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Ammonia Formation in the Catalytic Reduction of Nitric Oxide by Hydrocarbons

I. Promotional Effects of Hydrogen

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The catalytic reduction of nitric oxide by methane and acetylene has been studied over a platinum–silica catalyst in the 200°–400°C temperature range under static conditions. The rate of ammonia formation was found to increase with increasing temperature. Increased nitric oxide concentration favored nitrogen formation at 250°C but had the reverse effect at 350°C. When a mixture of hydrogen and methane was used as the reducing gas, the selectivity for the reaction (ammonia concentration/nitrogen concentration) increased by a factor of 5 over that for pure methane and by a factor of 150 over that for pure hydrogen. Similar results were found for acetylene. Over a ruthenium–silica catalyst, these promotional effects were not observed. The promotional effect of hydrogen was barely observed at 250°C. Results are interpreted in terms of nitric oxide displacement from the surface by methane at the higher temperatures.

INTRODUCTION

Products formed in the catalytic reduction of nitric oxide with hydrogen have been the subject of many investigations, however, relatively few studies have appeared in the literature in which hydrocarbons are used as the reducing agent.

Variables which affect the rate of ammonia formation when hydrogen is used as a reducing gas have been carefully studied by Shelef and Gandhi (*1*), Ayen and Peters (*2*), Jones *et al.* (*3*), and Klimisch and Taylor (*4*). The production of ammonia depends critically on temperature, nitric oxide pressure, and catalyst composition. At temperatures below 200°C, the major nitrogen-bearing products are nitrous oxide and nitrogen with only trace amounts of ammonia being formed. The concentration of ammonia increases rapidly with temperature, usually going through a maximum between 350° and 450°C depending on the catalyst used (*4*). At higher temperatures, the decomposition of ammonia becomes thermodynamically favorable with a resulting increase in nitrogen formation. Ammonia formation also increases with decreasing nitric oxide pressure. This is consistent with the idea proposed by Shelef and Gandhi (*1*) that in order to form nitrogen, two nitrogen-containing species must be adsorbed on a dual site; a condition which can best be satisfied at high nitric oxide pressures. Kokes (*5*) has shown that when an excess of hydrogen is used at room temperature, ammonia is the main reduction product. In fact it is the sole nitrogen-bearing product when the ratio of hydrogen to nitric oxide is 100:1.

Ammonia formation in the reduction of nitric oxide by hydrocarbons has not been detected by all investigators. Ault and Ayen (*6*), using a series of paraffinic hydrocarbons from methane through octane, detected no ammonia on a barium-promoted copper catalyst in the temperature range 225°–525°C. This is in agreement with Malling (*7*) using methane and Sotoodehnia-Korrani and Nobe (*8*) who used ethylene as a reducing agent. Both obtained only nitrogen as the reduction product. On the other hand, Anderson *et al.* (*9*) detected ammonia formation in the catalytic treatment of nitric acid plant tail gas with methane in the presence of hydrogen over supported noble metal catalysts. These results have further been substantiated by Jaros and Krizek (*10*). Both of these investigations were carried out in a flow system with gases of fairly complex composition in the presence of oxygen, so that in addition to having a partially oxidized surface, other higher oxides of nitrogen may have possibly been present. In the catalytic reduction of nitric oxide with hydrocarbons, an additional source of hydrogen is available from the water–gas shift reaction which has been shown to proceed quite rapidly in a reducing atmosphere below 375°C (*11*). Minor products in past investigations using both methane and hydrogen, include hydrocyannic acid and hydroxylamine (*12*). Carbon dioxide and water are important products when methane is used with only trace amounts of carbon monoxide being reported.

We have chosen methane and acetylene to initiate a series of investigations on the catalytic reduction of nitric oxide by hydrocarbons. The reason for this choice is twofold. (a) Methane and acetylene exhibit different chemisorption properties over supported platinum. Whereas the adsorption of methane is necessarily dissociative, that of acetylene is mainly nondissociative. (b) Both methane and acetylene are important constituents of internal combustion engine effluents and information regarding the reduction process is of current interest. Methane should also serve as a good starting base in the comparison of hydrocarbon–nitric oxide reactivity to that for the nitric oxide–hydrogen reaction. A comparison of these results, should be helpful in evaluating the role of hydrocarbons in the formation of ammonia.

