, 18 (1969).
- Kudo, T., Manabe, T., Gejo, T., Seki, M., Yoshida, K., "New Oxide Catalyst with Perovskite-Related structure for Reduction of NO with NH₃," presented at 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974.
- Seidman, E. B., *Anal. Chem.*, **30**, 1680 (1958).

Received for review December 30, 1976

Accepted February 28, 1978

Work supported by a grant from the Environmental Protection Agency.