

KINETICS OF THE REDUCTION OF NITROGEN OXIDE AND DINITROGEN OXIDE BY AMMONIA ON A V_2O_5/Al_2O_3 CATALYST IN THE ABSENCE OF OXYGEN

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The kinetics of the reduction of NO and N_2O by ammonia on a V_2O_5/Al_2O_3 catalyst (15 mass % V_2O_5) have been measured over the temperature range 300–480°C at atmospheric pressure. The presence of water vapour in the reaction mixture retards the reduction rates of both NO and N_2O . The oxidation state of vanadium does not change within the concentration and temperature ranges investigated. From the results for the reaction kinetics and the oxidation state of vanadium it is concluded that the reduction of NO and N_2O by ammonia occurs by the associative Langmuir–Hinshelwood mechanism with the surface reaction as the rate-determining step.

The reduction of nitrogen oxides by ammonia to nitrogen on V_2O_5/Al_2O_3 catalysts is one of the most efficient methods for abating NO_x emissions. The advantage of ammonia as the reducing agent is that its reaction with nitrogen oxides occurs selectively over a wide temperature range even when excess oxygen is present, the oxidation of ammonia alone by oxygen being inappreciable under these conditions. For these reasons, a great deal of attention has been given to research studies on the catalytic reduction and its kinetics.

The kinetic data for the catalytic reaction of NO with NH_3 have been represented in the literature mainly by empirical power law expressions or by equations derived from the Langmuir–Hinshelwood concepts. Murakami¹ divides transition metal oxides into two groups according to the form of the power law expression for the $NO + NH_3$ reaction, the N_2O content of the reaction products, and the ratio of the catalytic activities for the $NO + NH_3$ and $NO + H_2$ or $NO + CO$ reactions. For the group involving MoO_3 , WO_3 , SnO_2 , and TiO_2 in addition to V_2O_5 , empirical rate laws that give the best fit with the data involve the NO concentration to a power close to 1. Power law rate expressions in which the NO concentration enters to the power ≈ 1 and the NH_3 concentration to a power between 0 and 1 have also been used by Inomata² for other catalysts, including supported vanadium catalysts. From these dependences it has been concluded that the adsorption of NO, if any, occurs to only a very small extent and gas-phase NO reacts directly with adsorbed ammonia. This conclusion is also supported by adsorption measurements made by

the above workers on these catalysts. The assumption of gaseous NO reaction is also involved in a Langmuir type equation derived by Stringaro³ for the reaction over a V₂O₅/Ce₂O₃/Al₂O₃ catalyst:

$$R_{\text{NO}} = \frac{kx_{\text{NH}_3}x_{\text{NO}}}{(1 + K_{\text{NH}_3}x_{\text{NH}_3})} \quad (1)$$

Wu⁴ has derived an equation for the rate of the NO + NH₃ reaction on a V₂O₅/Al₂O₃ catalyst in the absence of oxygen in the form

$$R_{\text{NO}} = kP_{\text{NO}}^{0.2}P_{\text{NH}_3}^{0.12} \quad (2)$$

That the exponent of the NO concentration is different from unity is due to significant adsorption of NO on the reduced V₂O₅/Al₂O₃ catalyst under the conditions of the NO + NH₃ reaction.

The different activities of vanadium catalysts prepared in similar ways by various workers, which are reflected primarily in different preexponential terms and activation energies in the power law equations, can be attributed to different trace concentrations of oxygen in the NO + NH₃ reaction mixtures. It is well known that oxygen significantly increases the rate of NO reduction by ammonia starting from O₂ concentrations of tens of ppm (ref.⁵), yet many workers made no check on the oxygen content of the carrier gas and other components of the reaction system when studying the kinetics of the NO + NH₃ reaction "in the absence of oxygen". No significant change in the exponent of the NO concentration in the equation of Inomata² occurs even at high levels of oxygen in the reaction mixture, consistent with Inomata's observation of a negligible extent of NO adsorption on vanadium catalysts in the presence of excess oxygen at the temperature of the NO + NH₃ + O₂ reaction.