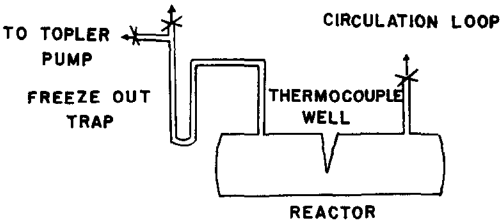

FIG. 1. Catalytic reactor.

EXPERIMENTAL

Apparatus

A static catalytic reactor (Fig. 1), consisting of a U-shaped Pyrex tube, was incorporated into the reaction loop of a conventional high vacuum system capable of attaining an ultimate pressure of 1×10^{-6} torr. The reactor was made from 25-mm Pyrex tubing and was about 10 cm in length. The side arms consisted of 10-mm Pyrex tubing connected to the vacuum system through two stopcocks. The catalyst was held in place by two quartz wool "plugs" which had previously been treated in a boiling solution of 9 *M* nitric acid and washed several times in deionized water. The purpose of this treatment was to remove traces of hydrocarbons present in the quartz wool. The reaction loop was placed in an oven and the temperature monitored through a thermocouple inserted in a thermocouple well in the catalytic bed. The temperature could be controlled to within five degrees over the entire catalytic bed.

Materials

The catalyst was prepared by impregnating Cab-O-Sil, grade M-5, obtained from the Cabot-Corporation of Boston, Mass., with chloroplatinic acid obtained from the Engelhard Industries of New Jersey. Spark spectra analysis of Cab-O-Sil, a high grade silica, indicated a total metallic impurity content of less than 100 ppm. The chloroplatinic acid solution was prepared by dissolving the appropriate amount of chloroplatinic acid in deionized water. The catalyst used in this study had a nominal 2% platinum content. The mixture was dried in an oven at 110°C and stirred regularly to retain uniformity. The dried mixture was then ground and screened to a 35/60 mesh and a 2-gm aliquot was sealed into the reactor. The metal surface area was determined by H_2–D_2 exchange. The particle size was determined to be between 10 and 30 Å. In three runs, a silica supported ruthenium catalyst was used. $RuCl_3 \cdot 3H_2O$ was obtained from Engelhard Industries of New Jersey. The same method of impregnation as the chloroplatinic acid was used except that the $RuCl_3 \cdot 3H_2O$ was dissolved in HCl rather than in deionized water. The composition of this catalyst was a nominal 2% ruthenium.

Ultrapure methane (99.97%) and technical grade nitric oxide (98.5%) were obtained from the Matheson Corporation. The methane was passed through a dry ice trap prior to storage in the vacuum system. The nitric oxide was purified using the freeze thaw technique. It was found that at least five thaws were necessary to remove nitrogen. Prior to storage, the nitric oxide was subjected to a vacuum distillation treatment in which only the middle cut was retained. Regular tank hydrogen was used in the catalytic reaction as well as in the reduction of the catalyst. It was purified by passing sequentially through a deoxo unit to remove traces of oxygen and then a molecular sieve and a liquid nitrogen trap to remove water. Carbon dioxide and ammonia used in analytical calibrations were obtained locally and were purified by standard vacuum distillation techniques. All gases were periodically checked for purity with a mass spectrometer.

Techniques

The catalyst was briefly outgassed at room temperature and then the temperature was gradually increased to 300°C in flowing hydrogen (150 ml/min). Reduction time at 300°C was for 4 hr. The hydrogen was then evacuated and the catalyst gradually heated to 400°C and outgassed for 4 hr at that temperature. The catalyst was then cooled to the temperature of the run. Separate predetermined amounts of nitric oxide and methane and/or hydrogen were introduced into the reaction cell at the start of the reaction. In an attempt to investigate the relative importance of the water–gas shift reaction in the production of ammonia, runs were made with and without a dry ice trap in the reaction loop. This should remove water from the reaction loop and depress the concentration of hydrogen available as a result of the water–gas shift reaction. The reactions were stopped by placing a liquid nitrogen trap in the reaction loop to remove condensable gases. Noncondensables were transferred over to a measured volume using a Topler pump. The reactor was then sealed off and the remaining condensable gases were toplered over to the measured volume. An aliquot sample was taken and analyzed mass spectrometrically on a C.E.C. (Dupont) Model 21-104 mass spectrometer equipped with an electron multiplier. Calibration curves relating the ratio of mass spectral lines of the major components to their absolute values were obtained and the raw data was programmed and processed in an IBM model 360 computer. The major components for the nitric oxide–methane reaction included nitric oxide, methane, carbon dioxide, nitrogen, and ammonia and when hydrogen was added to methane, the six components then included hydrogen. For the nitric oxide–hydrogen reaction, only one curve relating ammonia and nitrogen concentration was used as there were no interfering mass spectral lines. Positive product identification was obtained using a Perkin-Elmer model 521 Grating Infrared spectrophotometer. A material balance for nitrogen and carbon was made for each run.

