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Molecular Oxygen Induced Crystallite Size Effect in Reduction of Nitric Oxide with Ammonia Over Supported Platinum

The effect of changing platinum crystallite size from 2.7 to 15.5 nm on the specific catalytic activity in NO reduction by NH_3, with and without added O_2, was studied over alumina supported platinum catalysts between 423 and 473°K. In the NO-NH_3 system both specific catalytic activity and selectivity to N_2 are independent of crystallite size. In the NO-O_2-NH_3 system the specific catalytic activity of the 15.5 nm crystallites is about six times that of the 2.7 nm crystallites. The NO reduction rate shows dependence on NO to the first power and on NH_3 to the one-half power.

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SCOPE

Supported noble metal catalysts find wide and important application in industry and are gaining importance in pollution control applications including the reduction of NO in automotive exhaust and in tail gas streams. Because of the high cost of noble metals, these catalysts usually contain only a small amount of highly dispersed metal on a support. The metal crystallites typically range from 1.0 to 50 nm in diameter (1 nm = 10Å). The literature provides little quantitative information on their kinetic behavior in NO reduction, and it provides no information on the effect of the degree of dispersion of the metal on its specific catalytic activity (rate of reaction per unit metal surface area) in such reactions. In many reactions involving H_2 and hydrocarbons the specific catalytic activity is independent of the size of the metal crystallites. However, it has recently been shown that in oxidation with O_2, including NH_3 oxidation, the specific catalytic activity is markedly dependent on crystallite size. The cause of this effect can be better understood if information on related oxidation-reduction reactions is available; yet there are no data with other oxidants such as NO. This work sought to determine if a crystallite size effect exists for a platinum on alumina catalyst in the reduction of NO by NH_3 with and without added O_2. Another purpose of the work was to quantitatively determine the kinetics of the NO-NH_3 reaction.

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CONCLUSIONS AND SIGNIFICANCE

Increasing the platinum crystallite size from 2.7 to 15.5 nm does not affect the specific catalytic activity in the reduction of NO by NH_3 without O_2 present between 423° and 473°K. N_2 and N_2O are the only nitrogen-containing products of reaction. In the presence of O_2 larger crystallites have a higher specific activity. This is similar to observations in low-temperature NH_3 oxidation by O_2 and is opposite in trend to most cases of crystallite size effect under reducing conditions. The absence of a crystallite size effect in the oxygen-free system indicates that reaction involves unspecific sites on the metal surface and is thus insensitive to changes in surface detail, which occur with changes in crystallite size. The crystallite size effect in the presence of O_2 is interpreted in terms of an involvement of O_2 directly in the reaction and of the greater ability of large crystallites to chemisorb active oxygen species. The work shows that in the absence of O_2 the most efficient use of the metal occurs at very high degrees of dispersion, whereas in the presence of O_2 crystallites somewhat larger than 5.0 nm result in the most efficient use of the metal.

The rate of reaction is satisfactorily described by a single-site Langmuir-Hinshelwood kinetic model involving associative NO adsorption and dissociative NH_3 adsorption. The rate limiting step appears to be reaction between adsorbed NO and an adsorbed nitrogen containing fragment of NH_3. O_2 causes a considerable rate enhancement. This can be attributed to a change in the relative concentration of surface species resulting from reaction of oxygen with adsorbed nitrogen-containing fragments from NH_3.

The effect of metal crystallite size on the specific catalytic activity of highly dispersed, supported metal catalysts is of considerable interest and importance for both practical and theoretical reasons. If specific catalytic activity is independent of crystallite size for very small crystallites, it is reasonable to assume that the metal atoms are acting individually or are involved only in simple sites. If crystallite size affects specific catalytic activity, special surface sites are probably the source of the catalytic activity, and studies of such effects can offer insight into the nature of such sites and the nature of the reactant-catalytic surface interactions. Currently it is not possible to predict whether specific catalytic activity of a given reaction over a metal will change with crystallite size although some rationale for the presence of change is available (Poltorak and Boronin, 1966; van Hardeveld and Hartog, 1971; Boudart, 1971; Bond, 1971). Under reducing conditions many reactions involving H_2 and hydrocarbons (Boudart, 1969; Aben et al., 1970; Boudart et al., 1966; Poltorak et al., 1971; Poltorak and Boronin, 1966; van Hardeveld and Hartog, 1971; Hughes et al., 1962; Kraft and Spindler, 1971; Cusumano et al., 1966; Dautzenberg and Platteeuw, 1970; Benson and Boudart, 1965) are not affected by metal crystallite size, that is, are facile (Boudart et al., 1966). Several other hydrocarbon reactions have been shown to be demanding (van Hardeveld and Hartog, 1971; Benson and Boudart, 1965; Corolleur et al., 1972) in that the specific catalytic activity is dependent on metal crystallite size. Oxidation reactions involving O_2 also appear to be demanding (Boudart, 1969; Poltorak and Boronin, 1965, 1966; Poltorak et al., 1971; Ostermaier et al., 1974a). The reason for the crystallite size dependence in oxidation reactions with O_2 can be better understood if information is available on related oxidation reactions such as the crystallite size behavior if the oxidant is an oxygen containing molecule such as NO.

The reduction of NO by NH_3 is of practical interest as a technique for removing pollutant NO from gas streams containing O_2 because NH_3 reacts selectively with NO in the presence of O_2 (Andersen et al., 1961; Griffing et al., 1969; Andersen and Kieth, 1961; Cohen et al., Bartok et al., 1971; Shelef and Kummer, 1969, 1971). This paper presents a study of the effect of platinum crystallite size on specific catalytic activity in the oxidation of NH_3 by NO with and without O_2 present in the feed gas. Kinetic studies which quantify the NO reduction reaction and support the proposed reaction mechanism are described.

