JOURNAL OF CATALYSIS **100**, 158–166 (1986)

Nitrogen Desorption in the Reaction of Nitric Oxide on Carbon-Supported Platinum Catalysts

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Received November 14, 1985; revised February 27, 1986

The catalytic decomposition of nitric oxide on carbon- and γ-alumina-supported platinum was studied in a quartz flow reactor between 423 and 623 K. The measured turnover frequency, defined as the number of nitric oxide molecules reacting per surface platinum atom per second, was an order of magnitude higher on the carbon-supported catalysts than on the alumina-supported catalyst or than that projected from earlier work on platinum foil. The rate-determining step for nitric oxide decomposition on Pt/Al_2O_3 or Pt foil appears to be the chemisorption of NO on platinum, with inhibition by oxygen, the most abundant reaction intermediate (mari) in equilibrated chemisorption on the same sites as those required for NO chemisorption. By contrast, it appears that on Pt/C, the inhibition product oxygen is removed continuously from the platinum surface by the surrounding carbon support, producing CO and CO_2. The kinetic data suggest that the mari now consists of adsorbed nitrogen atoms. The second-order rate constant k for the associative desorption of nitrogen from platinum obtained from our work is compared with that extracted from published data on NH_3 decomposition or that measured directly by temperature-programmed desorption of nitrogen from platinum. We find for k a preexponential factor of 5×10^{-9} cm^2 s^{-1} and an activation energy of 88 kJ mol^{-1}, in remarkable agreement with those reported by others.

INTRODUCTION

It has long been established, since the pioneering work of Green and Hinshelwood (*1*), that while platinum is an active catalyst for the decomposition of nitric oxide on platinum, the reaction is retarded by product oxygen (*2–5*). More recently this inhibition by oxygen has been quantitatively established on supported platinum catalysts and platinum foil by Amirnazmi and Boudart (*6, 7*) and on platinum foil (ribbon) by Mummey and Schmidt (*8*). The interaction of NO with single crystal platinum surfaces has been studied extensively by many investigators using a variety of spectroscopic techniques, notably temperature-programmed desorption (*9–20*). It is generally agreed that NO adsorbs and desorbs in the molecular state at low and moderate temperatures and does not begin to dissociate until above 400 K.

The objective of this study was to investigate the rate of decomposition of NO on carbon and its acceleration by platinum supported on carbon. Carbon blacks have been used as a noble metal support in many applications because of their high surface area and low chemical reactivity (*21–22*). The present investigation was based on the idea that the carbon support would serve as a "sink" for the product oxygen from the NO decomposition reaction, thereby removing the inhibitor from the active platinum surface.

EXPERIMENTAL

The decomposition of NO was studied in a differential quartz flow reactor at a total pressure of 128 kPa and between 423 and 623 K. The catalyst under study was confined to a quartz tube of 20 mm i.d. and supported by a fritted quartz disc. The experimental setup, gas chromatograph analytic system, and gas mixtures have been described previously (*6*) except as noted.

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0021-9517/86 $3.00

Premixed 10% NO in He 99.90% was diluted with He 99.995% as needed and passed through Ascarite, a high-purity commercial adsorbent consisting of NaOH imbedded in asbestos, and silica gel traps cooled in a dry ice/acetone bath. The impurities in the NO mixtures were typically 400 ppm N_2, 200 ppm N_2O, 250 ppm CO_2, 50 ppm NO_2, and less than 50 ppm H_2O. The Ascarite trap removed NO_2 and CO_2 while N_2O and H_2O were adsorbed by the silica gel trap; the background N_2 was measured and accounted for in the calculation of the NO decomposition rate.

The gases were analyzed before and after passing over the catalyst by a gas chromatograph–thermal conductivity detector system which was attached to the flow system. Gas analyses were accomplished using two stainless-steel chromatograph columns prepared using a variation of the techniques of Dietz (*23*) and Amirnazmi *et al.* (*6*). One column packed with Linde molecular sieve 5A preceded by a short Porapak Q (microporous polymer beads) section was used to separate N_2 and NO, while the second column packed with Porapak Q separated CO, NO, CO_2, and N_2O. The analysis for CO was not quantitative because of the proximity of its small gas chromatogram peak to an orders-of-magnitude larger NO peak.