RESULTS

Shelef and Gandhi (*1*) have used the terms "fixed" and "unfixed" nitrogen in defining selectivity in their study on the catalytic reduction of nitric oxide with hydrogen. "Fixed" nitrogen does not contain a nitrogen to nitrogen bond so that molecular nitrogen is an "unfixed" product while ammonia is a "fixed" product. Once "unfixed" it is unlikely that nitrogen will revert back to the "fixed" state. Rather than "fixed" and "unfixed" nitrogen, we have chosen to express our results in terms of a selectivity ratio defined here as the ammonia to nitrogen concentration in the products. In this study, the effect of time, temperature and reactant concentration on selectivity was considered. In order to establish the relative importance of the catalytic reduction of nitric oxide with hydrocarbons in a competitive situation with hydrogen, reducing gas mixtures consisting of methane or acetylene and hydrogen of varying composition were used.

Effect of Time

At a constant initial concentration of nitric oxide and methane, several runs were made to investigate the effect of percent conversion on the distribution of products. The total initial pressure in the reactor was approximately 120 Torr. Initial partial pressures of nitric oxide and methane were approximately 53 and 67 Torr, respectively. The results are shown in Fig. 2. Conversion of nitric oxide, based on initial concentrations, increased from 60% for a 2-hr run to over 80% for the 12-hr run. Of significance here is that the concentration of ammonia does not go through a maximum and decrease with time. This implies that the ammonia does not decompose or react further with nitric oxide. This is rather surprising in view of the results of Otto, Shelef, and Kummer (*13*) who have shown that ammonia reacts readily with nitric oxide over a supported platinum catalyst in the 200°–250°C temperature range. We confirmed these results on a blank run in which nitric oxide and ammonia were reacted over the catalyst for a period of 4-hr. An analysis of the products showed large quantities of nitrogen and nitrous oxide in agreement with the results of Otto, Shelef, and Kummer (*13*). Nitrous oxide was never observed as a product in the reduction with methane. It is conceivable that it could have been formed and underwent secondary reactions with methane. That the concentration of ammonia always increased with time, precluded secondary reactions involving ammonia. Possibly ammonia is excluded from the surface under the experimental conditions of this investigation.

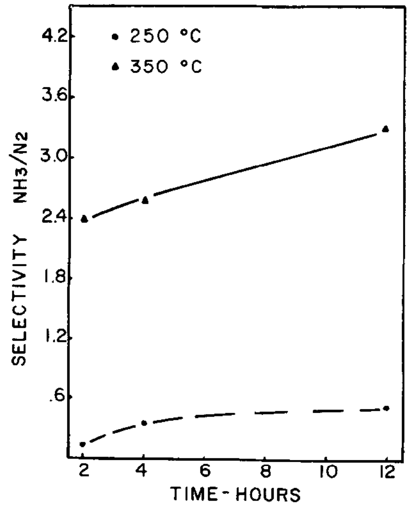

FIG. 2. Selectivity as a function of time for the reduction of nitric oxide with methane.

Effect of Temperature

Reduction of nitric oxide with methane and hydrogen. The reduction of nitric oxide with methane was studied over a 200° to 400°C temperature range at a constant initial methane to nitric oxide mole ratio of 5:4. The total pressure in the reaction loop at the start of each reaction was approximately 120 torr. Reaction times for all runs were 4 hr and a conversion of better than 80% based on initial nitric oxide concentration was obtained in all cases. Products other than ammonia, carbon dioxide, nitrogen, and water were not found. Carbon monoxide, hydroxylamine, and nitrous oxide were notably absent from the reaction products. This was encouraging as interference due to secondary reactions were relatively unimportant. The results of this study are shown in Table 1. It is apparent that high temperatures favor the formation of ammonia at the expense of a decrease in the amount of nitrogen formed.