EXPERIMENTAL METHODS

Apparatus and Procedure

The apparatus consisted of a manifold system for measuring and controlling the flow of premixed gases to the reactor; a packed bed, flow, micro-reactor operated at atmospheric pressure and immersed in a fluidized sand bath for temperature control (± 1°C) (Pusateri, 1973). A thermocouple in the catalyst bed demonstrated equality with sand-bath temperature. The system was entirely of 316 stainless steel. A dual-column gas chromatograph with dual gas sample valves permitted samples of effluent gas to be analyzed with either of the two columns allowing complete separation of components and determination of point rates of reaction.

Because oxygen enhances the rate of NO-NH_3 reaction (Wanner, 1972; Markvart and Pour, 1967), extreme care was taken to eliminate it from the system, and tests indicated less than one ppm O_2 under reaction conditions. Freshly prepared catalyst as 30-40 mesh range particles was reduced under flowing hydrogen by heating at 1°K/min to 623° and 773°K for the unsintered and sintered catalyst and holding for 12 hr. before placing in the reactor. Rereduction in the reactor did not affect the steady state activity of the catalyst although it did affect initial activity. Typically several tenths of a gram of catalyst were used. Space velocities based on the feed stream at 298°K were varied from 47 to 108 s^{-1} for the unsintered catalyst and from 3.75 to 42.8 s^{-1} for the sintered catalyst. Conversion of limiting reactant was maintained below 10% in all cases, and differential reactor operation was demonstrated in this region by showing that rate was independent of space velocity. Because the catalysts underwent deactivation to steady state activity in about 12 hr., they were always deactivated under 0.25% NO and 2.0% NH_3 for 18 hr. Kinetic data were obtained with one-half hour allowed for equilibration after each concentration change. The rate at the conditions of the initial deactivation was shown to reproduce after all kinetic data were obtained. Concentration ranges of 0.25 to 1.0% NO and 0.1 to 2.0% NH_3 were studied at 423°, 448°, and 473°K.

For the NO-NH_3-O_2 system the stream containing O_2 was mixed with other reactants just prior to the catalyst bed to prevent formation of reactive NO_2 prior to the catalyst, and a liquid nitrogen cold trap placed immediately behind the reactor trapped out NH_3 and NO preventing the formation of NO_2 and the subsequent formation of significant amounts of N_2 from gas-phase reaction between NH_3 and NO_2. A run employing an equivalent weight of platinum-free alumina in the reactor quantitatively demonstrated that the amount of N_2 formed independent of platinum was small. N_2O was not produced without the platinum catalysts. Space velocities of 189 and 238 s^{-1} were used for the unsintered and sintered catalysts. The feed composition was 0.25% NO, 2% NH_3 and 0.5% O_2 in helium, and the temperature was 423°K.

All analyses were by gas chromatography. Nitrogen and nitric oxide were separated by a 4 m Chromasorb 104 column followed by a 3.1 m Porapak Q column. Nitrous oxide was separated from the other species by a 2 m Chromasorb 104 column. Both columns were operated at room temperature. The oxygen-nitrogen separation was achieved with a 2 m 5A molecular sieve column operated at 313°K.

Rates are given as turnover numbers which are defined as the number of gmoles of N_2 or N_2O produced per second per gram mole of calculated surface sites. Each surface site was assumed to consist of two surface platinum atoms where surface platinum atoms were determined by hydrogen chemisorption.

Materials

High purity helium (<20 ppm O_2), and 10% NO (<40 ppm air), 6% NH_3 (<25 ppm N_2) and 25% high purity O_2 in high purity helium were used. Helium was passed through a heated (473°K), reduced copper oxide catalyst bed followed by a 4A molecular sieve column to remove O_2 and H_2O. H_2 was electrolytic grade further purified with a reduced copper catalyst and molecular sieve unit.

Three catalysts were studied. Two were 1 wt. % Pt on alumina prepared and characterized by Ostermaier (1973; Ostermaier et al., 1974a). The unsintered catalyst had a platinum dispersion of 0.38 corresponding to a surface average platinum crystallite size of 2.7 nm assuming a cube with five sides available for hydrogen chemisorption (Adams et al., 1962) and a 1:1 hydrogen atom to surface platinum atom stoichiometry (Wilson and Hall, 1970, 1972). It chemisorbed 9.83×10^{-6} gmole H_2/g cat. Electron micrographs of this catalyst indicated that essentially all the platinum crystallites fell between 2.0 and 3.0 nm. A portion of this catalyst was sintered in air at 923°K for 24 hr. causing a decrease in H_2 chemisorption to 1.71×10^{-6} gmole H_2/g cat and in platinum dispersion to 0.065 corresponding to a surface average platinum crystallite size of 15.5 nm. X-ray indicated a volume average crystallite diameter of 14 nm and electron micrographs a crystallite size range 8.0 to 20 nm. The third catalyst was a commercial 0.5% Pt on alumina catalyst (referred to as type M). It chemisorbed 2.78×10^{-6} g-mole H_2/g cat and had a dispersion of 0.236 corresponding to a crystallite size of 4.3 nm.

RESULTS

Nitric Oxide-Ammonia System

At 473°K no measurable reaction occurred in either the empty reactor or the reactor filled with alumina. Reproducibility of rate across the entire concentration range was typically better than 15% for independent runs carried out several weeks apart. Diffusion calculations indicated mass transfer limitations were not important.

A marked decline in activity occurred during the first few hours on stream. Catalyst activity had typically decreased by a factor of about 3.3 independent of temperature when steady state activity was reached. The characteristics and probable cause of the deactivation, thought to result from surface oxidation, are discussed elsewhere (Ostermaier et al., 1974b; Pusateri, 1973). Table 1 gives the initial specific catalytic activities, obtained by extrapolation of semi-log plots of rate to zero time, and the extents of deactivation observed. Initial specific catalytic activity is independent of platinum crystallite size within the estimated error of the zero time extrapolation of ± 25%. Thus the $NO\text{-}NH_3$ reaction over platinum is facile.