The N₂O + NH₃ reaction has so far been studied only exceptionally, mainly at high temperatures as a gas-phase homogeneous reaction. There has been no systematic study of the heterogeneous catalytic reduction of N₂O by ammonia. However, some of the studies on the kinetics of the NO + NH₃ reaction may serve as a guide for estimating the rate of the N₂O + NH₃ reaction. Under certain conditions of the NO + NH₃ reaction, N₂O is produced in addition to nitrogen and water, and if sufficient data are available on the N₂O content of the reaction products, it is possible to draw inferences concerning the dependence of the rate of the N₂O + NH₃ reaction on the reaction conditions.

The aim of the present work was to measure the kinetics of the reduction of NO by ammonia on a V₂O₅/Al₂O₃ catalyst (15 mass % V₂O₅) in the absence of oxygen (with a maximum level of O₂ in the inlet mixture of 5 ppm). Since N₂O also formed in a non-negligible amount under the conditions employed, the kinetics of the N₂O + NH₃ reaction were also evaluated. In addition, changes in EPR spectra

were followed for catalyst samples treated in the same way as in measuring the kinetics of both reactions.

EXPERIMENTAL

A V_2O_5/Al_2O_3 catalyst was prepared by mixing and kneading γ -alumina (Condea SC) with a suspension of vanadyl oxalate containing oxalic acid as a peptizing agent⁶. After forming, the catalyst was dried at 120°C and calcined in air at 575°C for 3 h. The specific surface area of the catalyst was 193 m²/g.

The kinetics of the $NO + NH_3$ and $N_2O + NH_3$ reactions were measured at atmospheric pressure and 300–480°C, using a flow-through all-glass apparatus with an integral reactor. The gas space velocities ranged from 5 to 100 l NTP/h g. The overall inlet concentrations of the components were varied up to 3 mole % in such a manner that either NO (or N_2O) or NH_3 was in excess. The competitive $NO + N_2O + NH_3$ reduction was also investigated. The carrier gas was nitrogen purified by passing over a Cu catalyst (BTS, Merck).

The region of kinetic control was determined by measuring the activities of catalysts of grain sizes 0.5–1 and 0.3–0.5 mm at various linear flow rates of the gas mixture and various dilutions of the catalyst with crushed glass of the same grain size. The measurements for the 0.5–1.0 mm catalyst demonstrated that, over the whole range of space velocities used, there were no mass transfer effects due either to external or internal diffusion. For dilution with crushed glass by a ratio of 1 : 1, the temperature was found to be constant throughout the catalyst bed within a maximum vertical deviation of $\pm 3^\circ C$.

Gases. NO was prepared by the reaction of an $NaNO_2$ solution with an $H_2SO_4 + FeSO_4$ solution, and was freed from NO_2 by absorption in a concentrated KOH solution. NH_3 and N_2O were taken from cylinders. All the gases were dried by passing over solid KOH or a 5A molecular sieve. In studying the effect of water vapour, a defined amount of the vapour was introduced into the reaction mixture by saturating part of the carrier gas in a water-sprayed saturator maintained at a constant temperature.

Analysis. The course of the reaction was followed by measuring the concentrations of the components at the reactor outlet. The concentration changes during the reaction were followed continuously by means of an ion-selective electrode (Orion). The concentrations of NO and N_2O were determined with the aid of a Chrom-4 gas chromatograph (Laboratorní přístroje, Prague) using columns packed with a 5A molecular sieve treated as described by Dietz⁷ and with Porapac Q respectively. After a steady state had been attained in the system, a measured amount of gas was absorbed in an $H_2SO_4 + H_2O_2$ solution and the concentrations of NH_3 and NO were determined by titration.