Even though the catalytic reduction of nitric oxide with hydrogen has been well characterized (*1*), we felt that a comparison of selectivities obtained for hydrogen reduction to those for methane reduction would be helpful. These results are included in Table 1. Temperature has very little

TABLE 1

THE EFFECT OF TEMPERATURE ON THE REDUCTION OF NITRIC OXIDE BY METHANE AND HYDROGEN OVER A 2% PLATINUM–SILICA CATALYST[a]

Temperature (°C)	Reactants total amounts (μmoles)			Products[b] total amounts (μmoles)					% Conversion (based on nitric oxide conversion)	Selectivity NH_3/N_2
	NO	CH_4	H_2	N_2	NH_3	CO_2	NO	CH_4		
200	284	363	—	114	4.5	69.6	39.2	267	82	0.039
250	290	356	—	107	40	82.9	21.4	243	88	0.37
300	290	353	—	68.7	122	102	22.7	220	89	1.77
350	291	363	—	58.2	144	121	28.7	202	89	2.47
400	284	357	—	49.5	165	139	18.7	184	93	3.34
200[c]	280	—	350	—	—	—	—	—	—	0.069
250	284	—	356	—	—	—	—	—	—	0.045
300	285	—	353	—	—	—	—	—	—	0.043
350	271	—	352	—	—	—	—	—	—	0.083
400	275	—	341	—	—	—	—	—	—	0.21

[a] Reaction time = 4 hr.

[b] Water was not analyzed for.

[c] Absolute amounts of products were not obtained for the reduction with hydrogen. Conversions were about 90%.

effect on the selectivity for hydrogen reduction.

An identical set of runs with a dry ice trap placed in the reaction loop to freeze out water formed during the reaction are shown in Table 2. Partial pressures of ammonia were low enough so that no ammonia was condensed in the dry ice trap. That ammonia did not appreciably go into solution, was established by a nitrogen material balance (good to within 5%). The effect here is to enhance nitrogen formation, especially at the higher temperatures, at the expense of ammonia formation. Carbon dioxide formation was also depressed in the presence of the dry ice trap. Lower methane conversions, based on initial methane concentrations, coincided with this observation. This is due to the fact that it takes less methane to convert nitric oxide to nitrogen than to ammonia. A glance at Table 3 shows that at the temperatures

TABLE 2

THE EFFECT OF TEMPERATURE ON THE REDUCTION OF NITRIC OXIDE BY METHANE OVER A 2% PLATINUM–SILICA CATALYST WITH A DRY ICE TRAP PLACED IN THE REACTION LOOP[a]

Temperature (°C)	Reactants total amounts (μmoles)		Products[b] total amounts (μmoles)					% Conversion (based on nitric oxide conversion)	Selectivity NH_3/N_2
	NO	CH_4	N_2	NH_3	CO_2	NO	CH_4		
200	289	349	121	5.1	56.5	23.4	281	85	0.042
250	291	377	112	37	68.7	22.4	283	90	0.33
300	281	345	91.9	78	75.1	18.1	249	93	0.85
350	281	370	766	107	88.5	17.4	271	93	1.40
400	289	359	64.3	147	126	10.8	205	96	2.29

[a] Reaction time = 4 hr.

[b] Water was not analyzed for.

TABLE 3
LOGARITHMS OF EQUILIBRIUM CONSTANTS

Temperature (°K)	Log Kp
400	3.191
500	2.139
600	1.454
700	0.977

$CO + H_2O \rightleftarrows H_2 + CO_2$

of this investigation, the equilibrium for the water gas shift reaction is thermodynamically favorable for the production of additional hydrogen and enhances rates of ammonia formation. Our results using the dry ice trap also suggest that the water gas shift reaction may be an important source of hydrogen for ammonia formation. In any case, it is clear that water is a co-catalyst in the formation of ammonia.

Acetylene reduction. The reduction of nitric oxide with acetylene was studied over a 200°–400°C temperature range over a 2% platinum–silica catalyst. The results are shown in Table 4. The initial concentration ratio of acetylene to nitric oxide was 5:4 and the total pressure in the reaction loop was approximately 120 torr at the start of each experiment. A conversion of better than 80%, based on initial nitric oxide concentration, was obtained in all runs above 200°C and other runs at 100°C, the conversion of nitric oxide decreased to 50% at 200°C and 20% at 100°C for a 4-hr run. No products other than ammonia, carbon dioxide, nitrogen, and water were found except for trace amounts of ethylene and ethane. The selectivity for acetylene reduction is independent of temperature over the range studied.