Figure 1 summarizes the effect of temperature and platinum crystallite size on the steady state specific catalytic activity of the three catalysts studies for the $NO\text{-}NH_3$ reaction. At 423° and 448°K the ratio of specific catalytic activity of the unsintered catalyst to that of the sintered catalyst ranges from 0.90 to 1.38 over all feed compositions studied, and the average ratio of 1.15 describes all the data within experimental error. At 473°K the initial specific catalytic activity of the two catalysts is the same but the sintered catalyst appeared to deactivate more severely. Since the data for the unsintered catalyst were duplicated and reproduced well, while that for the sintered catalysts were not repeated, the steady state results for the sintered catalyst are considered less reliable. Type M catalyst, which has an average platinum crystallite size 1.6 times that of the unsintered catalyst,

Table 1. Initial Specific Catalytic Activities and Extents of Deactivation for Nitrogen Formation*

Temp., °K	Catalyst	Initial activity, turnover no., s^{-1}	r_i/r_{ss}
423	Sintered 1% Pt	0.015	3.4
448	Unsintered 1% Pt	0.08	3.5
448	Sintered 1% Pt	0.07	3.0
473	Unsintered 1% Pt	0.22	3.3
473	Sintered 1% Pt	0.23	5.3
473	Type *M*	0.33	3.1

* Feed composition 0.25% NO, 2.0% NH_3 in helium. Estimated error in initial rate was ±25%.

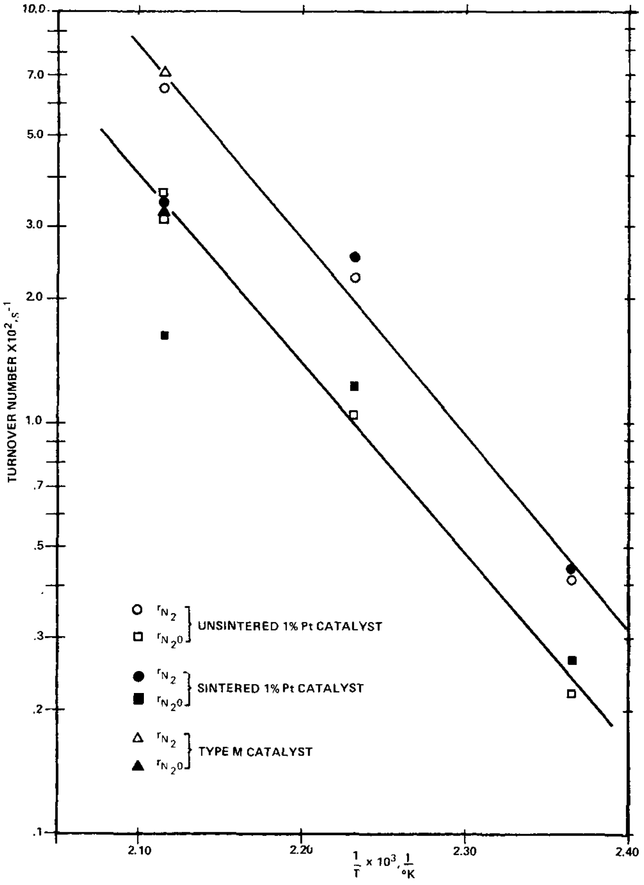

Fig. 1. Arrhenius temperature dependence of observed rate of reaction for 0.25% NO and 2.0% NH_3 in helium.

gave the same specific catalytic activity as the unsintered catalyst. We conclude from these data that specific catalytic activity is independent of crystallite size in the NO-NH_3 system. The activation energies calculated from Figure 1 are 21.6 ± 2 kcal/mole for nitrogen formation and 20.8 ± 2 kcal/mole for nitrous oxide formation excluding the 473°K data for the sintered catalyst. The difference is not significant. Selectivity to nitrogen, defined as the ratio r_{N_2}/r_{N_2O}, is independent of platinum crystallite size and temperature as shown in Table 2. Selectivity shows no trend with feed composition and under all conditions at steady state is about 1.8.

The NO-NH_3 reaction rate was fitted to several Langmuir-Hinshelwood models (Smith, 1970) using a nonlinear, least squares fitting technique. A dual-site dissociative NH_3 adsorption model and a single-site dissociative adsorption model both gave good fits as judged by standard error

$$\left[\text{standard error} = \left[\sum_{i=1}^{n} (r_{\text{obs},i} - r_{\text{pre},i})^2/(n-k) \right]^{1/2} \right] .$$

The single-site model was chosen because the absence of a crystallite size effect indicated the reaction involved only simple, unspecific sites and thus the requirement of two different sites seemed unlikely. The standard error was less than 10% of the rate for all conditions except with the sintered catalyst at 473°K and the unsintered catalyst at 423°K where the error was 20%. The single site rate models for N_2 and N_2O formation are

$$r_{N_2} = \frac{k_{s,N_2} K_{NO} K_{NH_3}^{1/2} P_{NO} P_{NH_3}^{1/2}}{(1 + K_{NO} P_{NO} + K_{NH_3}^{1/2} P_{NH_3}^{1/2})^2} \tag{1}$$

$$r_{N_2O} = \frac{k_{s,N_2O} K_{NO} K_{NH_3}^{1/2} P_{NO} P_{NH_3}^{1/2}}{[1 + K_{NO} P_{NO} + K_{NH_3}^{1/2} P_{NH_3}^{1/2}]^2} \tag{2}$$

The two rates are coupled due to constant selectivity. Kinetic analysis of a proposed reaction network for this system, discussed below, provides interpretation of the model parameters in terms of surface reaction rate constants and adsorption equilibrium coefficients.