EPR spectra of the catalysts were taken on an ESR-220 instrument (Academy of Sciences of the G.D.R., Berlin) at room temperature (X-band; field modulation, 100 kHz; modulation amplitude, 1 mT; microwave power output, 2 mW; time constant, 0.2 s; standards, Mn^{2+}/ZnO and DPPH).

RESULTS AND DISCUSSION

The results of the kinetic measurements for the $NO + NH_3$ and $N_2O + NH_3$ reactions were treated in the form of dependences of the conversions of NO, N_2O , and NH_3 defined as

$$\eta_i = 1 - x_i/x_i^0, \quad (3)$$

where x_i^0 and x_i are the mole fractions of the reaction components in the gas mixture at the inlet and outlet of the reactor, respectively, on the space time, W/F , at a constant temperature.

Characteristic plots of the conversions η_{NO} , η_{NH_3} and of the molar concentration of N_2O in the $\text{NO} + \text{NH}_3$ reaction against the ratio W/F at a temperature of 450°C are shown in Fig. 1. At lower temperatures, notably at 350 and 300°C , the N_2O concentration does not go through a maximum owing to a lower proportion of N_2O in the products of the $\text{NO} + \text{NH}_3$ reaction and simultaneously a lower rate of the consecutive reduction of N_2O by ammonia.

The rates of removal and formation of individual components were calculated by differentiating the conversion data graphically in accordance with the equation

$$R_i = \frac{x_i^0}{22 \cdot 4} \frac{d\eta_i}{d(W/F)} \quad (4)$$

The rate data obtained were correlated by empirical power law equations of the type

$$R_i = kx_{\text{NO}}^a x_{\text{NH}_3}^b x_{\text{H}_2\text{O}}^c x_{\text{N}_2\text{O}}^d \quad (5)$$

by equations for the oxidation-reduction mechanism taking into account the total number of active sites, and by equations derived from the Langmuir-Hinshelwood models for various rate-determining steps (adsorption of NO , NH_3 , and N_2O ; desorption of H_2O ; surface reactions between adsorbed NO (or N_2O) and NH_3 , and between adsorbed NH_3 and gas-phase NO or N_2O). Both molecular and dissociative adsorption was considered; ammonia was assumed to be dissociatively adsorbed on two to three active sites, and for dinitrogen oxide adsorption onto active sites of the same and different kind was considered.

The rate data were processed using a multiple quasi-linear regression method⁸. The criteria used in assessing the adequacy of the proposed kinetic equations were the average absolute and relative deviations between calculated and measured reaction rates for individual inlet concentrations, the deviations for all measurements at each reaction temperature, and the deviations for measurements over the whole temperature range of the $\text{NO} + \text{NH}_3$, $\text{NO} + \text{N}_2\text{O} + \text{NH}_3$, and $\text{N}_2\text{O} + \text{NH}_3$ reactions.

It has been found that a power law expression of the type of Eq. (5) is unable to reproduce the whole set of data, even though at the lower reaction temperatures 300 and 350°C the results can be described approximately by the equation

$$R_{\text{NO}} = kx_{\text{NO}}^1 x_{\text{NH}_3}^0 \quad (6)$$

The deviations between measured and calculated reaction rates were least for Langmuir-Hinshelwood rate laws derived by assuming that the rate-determining step is the surface reaction between dissociatively adsorbed ammonia and gas-phase NO:

$$R_{\text{NO}} = \frac{k_0 x_{\text{NO}} (K_2 x_{\text{NH}_3})^{2/3}}{[1 + (K_2 x_{\text{NH}_3})^{1/3} + K_4 x_{\text{H}_2\text{O}}]^2} \quad (7)$$

For the $\text{N}_2\text{O} + \text{NH}_3$ reaction, the best fit was given by a kinetic equation considering as the rate-determining step a surface reaction between adsorbed ammonia and a molecule of N_2O adsorbed on different active sites:

$$R_{\text{N}_2\text{O}} = \frac{k_{00} K_3 x_{\text{N}_2\text{O}} (K_2 x_{\text{NH}_3})^{2/3}}{[1 + (K_2 x_{\text{NH}_3})^{1/3} + K_4 x_{\text{H}_2\text{O}}]^2 (1 + K_3 x_{\text{N}_2\text{O}} + K_5 x_{\text{H}_2\text{O}})} \quad (8)$$

The values of the rate constants and adsorption coefficients in Eqs (7) and (8) and their temperature dependences are presented in Table I and Fig. 2.