The Promotional Effect of Hydrogen

Because of the somewhat surprising results in comparing the reactivity of the various reducing gases, and in view of the availability of hydrogen (from the water gas shift reaction), it was decided to study selectivity as a function of reducing gas composition, i.e., a competitive situation. Two temperatures (250° and 350°C) were used in this study and reaction times were for 4 hr. The reducing gas mixture was taken such that the initial concentration ratio of reducing gas to nitric oxide was 5:4. The results are shown in Table 5 for methane and Table 6 for acetylene. These data are also plotted in Figs. 3 and 4. It should be pointed out that there is a decrease in the total atom % hydrogen for the methane–hydrogen mixtures with increasing mole % hydrogen, whereas for acetylene, the atom % hydrogen is constant throughout the mixture. At 350°C there is a sharp increase in ammonia formation which shows a maximum at about 55% hydrogen and 45% methane. The selectiv-

TABLE 4
THE EFFECT OF TEMPERATURE ON THE REDUCTION OF NITRIC OXIDE BY ACETYLENE OVER A 2% PLATINUM–SILICA CATALYST[a]

Temperature (°C)	Reactants total amounts (μmoles)		Products total amounts (μmoles)					% Conversion (based on nitric oxide conversion)	Selectivity NH_3/N_2
	NO	C_2H_2	N_2	NH_3	CO_2	NO	C_2H_2		
100	286	358	19.3	Trace	—	229	343	14	Not determined
200	285	357	75	2.32	—	123	329	53	0.031
250	288	361	122	6.03	—	23.1	325	87	0.049
300	284	363	122	15.6	33.4	8.7	304	91	0.128
350	284	355	130	15.4	53.5	7.0	275	97	0.120
400	287	357	129	15.5	54.0	6.73	273	95	0.120

[a] Reaction time = 4 hr.

TABLE 5

Effect of Reducing Gas Composition on Selectivity for the NO-CH_4-H_2 Reaction[a]

Temperature (°C)	Reactants total amounts (μmoles)			Products total amounts (μmoles)					% Conversion (based on nitric oxide conversion)	Selectivity NH_3/N_2
	NO	CH_4	H_2	N_2	NH_3	CO_2	NO	CH_4		
250	285	320	39.8	112	47.5	31.8	31.8	268	95	0.42
250	285	282	80.0	112	45.1	27.3	10.6	241	95	0.40
250	288	239	121	113	46.9	21.0	8.96	198	95	0.42
250	286	211	161	110	42.7	21.9	9.08	173	91	0.39
250	285	160	205	108	58.1	15.9	7.37	143	96	0.54
250	289	121	240	105	62.9	14.1	6.50	94.5	95	0.60
250	286	80.3	282	104	66.3	16.5	5.64	55.6	96	0.63
250	291	40.2	321	111	49.9	19.9	8.57	16.3	93	0.45
350	285	320	40.0	64.2	140	103	20.9	196	94	2.18
350	284	280	80.1	36.4	178	93.7	18.5	159	89	4.90
350	269	246	121	28.1	189	88.7	16.5	141	91	6.72
350	287	207	159	24.4	227	71.6	168	119	95	9.30
350	286	166	215	20.9	238	58.8	10.3	96.0	98	11.4
350	288	121	241	23.2	220	52.4	12.1	47.9	92	9.48
350	284	79.8	278	55.1	168	41.2	6.27	19.6	98	5.92
350	287	40.0	322	105	63.8	27.4	6.51	8.51	96	0.61

[a] Reaction time = 4 hr.

TABLE 6

EFFECT OF REDUCING GAS COMPOSITION ON SELECTIVITY FOR THE NO–C_2H_2–H_2 REACTION[a]

Temperature (°C)	Reactants total amounts (μmoles)			Products total amounts (μmoles)					% Conversion (based on nitric oxide conversion)	Selectivity NH_3/N_2
	NO	C_2H_2	H_2	N_2	NH_3	CO_2	NO	C_2H_2		
250	284	315	39.9	124	9.01	29.3	15.2	275	90	0.073
250	290	275	80.3	130	10.8	28.4	12.3	244	93	0.083
250	289	243	119	132	10.9	26.8	8.98	218	95	0.083
250	287	208	160	132	11.3	26.1	7.98	181	96	0.086
250	286	160	208	131	11.2	27.9	7.11	132	95	0.086
250	282	119	241	127	18.2	18.72	5.5	95.1	95	0.143
250	283	80.3	280	121	20.3	13.2	8.36	63.6	93	0.168
250	285	40.0	320	120	28.7	13.0	6.67	18.9	95	0.238
350	283	321	40.2	120	30.1	51.5	8.09	261	95	0.252
350	288	280	80.3	116	46.2	68.0	8.13	228	96	0.398
350	289	244	121	103	60.9	72.1	10.6	202	92	0.590
350	293	205	160	98.6	76.2	83.7	14.3	152	93	0.770
350	285	159	203	88.0	88.7	103	10.5	98.4	93	1.01
350	282	119	243	79.1	97.5	190	12.6	64.6	87	1.23
350	285	79.7	278	72.4	109	70.1	16.6	35.7	90	1.51
350	286	39.9	322	65.8	132	37.1	10.2	12.9	92	2.00
350	283	205	336	110	51.5	29.5	9.73	6.73	96	0.47