Figure 2 demonstrates that the reaction is clearly dependent on the NH_3 partial pressure to the one-half power further indicating the validity of applying a model involving dissociative adsorption of NH_3. Figure 3 is a plot of linearized Equation (1) (Kittrell, 1970) illustrating that the rate is dependent on the first power of NO partial pressure. The NO dependence cannot be shown directly as can that for NH_3 because NO appears to be more

TABLE 2. STEADY STATE SELECTIVITY TO NITROGEN FOR NO-NH_3 REACTION OVER PLATINUM

Temp., °K	Catalyst	Average selectivity*, r_{N_2}/r_{N_2O}	Standard deviation
423	Unsintered 1% Pt	1.99	0.14
423	Sintered 1% Pt	1.70	0.14
448	Unsintered 1% Pt	1.78	0.04
448	Sintered 1% Pt	1.92	0.04
473	Unsintered 1% Pt	1.81	0.13
473	Sintered 1% Pt	1.79	0.27
473	Type *M*	1.86	0.17

* Average over 12 feed compositions covering 0.25 to 1% NO and 0.1 to 2% NH_3 in helium. No trend with feed composition was observed.

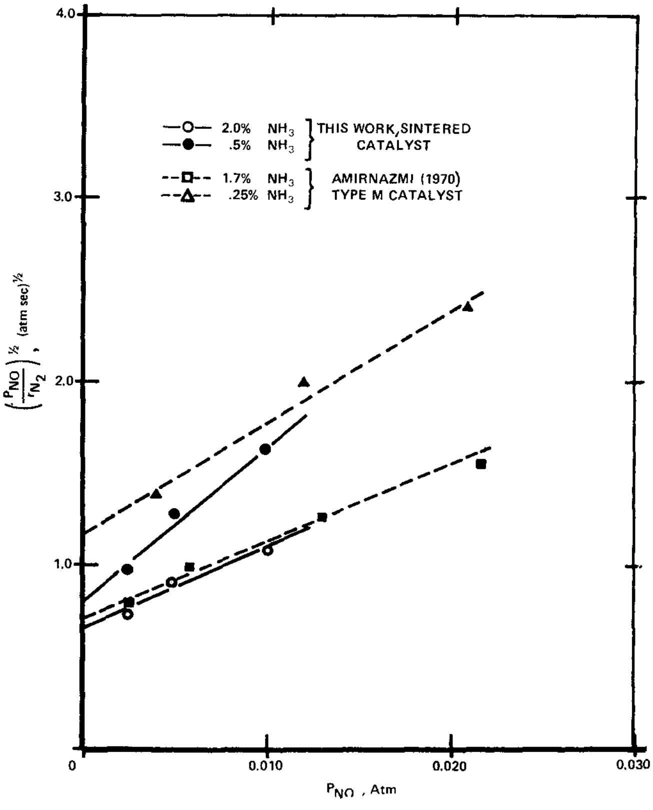

Fig. 3. First-order dependence with respect to nitric oxide of rate of reduction to nitrogen.

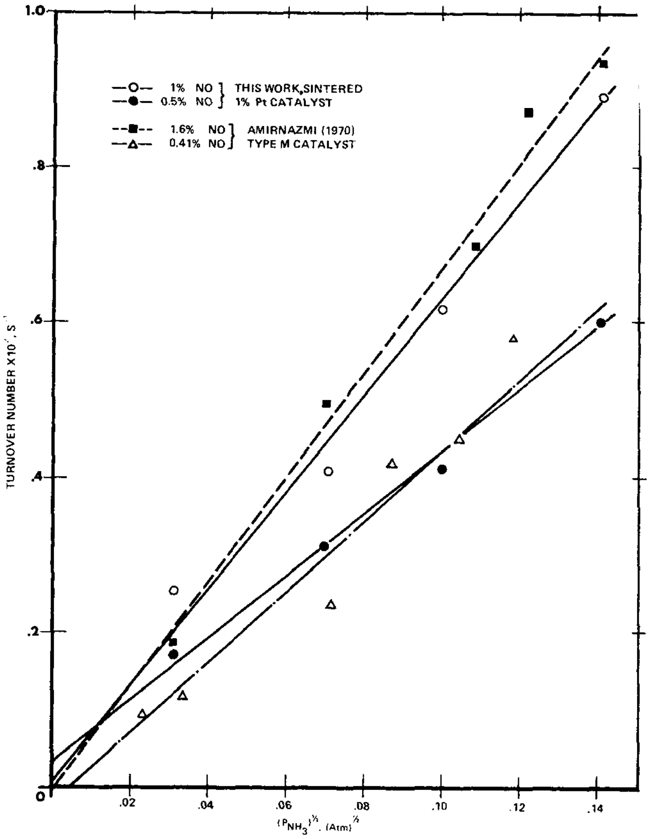

Fig. 2. Dependence of rate of nitric oxide reduction to nitrogen on square root of ammonia partial pressure.

strongly adsorbed. The dashed lines represent unpublished data taken in our laboratory two years earlier using the type M catalyst (Amirnazmi, 1970). At 423°K the turnover numbers observed by us for the unsintered and sintered catalyst and by Amirnazmi for the type M catalyst for 1% NO and 0.5% NH_3 are 0.0058, 0.0041 and 0.0044 s^{-1}. For 1% NO and 2% NH_3 they are 0.0088, 0.0081, and 0.0089 s^{-1}. These data show that specific rates are reproducible with changes in both catalyst and experimenter and further verify the absence of crystallite size effect in the NO-NH_3 system.