The proposed kinetic equations and the calculated rate and adsorption coefficients were checked by integration of Eq. (4), where rates R_{NO} and $R_{\text{N}_2\text{O}}$ calculated from Eqs (7) and (8) were substituted for R_1 . The experimental and calculated conversions in the $\text{NO} + \text{NH}_3$ reaction for some of the data sets are compared in Figs 1 and 3, and those for the $\text{N}_2\text{O} + \text{NH}_3$ reaction in Fig. 4. The dependences of the conversions of NO and NH_3 and of the molar concentration of N_2O on the inlet concentrations of H_2O and N_2O at constant W/F are shown in Figs 5 and 6, respectively.

The rate of the $\text{NO} + \text{NH}_3$ reaction can be described with an accuracy equal to that of Eq. (7) by using the equation

$$R_{\text{NO}} = \frac{k'_0 x_{\text{NO}} K_2 x_{\text{NH}_3}}{[1 + K_1 x_{\text{NO}} + K_2 x_{\text{NH}_3} + K_4 x_{\text{H}_2\text{O}}]^2} \quad (9)$$

derived on the assumption that the rate-determining step is a surface reaction between molecularly adsorbed ammonia and adsorbed NO. Of the possible equations for the rate of the $\text{N}_2\text{O} + \text{NH}_3$ reaction, the best fit with experimental data is given by

$$R_{\text{N}_2\text{O}} = \frac{k_{00} K_3 x_{\text{N}_2\text{O}} K_2 x_{\text{NH}_3}}{(1 + K_1 x_{\text{NO}} + K_2 x_{\text{NH}_3} + K_4 x_{\text{H}_2\text{O}})^2 (1 + K_3 x_{\text{N}_2\text{O}} + K_5 x_{\text{H}_2\text{O}})} \quad (10)$$

even though with deviations exceeding at low temperatures those found for Eq. (8).

The values of the rate constants and adsorption coefficients in Eqs (9) and (10), as well as the activation energy and the heats of adsorption, are listed in Table II.

Electron paramagnetic resonance investigation of the oxidation state of vanadium

has revealed that the original pentavalent vanadium undergoes a reduction in the course of the reaction. It has been found that the time required for a steady-state

TABLE I

Rate constants and adsorption coefficients in Eqs (7) and (8)

Temperature, °C	k_0	k_{00}	K_2	K_4	K_3	K_5
480	—	0.0182	137	52	540	73
450	6.95	$3.9 \cdot 10^{-3}$	315	73	1 130	122
400	1.82	$2.2 \cdot 10^{-4}$	1 550	144	4 420	319
350	0.47	$7.8 \cdot 10^{-6}$	9 200	301	22 000	970
300	0.091	—	81 000	740	—	—
Activation energy kJ mol ⁻¹	98.9	233	—	—	—	—
Heat of adsorption kJ mol ⁻¹	—	—	127	53	111	78

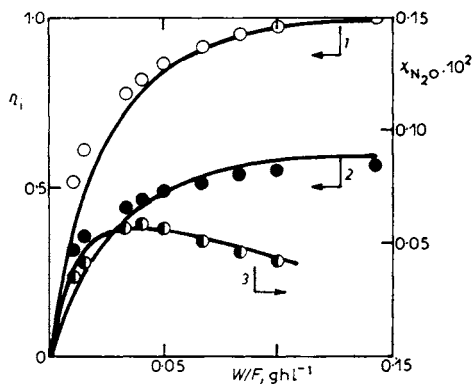


FIG. 1

Plots of conversions of NO (1) and NH₃ (2) and of the N₂O concentration (3) in the NO + NH₃ reaction at 450°C as functions of W/F . Inlet concentration: 0.5% NO + 0.5% NH₃