[a] Reaction time = 4 hr.

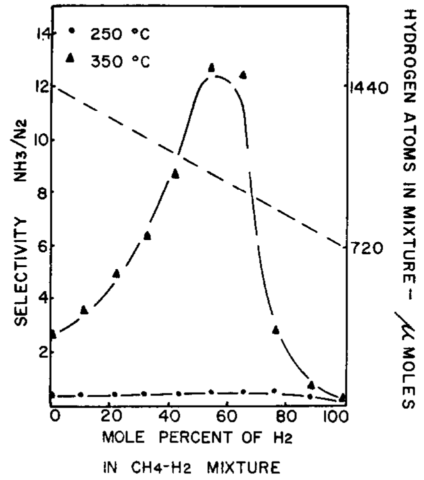

Fig. 3. Selectivity as a function of mole % H_2 for the NO-CH_4-H_2 reaction at 250° and 350°C.

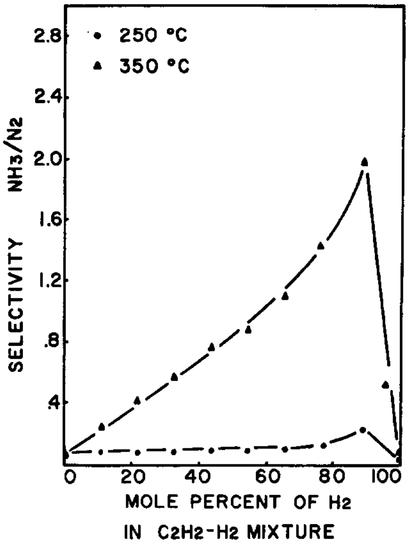

Fig. 4. Selectivity as a function of mole % H_2 for the NO-C_2H_2-H_2 reaction at 250° and 350°C.

ity for this mixture is five times that for the reduction with methane and over 150 times that for pure hydrogen. This promotional effect was barely observed at 250°C. For acetylene reduction (Table 6), the magnitude of the maximum selectivity value for this promotional effect is only 2 (as compared to 13 for the methane hydrogen mixture), however when this value is compared to that for the pure hydrocarbon, these ratios are similar (five times greater for methane–hydrogen and twelve times greater for acetylene–hydrogen).

Ruthenium Catalysts

Klimisch and Taylor (*4*) have shown ruthenium supported on alumina to be considerably more selective for nitrogen formation then either platinum or palladium. This was interpreted in terms of the greater activity for ammonia decomposition exhibited by ruthenium. In view of these results, we felt that it might be instructive to study the reduction of nitric oxide with methane at temperatures at which ammonia

TABLE 7

A Comparison of the Selectivity for Nitric Oxide Reduction over Ruthenium–Silica to That for Platinum–Silica

Catalyst	Temperature (°C)	Reactant composition NO:CH_4	Selectivity NH_3/N_2
2% Platinum–silica	350	4:5	2.5
2% Ruthenium–silica	350	4:5	0.38

Promotional Effect of Hydrogen for Nitric Oxide Reduction with Methane over Ruthenium–Silica

Catalyst	Temperature (°C)	Reducing gas composition CH_4:H_2	Selectivity NH_3/N_2
2% Platinum–silica	350	2:1	6.25
2% Ruthenium–silica	350	2:1	0.33

is thermodynamically stable. The results are shown in Table 7 for a 2% ruthenium–platinum catalyst. It is clear that ruthenium does not exhibit the promotional properties exhibited by platinum and that unlike platinum, it is not selective in promoting ammonia formation.