Figure 4 shows the temperature dependence of the surface rate constants for N_2 and N_2O formation for the unsintered and sintered catalysts. The anomalous data at 473°K for the sintered catalyst were not used in the data fitting. The results are correlated by the equations:

$$k_{s,N_2} = 1.37 \times 10^5\, e^{-11{,}800(\pm 3000)/RT}\, s^{-1}$$

$$k_{s,N_2O} = 1.56 \times 10^4\, e^{-10{,}300(\pm 1000)/RT}\, s^{-1}$$

Figure 5 shows the temperature dependence of the adsorption constants from both Equation (1) and (2) for NO and NH_3 for the unsintered and sintered catalysts. The NO adsorption coefficient for the unsintered and sintered catalysts agree very well, indicating independence of crystallite size. The NH_3 adsorption parameters agree reasonably well with the exception of 423°K. The NH_3 adsorption parameter is the square of the computed parameter so that scatter in the computed parameter is magnified. Further because the contribution of the NH_3 adsorption term in the denominator is small relative to that for NO, the term does not become dominant at low temperatures even at the highest NH_3 concentrations. This results in a coupling of k_s and $(K_{NH_3})^{1/2}$ and an inverse correlation between these parameters. This caused some difficulty in converging on realistic values of k_s and K_{NH_3} at 423°K. The data are correlated by the equations:

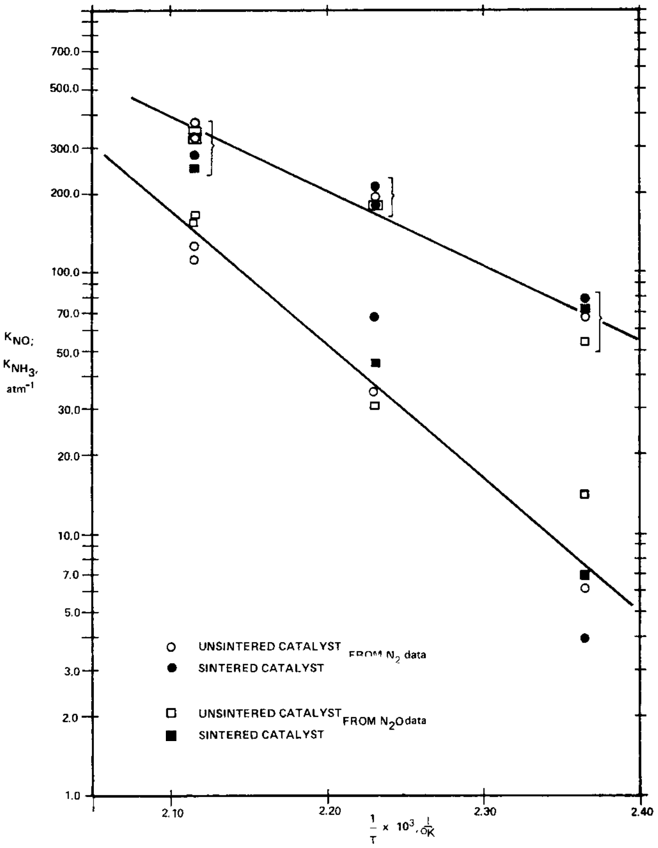

Fig. 5. Arrhenius plot of ammonia and nitric oxide adsorption parameters for single-site dissociative Langmuir-Hinshelwood kinetic model fit to NO-NH_3 data for 1% Pt catalyst. Bracketed data represent K_{NO} values.

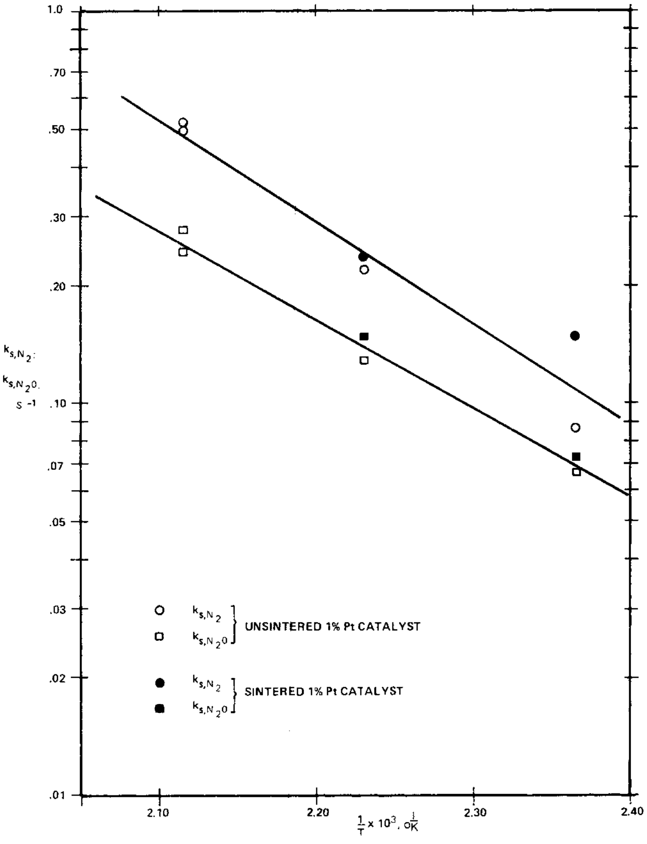

Fig. 4. Arrhenius temperature dependence of surface rate constants for single-site dissociative Langmuir-Hinshelwood kinetic model fit to NO-NH_3 data for 1% Pt catalyst.

$$K_{NO} = 4.89 \times 10^7\, e^{-\frac{11{,}300(\pm 1{,}000)}{RT}}\ \text{atm}^{-1}$$

$$K_{NH_3} = 1.04 \times 10^{13}\, e^{-\frac{23{,}500(\pm 4{,}000)}{RT}}\ \text{atm}^{-1}$$

A run at 548°K and 0.25% NO exhibited a rate maximum at about 0.1% NH_3 and weak dependence on NH_3 partial pressure between 0.5 and 0.07% NH_3, indicating that K_{NH_3} is quite large at this temperature.