High-purity supports were used to prepare the platinum catalysts: Spheron, an amorphous carbon black from the Godfrey Cabot Corporation; Graphon, the graphitic form of Spheron; Neo Spectra, a high-surface-area amorphous carbon black from the Cities Service Company; and finally, γ-alumina. The Pt/carbon catalysts were prepared by impregnation with chloroplatinic acid using the incipient wetness method as described by Robell *et al.* (*24*) and Bartholomew and Boudart (*25*). Catalysts of different dispersions, i.e., percentage of surface-exposed platinum atoms, were obtained by varying the amount of carbon burnoff achieved by the activation of the carbon support prior to impregnation. Carbon supports were activated in air at 693 to 773 K for 3 to 12 h, resulting in carbon burnoffs of 20 to 50%. It is well established that platinum particle size decreases as prior gasification of the carbon support increases (*21, 25*).

A 0.6 wt% Pt/γ-Al_2O_3 catalyst obtained from Cyanamid-Ketjen N.V. was used in this study. It came from the same batch that was used in the previous investigation of Amirnazmi *et al.* (*6*).

The surface area of the carbon materials was determined by the N_2 BET method. The platinum surface of the supported platinum catalysts was measured, before and after use, by the O_2–H_2 titration method of Benson and Boudart (*26*). Since the carbon support of the Pt/carbon catalysts was not a good absorbent for the water produced in the titration, high-purity silica gel was added to the catalyst prior to titration. Catalyst pretreatment consisted of a 4-h reduction in flowing dihydrogen followed by a 4-h evacuation, all at 673 K. A vacuum of better than 1.3×10^{-3} Pa (10^{-5} Torr) was achieved. For each catalyst, reaction rate

TABLE 1

Nitric Oxide Turnover Frequencies at 623 K and 13 kPa NO Partial Pressure

Catalyst	Dispersion (%)	Turnover frequency (s^{-1})
Spheron	($99\ m^2\ g^{-1}$)	7.5×10^{-6}
1% Pt/S	3.4	3.8×10^{-2}
1% Pt/S	20	3.8×10^{-2}
1% Pt/S	31	3.4×10^{-2}
Graphon	($84\ m^2\ g^{-1}$)	4.5×10^{-7}
0.9% Pt/G	8.0	3.0×10^{-2}
5% Pt/G	22	1.8×10^{-2}
10% Pt/G	8.3	3.7×10^{-2}
Neo Spectra	($500\ m^2\ g^{-1}$)	1.6×10^{-5}
2.1% Pt/NS	21	4.2×10^{-2}
5.3% Pt/NS	14	1.4×10^{-2}
5.3% Pt/NS	35	1.0×10^{-2}
5.3% Pt/NS	39	2.0×10^{-2}
0.6% Pt/Al_2O_3	33	1.2×10^{-3}

Note. Turnover rate defined as number of NO molecules reacting per second per surface atom (platinum for the supported catalysts and carbon otherwise).

measurements were made at the highest temperature first, following standard practice.

The reactor was operated in differential mode, with NO conversion generally less than 5%. The turnover frequency v, defined as the number of nitric oxide molecules reacting per surface platinum atom per second, is obtained directly by the relation

$$v\,(\mathrm{s}^{-1}) = \frac{N}{A \cdot L} 2 \cdot n \cdot (x_f - x_i) \quad (1)$$

where N is Avogadro's number, A is the platinum surface area, L is the platinum site density assumed to be 1.19×10^{15} cm^{-2}, n is the total molar flow rate (mol s^{-1}) and x_f and x_i are the mole fraction sums of N_2 and N_2O at exit and entrance of the reactor, respectively.

RESULTS

Turnover Frequency

Steady-state NO decomposition rates were measured on the supported platinum catalysts between 423 and 623 K. The initial rates decayed to the steady-state rates after approximately an hour on stream, and they remained at the steady state for at least 1 h. Table 1 summarizes the catalyst activity at 623 K for an NO partial pressure of 13 kPa for all the carbon-supported catalysts, the supports alone, and for comparison, Pt/Al_2O_3. It can be seen that the NO decomposition turnover frequency on the carbon support alone is several orders of magnitude less than that on carbon-supported platinum; i.e., the turnover frequency on carbon is negligible. In fact the turnover frequency on Pt/carbon is independent of the type of carbon support: amorphous or graphitic carbon, moderate- or high-surface-area carbon.