Discussion

Our results on the nitric oxide methane reaction are consistent with several features of the nitric oxide–hydrogen scheme proposed by Shelef and Gandhi (*1*). They have suggested that in order to obtain unfixed nitrogen, two molecules of nitric oxide must be adsorbed on adjacent surface sites. If this be true, the rate of nitrogen formation should increase with increasing nitric oxide pressure provided of course that the reaction occurs between two adjacent chemisorbed nitric oxide molecules. Using methane, this is certainly the case at low temperatures (Fig. 5). At 350°C however, the reverse is true (Fig. 6). We feel that this is in part due to a decrease in nitric oxide adsorption at the higher temperature in addition to an increase in the dissociative adsorption of methane (*14*).

Ayen and Peters (*2*) have found that the rate of nitrogen formation is

$$\text{rate} = \frac{kK_{\mathrm{NO}}P_{\mathrm{NO}}K_{\mathrm{R}}P_{\mathrm{R}}}{(1 + K_{\mathrm{NO}}P_{\mathrm{NO}} + K_{\mathrm{R}}P_{\mathrm{R}})^2},$$

where R can be hydrogen, a hydrocarbon, or carbon monoxide. This equation is strongly suggestive of a Langmuir-Hinshelwood type mechanism for nitrogen formation. Although it would be presumptuous of us to infer Langmuir adsorption equilibria under our set of experimental conditions, we feel that our data strongly suggests a Langmuir-Hinshelwood mechanism for nitrogen formation and an Eley-Rideal mechanism for ammonia formation. Figures 5 and 6 show the rate dependence of both nitrogen and ammonia formation on nitric oxide pressure. At 350°C, methane competes favorably with nitric oxide for adsorption sites. The concentration of dual sites remains roughly constant with increasing nitric oxide pressure with a resulting accumulation of nitric oxide in the gas phase. This nitric oxide may either abstract a hydrogen atom from an adsorbed alkyl radical or react with an adsorbed hydrogen atom via an Eley-Rideal mechanism. The hydrogenated nitric oxide intermediate (conceivably hydroxylamine) can then react to form ammonia. Additional support for the adsorption properties of methane were obtained in this laboratory (*14*). Methane–deuterium exchange over sup-

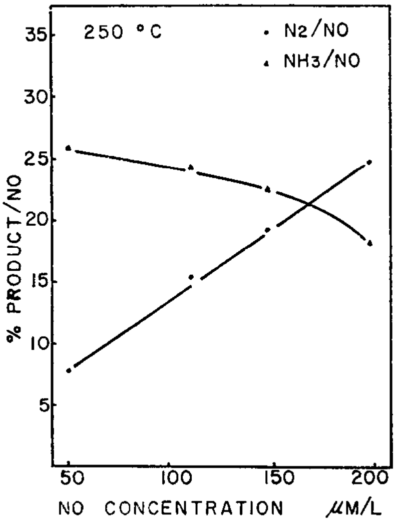

FIG. 5. Ammonia and nitrogen formation as a function of nitric oxide pressure at 250°C.

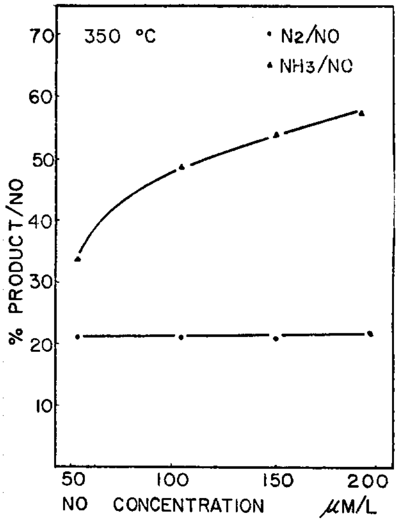

FIG. 6. Ammonia and nitrogen formation as a function of nitric oxide concentration at 350°C.

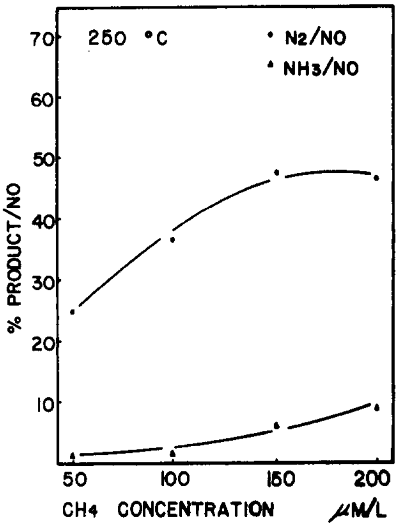

FIG. 7. Ammonia and nitrogen formation as a function of methane concentration at 250°C.