Nitric Oxide—Ammonia-Oxygen System

The NO-NH_3-O_2 system was studied at 423°K with a feed composition of 0.25% NO, 2.0% NH_3, and 0.5% O_2 (Table 3). When 0.5% O_2 is added to the feed, the rate of N_2 formation for the unsintered catalyst is increased by a factor of 12.5 and that of N_2O by a factor of 22. For the sintered catalyst the rates are increased by factors of 66 and 117. The ratio of steady state specific catalytic activity of the sintered to that for the unsintered catalyst is 5.8 and 6.6 for N_2 and N_2O formation respectively. Reproducibility was demonstrated with a separate catalyst charge. Thus a crystallite size effect is present indicating that the reaction becomes demanding in the presence of O_2. The selectivity to N_2 (r_{N_2}/r_{N_2O}) is 0.96 for the sintered catalyst and 1.11 for unsintered catalyst with 0.5% O_2 in the feed. This value is about one-half that without O_2. The increased formation of N_2O over the larger crystallites is small, but we believe the differ-

TABLE 3. EFFECT OF OXYGEN ON REACTION BETWEEN NITRIC OXIDE AND AMMONIA AT 423°K

Catalyst	Feed composition, mole %	Steady state specific rate of reaction, turnover no., s^{-1} N_2	N_2O	Selectivity r_{N_2}/r_{N_2O}
Unsintered 1% Pt	2.0% NH_3 0.25% NO 0.0% O_2	0.0042	0.0022	1.9
Sintered 1% Pt		0.0045	0.0027	1.7
Unsintered 1% Pt	2.0% NH_3 0.25% NO 0.5% O_2	0.052	0.047	1.11
Sintered 1% Pt		0.30	0.31	0.96

ence is real and consistent with other findings of this study.

Table 4 gives the initial specific rate of formation of unfixed nitrogen ($r_{N_2} + r_{N_2O}$) at 423°K for feeds containing 2% NH_3 and either 0.5% O_2, or 0.25% NO, or 0.5% O_2 and 0.25% NO in helium. Any effect of deactivation has been eliminated by comparing initial specific rates. The NH_3-O_2 data are from Ostermaier (1973). NH_3 reacts with O_2 and NO separately at about the same rate, particularly over the unsintered catalyst. When O_2 and NO are both present in the feed, the rate is markedly higher. This could not be predicted from the two-reactant feed data. The sum of rates of formation of unfixed nitrogen for the unsintered catalyst in the NH_3-O_2 and NH_3-NO systems is 42% of the rate for the same catalyst in the NH_3-NO-O_2 system. For the sintered catalyst the sum of rates for the first two systems is 12% of the rate in the NH_3-NO-O_2 system.

DISCUSSION

Nitric Oxide-Ammonia System

Product Distribution. Tracer studies of Otto et al. (1970) using ^{15}N suggest that the catalytic reduction of NO by NH_3 involves the following steps:

$$NH_3 \rightleftarrows NH_{3(ads)} \qquad (3)$$

$$NH_{3(ads)} \rightleftarrows NH_{2(ads)} + H_{(ads)} \qquad (4)$$

$$NO \rightleftarrows NO_{(ads)} \qquad (5)$$

$$NO_{(ads)} + NH_{2(ads)} \rightarrow [\text{surface complex I}] \rightarrow N_2 + H_2O$$
$$[\text{surface complex I}] \dashrightarrow N_2O + 2H_{(ads)} \qquad (6)$$

$$H_{(ads)} + NO_{(ads)} \rightarrow HNO_{(ads)} \qquad (7)$$

$$2HNO_{(ads)} \rightarrow [\text{surface complex II}] \rightarrow N_2O + H_2O$$
$$[\text{surface complex II}] + 2H_{(ads)} \dashrightarrow N_2 + 2H_2O \qquad (8)$$

Bold arrows in steps (6) and (8) represent major reaction paths, dashed arrows minor reaction paths. Product desorption steps are implicit, surface intermediates are those suggested by Otto et al. (1970). NH_3 adsorption is thought to be mostly associative at room temperature (Blyholder and Sheets, 1972; Melton and Emmett, 1964) with the extent of dissociation to $NH_{2(ads)} + H_{(ads)}$ increasing with temperature (Melton and Emmett, 1964; Mardaleishvili et al., 1967; Nutt and Kapur, 1969; May et al., 1969).

If the minor reaction pathways in steps (6) and (8) are neglected, the selectivity to N_2 is determined by the material balance on adsorbed NH_2 and H, and r_{N_2}/r_{N_2O} must equal 2.0. The data of Table 2 support this. Our selectivity data show better agreement with the simplified version of the mechanism proposed by Otto et al. (1970) than do their own data probably because of the lower temperature and lower concentrations used here and because our results are under steady state conditions. Additional support for the proposed reaction mechanism comes from the results of experiments in which the catalyst was reduced and cooled in flowing hydrogen. In the subsequent run the rate of N_2O formation initially was about twice that for N_2 presumably as a result of the chemisorbed hydrogen remaining on the platinum surface. When the catalyst was cooled in flowing helium after reduction in H_2, the rate of N_2O formation initially was only about one-half of that of N_2 formation. Otto et al. (1970) report the formation principally of N_2O in the reduction of NO by H_2 over platinum at 473°K. However, Otto and Shelef (1973) report that adsorbed hydrogen on platinum reduces NO almost exclusively to N_2 at 195 and 273°K. Since steady state selectivity is not dependent on crystallite size, the relative importance of the minor reaction paths must be independent of crystallite size.

TABLE 4. EFFECT OF DIFFERENT REACTION COMPONENTS ON RATE OF FORMATION OF UNFIXED NITROGEN AT 423°K

System	Feed composition, mole %	Catalyst	Initial specific rate* turnover no., s^{-1}
NH_3-O_2†	2% NH_3 0.5% O_2	Unsintered 1% Pt	0.014
		Sintered 1% Pt	0.049
NH_3-NO	2% NH_3 0.25% NO	Unsintered 1% Pt	0.022
		Sintered 1% Pt	0.022
NH_3-NO-O_2	2% NH_3 0.25% NO 0.5% O_2	Unsintered 1% Pt	0.099
		Sintered 1% Pt	0.61

* Rate equals ($r_{N_2} + r_{N_2O}$), initial rates were obtained by extrapolation to zero time. For NH_3-NO-O_2 system no deactivation was observed.