Furthermore, the turnover frequency on Pt/carbon is independent of platinum particle size (as measured here by the catalyst dispersion) and platinum metal loading for the range and conditions of this study. The absence of any significant change in turnover frequency as the amount of surface metal was increased tenfold is a convincing test of the lack of influence of transport phenomena in the pores of the catalyst (*27*).

TABLE 2

Catalyst Activity as a Function of Reactor Space-time

Run	SPCT (s)	Turnover frequency (s^{-1})	$\frac{X_{N_2}{}^a}{X_{N_2O} + X_{N_2}}$	$\frac{X_{CO_2}}{X_{CO_m} + X_{CO_2}}$
1	8.5	3.7×10^{-2}	0.55	0.74
2	11	3.8×10^{-2}	0.55	0.69
3	13	3.8×10^{-2}	0.57	0.63
4	20	3.6×10^{-2}	0.56	0.66

Note. Catalyst: 1% Pt/Spheron, $D = 3.4\%$, $T = 623$ K, 16.1 g catalyst charge, bed volume 42.2 cm^3. Reactant mixture: 10.2% NO in helium, 13 kPa NO partial pressure.

[a] X_{N_2}, X_{N_2O}, X_{CO_2}, and X_{CO} are the respective mole fractions at the reactor exit. X_{CO_m} represents the maximum CO based on an oxygen mass balance.

Perhaps the most significant observation is that the NO turnover frequency on carbon-supported platinum is an order of magnitude higher than that of the alumina-supported platinum. Previous work by Amirnazmi and Boudart indicated that the turnover frequency for NO decomposition on Pt/Al_2O_3 is independent of the alumina support and indeed is the same as that measured on platinum foil (*7*).

Table 2 shows that the measured NO turnover frequency on Pt/Spheron is independent of the reactor space-time, lending credence to the absence of external mass transfer limitations and to the validity of the differential reactor assumption. Space-time is defined here as the catalyst bed volume divided by the volumetric flow rate of the reactant mixture. The fractional distribution of nitrogen-based product, N_2 or N_2O, indicates that the reaction products were shifted toward N_2, at any value of the space-time. The same behavior was exhibited by the other carbon-supported catalysts. For the Pt/Al_2O_3 catalyst with a platinum dispersion of 33% under the same conditions, the nitrogen-based product was approximately 90% N_2O at a reactor space-time of 9 s. Amirnazmi observed on Pt/Al_2O_3 that the N_2 selectivity increased with increasing space-time, leading to the speculation when coupled with other kinetic evidence that N_2O is an intermediate in the NO decomposition reaction (*28*), contrary to the results of this study on Pt/carbon.

Table 2 also indicates that the carbon oxide product is mainly CO_2, again independent of reactor space-time. It should be noted that the CO_2 selectivity indicated in the table represents only a qualitative lower bound due to the measurement errors inherent in the CO chromatographic analysis discussed earlier. Nevertheless the X_{CO_m} of Table 2 is the upper bound CO mole fraction at the reactor exit, as calculated by a simple mass balance on the known maximum quantity of oxygen available from the dissociation of NO.

Kinetics

The NO turnover frequency and kinetic data on the carbon-supported platinum catalysts were examined in detail, and numerous rate expressions were tested. A few fitted the data numerically but were rejected because they yielded physically unreasonable results (e.g., positive enthalpy and entropy changes for NO adsorption). The following rate expression did adequately fit the data:

$$v\,(\mathrm{s}^{-1}) = \frac{k_{\mathrm{II}} \cdot K_{\mathrm{I}} \cdot [\mathrm{NO}]}{\left\{1 + \left(\dfrac{k_{\mathrm{II}} \cdot K_{\mathrm{I}}}{k_{\mathrm{III}}} \cdot [\mathrm{NO}]\right)^{1/2}\right\}^2}. \quad (2)$$