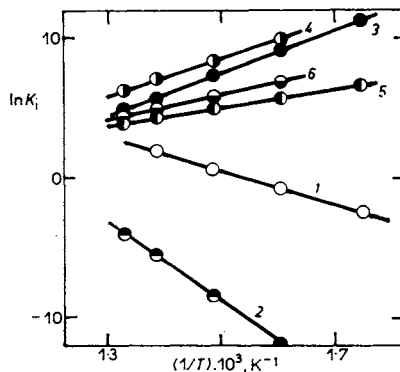


FIG. 2

Arrhenius and van't Hoff dependences of the rate constants and adsorption coefficients, respectively, in Eqs (7) and (8). 1 k_0 ; 2 k_{00} ; 3 K_2 ; 4 K_3 ; 5 K_4 ; 6 K_5

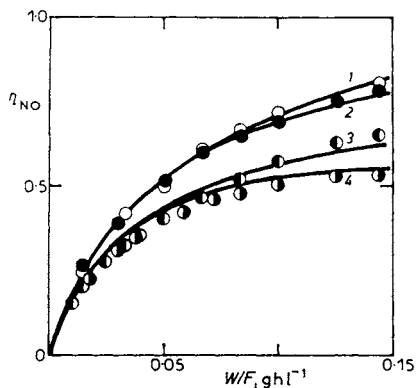


FIG. 3

A plot of NO conversion against W/F for the $\text{NO} + \text{NH}_3$ reaction at 400°C and various inlet concentrations of components: 1 0.6% NO + 0.4% NH_3 ; 2 1.8% NO + 1.2% NH_3 ; 3 0.75% NO + 0.25% NH_3 ; 4 2.25% NO + 0.75% NH_3

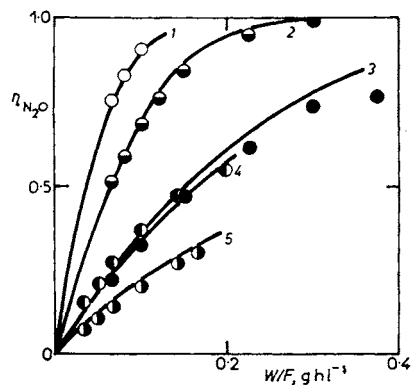


FIG. 4

A plot of N_2O conversion against W/F for the $\text{N}_2\text{O} + \text{NH}_3$ reaction at 450°C and various inlet concentrations of components: 1 0.1% N_2O + 1% NH_3 ; 2 0.25% N_2O + 1% NH_3 ; 3 0.25% N_2O + 1% NH_3 + 1% H_2O ; 4 0.6% N_2O + 0.6% NH_3 ; 5 0.6% N_2O + 0.2% NH_3

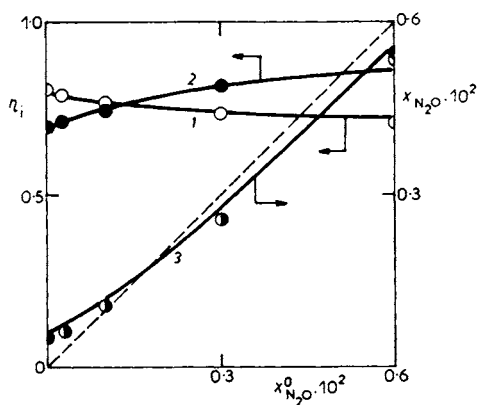


FIG. 5

Plots of η_{NO} (1), η_{NH_3} (2) and the molar concentration of N_2O (3) as functions of the inlet concentration of H_2O . Conditions: 450°C ; 1 g of catalyst; 20 l/h; inlet concentration, 0.5% NO + 0.5% NH_3 + $x\%$ H_2O