† From Ostermaier (1973).

Kinetics. The rate of reaction depends on $P_{NH_3}^{1/2}$ (Figure 2), on P_{NO} (Figure 3), and is represented satisfactorily by a single-site Langmuir-Hinshelwood kinetic model involving associative NO and dissociative NH_3 adsorption. If it is assumed that reaction steps (6) and

(7) are rate limiting, the Langmuir-Hinshelwood kinetic model [Equation (1)] can be readily derived by setting $r_{N_2} = k_6 \theta_{NH_2} \theta_{NO}$, writing a steady state balance on θ_H, and expressing surface coverages in terms of gas-phase partial pressures using a Langmuir isotherm (Smith, 1970). K_{NH_3} is a product of K'_{NH_3}, K_{s4} and the ratio of surface rate constants for steps (6) and (7). If the rate of surface dissociation of NH_3 were rate limiting as suggested by Otto et al. (1971), the observed rate of reaction should be first order in NH_3, zero order in NO, and should tend to minus first order in NO at high NO pressure. The apparent zero order in both reactants observed by Otto et al. (1971) is explained by the fact that the rate of reaction is near its maximum at the reactant concentrations used in their study and thus is quite insensitive to changes in reactant concentration over their range of concentrations. Other surface reaction steps can give a kinetic isotope effect. The turnover number of Otto et al. (1971; Otto and Shelef, 1973a) for platinum at 473°K and 60 Torr NO and NH_3 is 0.05 NO molecules per surface platinum atom per second. At 473°K and 1% NO and NH_3 we observed a turnover number of 0.063 NO molecules per surface platinum atom per second at steady state.

Since K_{NH_3} in Equation (1) contains a ratio of rate constants, the positive temperature coefficient (23,500 kcal/mole) is not surprising. The positive temperature coefficient for K_{NO} is consistent with similar values reported by others (Ayen and Peters, 1962; Gupta, 1970) although the reason for this is not clear.

Additional support for the model based on reaction step (6) as rate limiting comes from a reevaluation of the data of Michailova (1939) by Wanner (1972) in our laboratory. Michailova fitted data for the NO-NH_3 reaction over a platinum wire to a single-site Langmuir-Hinshelwood associative adsorption model. Wanner showed that her data fit Equation (1) equally well. She reported an observed activation energy for reaction of 24.8 kcal/mole which is close to our value of 21 kcal/mole. The agreement is perhaps surprising since Michailova's studies were in batch apparatus, and the importance of deactivation was not determined. Also in favor of reaction step (6) as rate limiting is the fact that the reaction of H_2 with NO is more rapid than that of NH_3 (Otto et al., 1970), suggesting that reaction steps (7) and (8) are not rate limiting. The apparently satisfactory agreement of the observed kinetics with a model based on reaction step (6) as rate limiting suggests that this step may indeed be the important step kinetically. The absence of a crystallite size effect in the NO-NH_3 reaction suggests that this reaction step does not require a complex ensemble of surface platinum atoms to form a reaction site or more than two catalytic sites (Bond, 1973; Boudart, 1971). An additional factor might be that the activation of O_2 is not required in the reaction sequence (Ostermaier et al., 1973).

Nitric Oxide-Ammonia-Oxygen System

Product Distribution. The results of this study are in agreement with previous reports of the selective reduction of NO by NH_3 in the presence of O_2 (Cohen, 1961; Griffing et al., 1969; Andersen et al., 1961; Andersen and Kieth, 1961; Markvart and Pour, 1967, 1969) and enhancement of the NO-NH_3 reaction rate (Markvart and Pour, 1967, 1969; Wanner, 1972). Our report of the effect of O_2 on the selectivity is believed to be new. The literature offers no satisfactory explanation for the rate enhancement by the presence of O_2. Selectivities with O_2 in the feed (Table 3) are not due to gas-phase reactions since these produce only N_2 below 473°K (Falk and Pease, 1954) and only small amounts of N_2O above 473°K (Bedford and Thomas, 1972). Only small amounts of N_2 were produced in the absence of the platinum catalyst. Homogeneous N_2 production was subtracted from the observed rates of N_2 formation.

In the presence of O_2 the following additional reaction steps are proposed (Fogel et al., 1964); Ostermaier et al., 1974a):

$$O_2 \rightleftarrows 2O_{(ads)} \tag{9}$$

$$O_{(ads)} + NH_{2(ads)} \rightarrow NH_2O_{(ads)} \tag{10}$$

$$NH_2O_{(ads)} + O_{(ads)} \rightarrow NO_{(ads)} + H_2O \tag{11}$$

Surface species are speculative (Ostermaier et al., 1974a); but since NO is observed to be the first product of interaction between NH_3 and O_2 on platinum, more complex reaction mechanisms are not indicated (Nutt and Kapur, 1968; 1969; Fogel et al., 1964). Steps (9), (10), and (11) may instead involve $O^-{}_{2(ads)}$ (Clarkson and Cirillo, 1972, 1973) and reaction of this species with $NH_{2(ads)}$ (Fogel et al., 1964) but this is not in accord with the observed dependence of the rate of NH_3 oxidation on P_{O_2} (Ostermaier et al., 1973). Further Wanner (1972) observed that the reaction rate in the NO-NH_3-O_2 system was proportional to $P_{O_2}{}^{1/2}$ indicating dissociative adsorption.