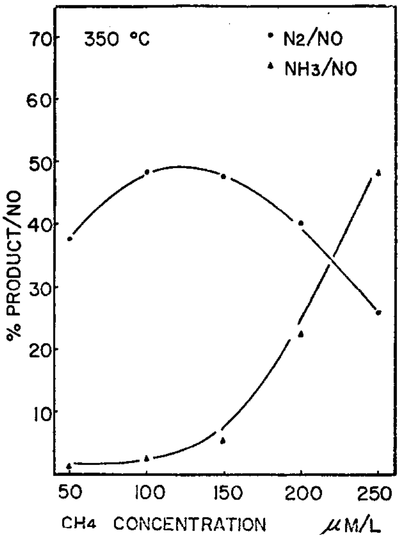

FIG. 8. Ammonia and nitrogen formation as a function of methane concentration at 350°C.

ported nickel yield predominantly methane d-1 at 250°C and methane d-2, d-3, and d-4 at 350°C. Experiments on platinum, although incomplete, substantiate these results. Below 250°C there is little or no methane–deuterium exchange which would rule out methane chemisorption at temperatures lower than 250°C. An increase in the rate of ammonia formation with temperature provides additional evidence that dissociative methane chemisorption is a requirement for ammonia formation.

When the pressure of methane is varied (Figs. 7 and 8), the rate of nitrogen formation goes through a maximum at both 250° and 350°C. The maximum observed at 350°C is much sharper than that at 250°C as one might expect since methane displaces nitric oxide more readily at 350°C than at 250°C. As nitric oxide is displaced into the gas phase, the population of dual sites decreases leading to a tailing off in nitrogen formation and an increase in ammonia formation through an enhancement of an Eley-Rideal mechanism.

The enhanced selectivity for methane as compared to hydrogen reduction of nitric oxide can be rationalized in terms of an additional source of hydrogen. Such a source is the water gas shift reaction. The depressed rate of ammonia formation in the presence of a dry ice trap shows that the water gas shift reaction may play a significant role in the reduction of nitric oxide with methane since carbon monoxide must undoubtedly be an intermediate. The hydrogen evolved, when placed in a competitive situation with methane (Fig. 3), produces an enhancement in the selectivity.

The role of acetylene in the catalytic reduction of nitric oxide is similar to that for methane. Both methane and acetylene are capable of displacing nitric oxide from the surface at high temperatures, however, acetylene exhibits the same chemisorption properties at low temperatures that methane does at high temperatures. This is in part due to the dissociative adsorption requirement for methane in contrast to acetylene. Acetylene is adsorbed strongly enough to inhibit nitrogen formation in the 100°–200°C temperature range. That ammonia is not a major product in this temperature range may be due in part to the higher activation energy requirement for ammonia formation and possibly the unavailablility of hydrogen if the adsorption of acetylene in predominantly nondissociative. Conversion at these lower temperatures were much lower than for the high temperature reduction.

The promotional effect of hydrogen observed in the methane reduction of nitric oxide was again evident when gas mixtures of acetylene and hydrogen were used. The promotional effect observed at 350°C for mixtures of acetylene and hydrogen was not as great as that observed for methane, however, enhancement of the selectivity ratio over that for pure acetylene was comparable to that for methane–hydrogen reducing mixtures and pure methane. It is reasonable to expect a greater concentration of surface hydrogen atoms when saturated hydrocarbons are used as they tend to adsorb dissociatively to a greater extent than unsaturated hydrocarbons. This extra availability of surface hydrogen atoms could enhance this promotional effect on the ammonia formation at the high temperature reduction. In fact, we feel that possibly saturated hydrocarbons formed in competing hydrogenation reactions in the acetylene–hydrogen mixtures, may have contributed significantly to the enhancement of the selectivity ratio.

The results of the methane reduction over a ruthenium–silica catalyst are significant in that there was virtually no ammonia formation at 350°C and the promotional effect of hydrogen found for platinum was not observed. We interpret this to mean that nitric oxide is very strongly adsorbed over ruthenium and is less readily displaced by hydrocarbons. It should be reemphasized here, that even though ruthenium is a good ammonia decomposition catalyst, the decomposition of ammonia is not thermodynamically favorable below 350°C. It must be assumed that ammonia is not formed in significant amounts over supported ruthenium. This may well be an important factor to consider when catalytic materials are evaluated for possible use in catalytic converters.

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