The above rate expression can be obtained by assuming the reaction sequence

$$\mathrm{NO} + * \overset{K_{\mathrm{I}}}{\rightleftharpoons} \mathrm{NO}^* \qquad \mathrm{(I)}$$

$$\mathrm{NO}^* + * \xrightarrow{k_{\mathrm{II}}} \mathrm{N}^* + \mathrm{O}^* \qquad \mathrm{(II)}$$

$$\mathrm{N}^* + \mathrm{N}^* \xrightarrow{k_{\mathrm{III}}} \mathrm{N}_2 + 2^* \qquad \mathrm{(III)}$$

and that the absorbed nitrogen atoms, N*, are the most abundant reaction intermediates (mari). In the above sequence * represents an active site on the catalyst.

It is important to note that the rate constant for associative nitrogen desorption from platinum, step III, can be calculated from our kinetic data and compared to values obtained in independent studies. Indeed, Eq. (2) can be rearranged to

$$\left(\frac{[\mathrm{NO}]}{v}\right)^{1/2} = \frac{1}{k_{\mathrm{III}}^{1/2}} \cdot [\mathrm{NO}]^{1/2} + \frac{1}{[k_{\mathrm{II}} \cdot K_{\mathrm{I}}]^{1/2}}. \qquad (3)$$

Figure 1 is a fit of Eq. (3) for the 1% Pt/Spheron catalyst with 3.4% dispersion at 523 and 573 K; the slope is equal to $k_{\mathrm{III}}^{-1/2}$, where k_{III} is the nitrogen desorption rate constant. When combined with the results from similar plots for all the other Pt/carbon catalysts and other temperatures, an

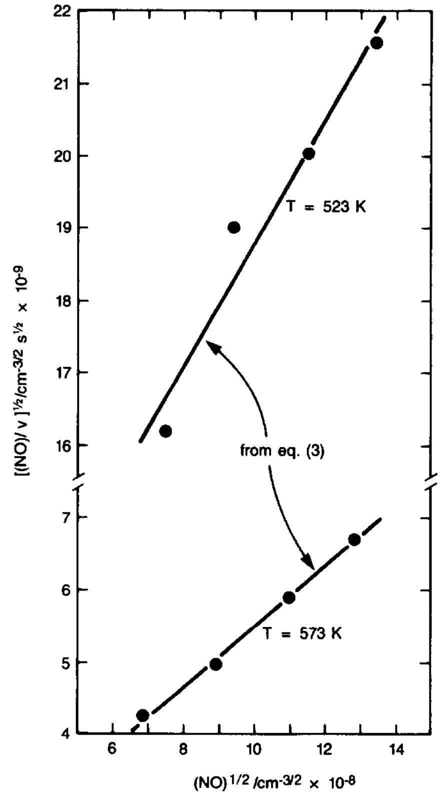

FIG. 1. Correlation of turnover frequency v and nitric oxide concentration (NO) at 523 and 573 K. Catalyst, 1% Pt/Spheron; platinum dispersion, 3.4%; NO partial pressure, 13 kPa.

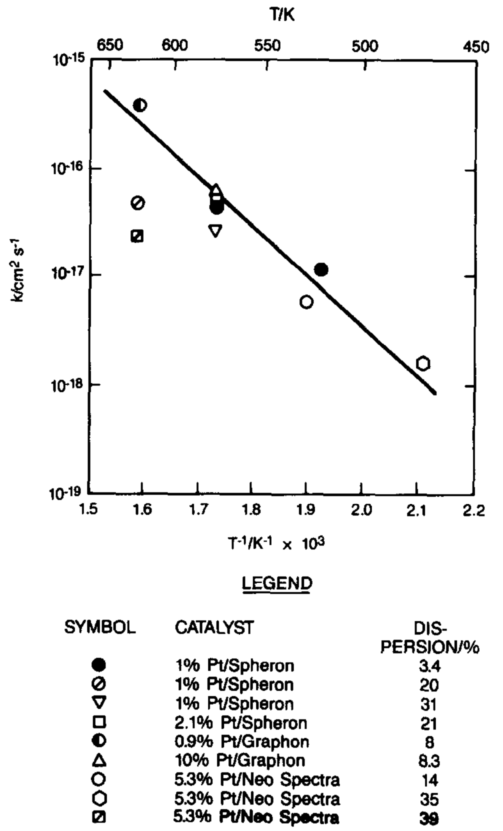

FIG. 2. Combined Arrhenius plot for the nitrogen desorption rate constants for all the Pt/carbon catalysts.