The decreased selectivity to N_2 in the presence of gas-phase O_2 may result from the intervention of oxygen in the reaction via steps (10) and (11) to increase the amount of $H_{(ads)}$ available on the surface for steps (7) and (8) eliminating the material balance requirement that $r_{N_2}/r_{N_2O} \cong 2.0$ as observed in the absence of O_2. All additional $H_{(ads)}$ resulting from steps (10) and (11) which is not oxidized to H_2O by adsorbed oxygen should result in additional N_2O. Thus r_{N_2}/r_{N_2O} can be considerably less than 2.0. This is consistent with the observations that H_2 reacts selectively with NO in the presence of O_2 (Jones et al., 1971; Shelef and Gandhi, 1972); selectivities to N_2 which are much less than one are observed when gas-phase H_2 is added to the NO-NH_3 system (Otto et al., 1970); and starting a run with the platinum surface covered with chemisorbed hydrogen results in high rates of N_2O formation relative to N_2 formation initially. If the O_2 had reacted with a large fraction of the $H_{(ads)}$, the selectivity to N_2 would have increased.

Kinetics. Since the rate limiting step in the NH_3-NO system appears to be step (6) and since this system does not show a crystallite size effect the crystallite size effect in the presence of oxygen appears to enter earlier in the reaction network. Steps (10) and (11) are the most logical candidates for kinetically important steps which may exhibit crystallite size dependence. Since steps (7) and (8) appear rapid relative to step (6), steps (10) and (11) may provide another mechanism of reducing the concentration of $NH_{2(ads)}$ and altering the relative concentrations of adsorbed NH_2 and NO-like species. This shift in relative surface concentrations could explain the rate enhancement by O_2 and also explain the crystallite size effect in a manner consistent with that in the NH_3-O_2 system (Ostermaier et al., 1974a). Another explanation involves the claimed formation of reactive NO_2 from O_2 and NO over platinum (Andersen and Haley, 1963). The mechanism of the O_2 effect is not clear, and its magnitude suggests that steps (9) through (11) may be simplistic.

The catalytic activity and selectivity to N_2O of oxide catalysts in NH_3 oxidation has been related to the concentration of extralattice or active oxygen on the surface

(Holbrook and Wise, 1972; Giordano et al., 1966; Krauss and Neuhaus, 1941; Krauss, 1949, 1950; Johnstone et al., 1954). This has recently been extended to low-temperature NH_3 oxidation over supported platinum, and the concept of more active and less active oxygen used to explain the effect of platinum crystallite size on activity and selectivity to N_2O. Oxygen adsorbed on plane surface platinum atoms is considered less strongly adsorbed and thus more active than that adsorbed on edge or corner platinum atoms, which should bind oxygen more strongly (Fassaert et al., 1972) making it less active. Thus large platinum crystallites, whose surface platinum atoms are predominantly plane atoms, should have a higher average surface concentration of active oxygen and a higher specific catalytic activity. For small platinum crystallites a large fraction of the surface platinum atoms are corner and edge atoms resulting in a lower average surface concentration of active oxygen and a lower specific catalytic activity. The observation that more oxygen is chemisorbed per surface platinum atom on large crystallites (Wilson and Hall, 1970, 1972) appears relevant to the interpretation of the crystallite size effect. The lower specific catalytic activity and higher selectivity to N_2 observed in this work for the smaller crystallite size catalyst is probably related to the lower average surface concentration of active oxygen on smaller crystallites. The correspondence of the effect of crystallite size on specific catalytic activity in the NH_3-NO-O_2 and the NH_3-O_2 systems is good, and the cause of the crystallite size effect in both systems appears to be the change in ability to activate oxygen with change in crystallite size.

CONCLUSIONS

The size of platinum crystallites in the critical size range of 1.5 to 10 nm does not affect specific catalytic activity in the NH_3-NO reaction. The absence of a crystallite size effect indicates that reaction involves rather unspecific sites on the metal surface and is thus insensitive to the detail of the surface. In the presence of O_2 larger crystallities have a higher specific activity. This is similar to observations in low-temperature NH_3 oxidation with O_2 and is opposite in trend to most cases of crystallite size effect under reducing conditions. The crystallite size effect is interpreted in terms of the greater ability of large crystallites to chemisorb molecular oxygen so as to produce an active oxygen species. Since for small crystallites specific activity increases considerably faster than the metal surface area decreases as crystallite size increases, larger crystallites result in more efficient use of the platinum. However the specific activity should be independent of size above ~ 5.0 nm (Poltorak and Boronin, 1966) resulting in the most efficient use of the platinum at a crystallite size somewhere around 5.0 nm. In the absence of O_2 the most efficient use of the metal occurs at high degrees of dispersion.

The rate of reaction in the NH_3-NO system is satisfactorily modeled by a single-site Langmuir-Hinshelwood kinetic model involving associative adsorption of NO and dissociative adsorption of NH_3. This is consistent with the reaction network proposed by Otto et al. (1970), and it indicates that the rate limiting step is reaction between adsorbed NO and an adsorbed nitrogen containing fragment of NH_3.

NOTATION

K_i = adsorption parameter in Langmuir-Hinshelwood kinetic model for species i, atm^{-1}
K'_{NH_3} = adsorption equilibrium coefficient for associative adsorption of ammonia, atm^{-1}
K_{s4} = surface dissociation equilibrium constant for reaction step 4
k = number of parameters to be fit in model
$k_{s,i}$ = surface reaction rate constant in Langmuir-Hinshelwood kinetic model for formation of species i, s^{-1}
k_i = surface reaction rate constant for reaction step i, s^{-1}
n = number of data points used in fitting
P_i = partial pressure of species i, atm
R = gas constant, cal/(gmol) (°K)
r_i = rate of formation of species i as turnover number, s^{-1}
$r_{obs,i}$ = observed rate of formation of species i, s^{-1}
$r_{pre,i}$ = rate of formation of species i predicted from the model, s^{-1}
T = temperature, °K

Greek Letters

θ_i = fraction of metal surface covered by species i

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