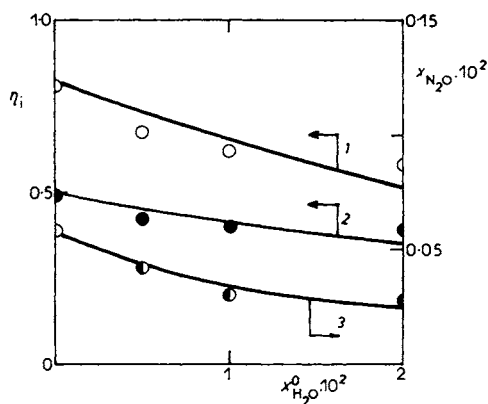


FIG. 6

Plots of η_{NO} (1), η_{NH_3} (2), and the molar concentration of N_2O (3) as functions of the inlet concentration of N_2O . Conditions: 450°C ; 1 g of catalyst; 20 l/h; inlet concentration, 0.6% NO + 0.4% NH_3 + $x\%$ N_2O

composition of the outlet reaction mixture to be established is practically identical with the time it takes for the character and intensity of the EPR spectra of a catalyst sample treated in the same way to become steady. The steady-state EPR spectra have the same character and signal intensity over the whole range of reaction conditions at the $\text{NO} : \text{NH}_3$ ratio from 0.01 to 100. Only when the catalyst is treated using component ratios lower or higher than those indicated above does further reduction or partial oxidation occur, respectively. Under these conditions, Eqs (7) to (10) are no longer valid.

CONCLUSIONS

The fact that the oxidation state of vanadium does not change under the reaction conditions investigated supports the assumption that the catalytic reaction $\text{NO} + \text{N}_2\text{O} + \text{NH}_3$ occurs by the associative Langmuir–Hinshelwood mechanism.

Kinetic equations (7) and (9) and their adsorption coefficients indicate that there is little or no adsorption of NO and the reaction involves gaseous NO. This is also in accord with results of an infrared study⁹ of NO adsorption on the same catalyst which show that the adsorption of NO decreases with increasing temperature, becoming negligible in the temperature range used in the present work. The fact that N_2O has no effect on the rate of NO reduction suggests that it is adsorbed on different active sites.

TABLE II
Rate constants and adsorption coefficients in Eqs (9) and (10) ($k'_0 = k_0K_1$; $K_1 < 1$)

Temperature, °C	k'_0	k_{00}	K_2	K_4	K_3	K_5
480	—	0.0189	125	88	704	25
450	10.8	$5.0 \cdot 10^{-3}$	133	89	960	46
400	3.7	$5.4 \cdot 10^{-4}$	149	92	1 980	149
350	1.10	—	170	96	—	—
300	0.262	—	198	100	—	—
Activation energy kJ mol ⁻¹	84.5	—	—	—	—	—
Heat of adsorption kJ mol ⁻¹	—	—	9.2	2.7	55	94

There remains the question of the mode of ammonia adsorption. Equations (7) and (8) suggest that dissociatively adsorbed ammonia is involved in the reaction. This would be in line with the mechanism proposed by Otto and coworkers¹⁰ for the reaction on platinum and copper catalysts and later adopted also for a vanadium catalyst⁴. This conclusion is further supported by results of an infrared study¹¹ on ammonia adsorption which indicate that, besides molecularly adsorbed ammonia, the NH_2 group may exist on the surface of reduced vanadium catalysts.

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LIST OF SYMBOLS

F	feed rate of reaction mixture (l(NTP) h^{-1})
k	rate constant (the dimension depends on the rate law)
K_i	adsorption coefficient of substance i (—)
P_i	partial pressure of substance i (MPa)
R_i	rate of removal of substance i ($\text{mol h}^{-1} \text{g}^{-1}$)
W	catalyst mass (g)
η	conversion (—)

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