Arrhenius plot for the nitrogen desorption rate constant can be prepared as shown in Fig. 2. While there is scatter in the data, the correlation appears to be excellent, considering the large variations in platinum loading and dispersion, and different carbon supports. The linear regression fit of the data, excluding the two anomalous data points at 623 K indicated in Fig. 2, yielded a preexponential factor A of 5.2×10^{-9} cm^2 s^{-1} and an activation energy E of 88 kJ mol^{-1}, where $k_{\mathrm{III}} = A \exp(-E/RT)$. The NO conversion for the two anomalous data points approached 10%, possibly invalidating the differential reactor assumption.

The nitrogen desorption rate constant found in this study is compared in Table 3 to those obtained in independent studies. Vajo *et al.* (*29*) examined the decomposition of ammonia on a heated platinum wire and found that for low temperatures and high NH_3 pressures, similar to the NO conditions of this study, the recombination and desorption of adsorbed nitrogen atoms were rate determining. Their reported rate constant for nitrogen desorption, obtained independently of our NO decomposition study, is in remarkable agreement with our results. Similarly, the NH_3 decomposition data of Löffler and Schmidt (*30*), who originally fitted their data to a Langmuir–Hin-

TABLE 3

Rate Constant for the Desorption of Nitrogen from Platinum Surfaces
$N^* + N^* \xrightarrow{k} N_2 + 2^*$, $k = A \exp(-E/RT)$

Investigator	Pt surface	Main reaction	Experimental method	Temp range (K)	A (cm^2 s^{-1})	E (kJ mol^{-1})	υ^a (s^{-1})
This study	Supported Pt/C	NO decomposition	Reaction kinetics	473–623	5×10^{-9}	88	0.07
Weinberg *et al.*, 1985	Pt wire	NH_3 decomposition	Reaction kinetics	400–800	6.4×10^{-8}	92	0.4
Löffler and Schmidt, 1976	Pt wire	NH_3 decomposition	Reaction kinetics	500–670^b	1.6×10^{-7b}	88^b	2.0
Wilf and Dawson, 1976	Pt wire	N desorption	TPD	400–650	4×10^{-8}	80	2.6
Sklyarov *et al.*, 1978	Pt wire	N desorption	TPD	440–800	1×10^{-6}	71	320 ?
Kislyuk *et al.*, 1984	Pt foil	N desorption	TPD	370–1000	3×10^{-5}–1×10^{-5}	75–85	4300–290 ?
Schwaha ad Bechtold, 1977	Pt single crystal (111)	N desorption	TPD	370–670	—	105	—

[a] Turnover frequency calculated at reference state of 623 K, half coverage N*; υ (s^{-1}) = k (N*)^2.

[b] Author's data refitted to reaction sequence with N* as mari.

shelwood rate expression, were refitted to a reaction sequence with N* as the mari (*31*), resulting in the desorption rate constant given in Table 3, again in good agreement with our results.

Our reported nitrogen desorption rate constant is also in good agreement with that reported by Wilf and Dawson (*32*), who measured the rate on a platinum wire directly, using temperature-programmed desorption (TPD), and the activation energy reported by Schwaha and Bechtold (*33*), who investigated nitrogen desorption from a platinum single crystal, also using TPD. Wilf and Dawson established that the recombination of adsorbed nitrogen atoms is second order; our proposed reaction sequence is consistent with that observation. The results of Sklyarov *et al.* (*34*) and Kislyuk *et al.* (*35*) appear to be anomalous when compared to all the other investigations, particularly when the calculated turnover frequencies of Table 3 are noted.

DISCUSSION

The reaction of NO on the carbon-supported catalysts, in the strictest sense, is not a classical catalytic decomposition in that ultimately, given sufficient time, the carbon support would be consumed. However, we were able to achieve quasi-steady-state NO turnover frequencies because of the very low differential rates studied here. Moreover, it is not a usual reduction reaction because the "reducing agent" is the support for the active catalytic surface, platinum. Indeed, the carbon does not appear to react directly with NO but rather serves as an "external agent" to maintain the platinum surface in a reduced state, as we discuss below.

The observed accelerated rate of NO decomposition on carbon-supported platinum as compared to that on alumina-supported platinum or that projected from earlier work on platinum foil (*7*) is explained by the role of the carbon support as an oxygen scavenger. While it is uncertain whether the product oxygen on the platinum surface is in atomic or molecular form, Amirnazmi *et al.* (*6, 7*) and Mummey and Schmidt (*8*) have established its inhibiting effect. Amirnazmi *et al.* have postulated that in the presence of oxygen the decomposition of NO on platinum proceeds through the reaction sequence

$$NO + * \xrightarrow{k_{IV}} NO^* \qquad (IV)$$

$$NO + NO^* \longrightarrow N_2O + O^* \qquad (V)$$

$$N_2O \longrightarrow N_2 + O_a \qquad (VI)$$

$$O_a + O^* \overset{K_{VII}}{\rightleftharpoons} O_2 + * \qquad (VII)$$

where O_a is surface mobile oxygen. When O* is assumed to be the mari, the following rate expression results:

$$v\ (s^{-1}) = \frac{k_{IV} \cdot [NO]}{1 + K_{VII} \cdot [O_2]}. \qquad (4)$$

The kinetic data of Amirnazmi *et al.* suggest that product oxygen, the most abundant reaction intermediate, is in equilibrated chemisorption on the same sites as those required for NO chemisorption.

On the other hand, the kinetic data in this study for NO decomposition on Pt/carbon (Eqs. (I)–(III)) suggest that the inhibition product oxygen is removed continuously from the platinum surface by the surrounding carbon support, producing CO and CO_2. It appears that the mari is then adsorbed nitrogen atoms and not oxygen. Derivation of the rate expression (Eq. (2)) which fits our Pt/carbon data and correctly predicts the second-order rate constant for the desorption of nitrogen does not require any assumptions about the sequence of carbon oxidation reactions other than that there be sufficient carbon to remove oxygen from the platinum surface, thereby leaving N* as the mari. Indeed, the result shown in Table 1 that the accelerated rate of NO decomposition on Pt/carbon is independent of the type of carbon support, platinum metal loading, and platinum dispersion lends credibility to the proposed reaction sequence. L'Homme *et al.* (*36*) have investigated the platinum-catalyzed oxidation of Spheron and suggested that oxygen dissociates on the platinum surface and the atoms produced migrate over the catalyst particle to the carbon. It is well known that platinum is an active catalyst for the oxidation of carbon (*37, 38*). It can be speculated that for NO decomposition on Pt/carbon the inhibition product oxygen migrates to the platinum–carbon interface where platinum catalyzes the oxidation of carbon.

The reaction sequence proposed by Amirnazmi *et al.* (*6*) for an oxygen-abundant platinum surface involves a bimolecular reaction between two NO molecules (Eq. (V)) yielding nitrous oxide N_2O. This nitrous oxide can then decompose to dinitrogen, but under the low temperature conditions of this study, the N_2O remains (*28*). Our proposed sequence (Eqs. (I)–(III)) for NO decomposition on oxygen-clean platinum (Pt/carbon) is consistent with experimental data showing dinitrogen as the dominant product. The observed shift of the nitrogen product distribution toward dinitrogen in the case of Pt/carbon as opposed to primarily nitrous oxide in the case of Pt/Al_2O_3 lends further support to our proposed reaction sequence. These observations are consistent with the recent work of Baldwin and Friend (*39*), who used TPD and isotope-exchange experiments to study NO chemistry on W(100) under ultrahigh vacuum conditions. They found that NO dimer formation and subsequent nitrous oxide product are favored on the oxygen-pretreated surface whereas direct NO dissociation to adsorbed nitrogen atoms and their desorption as dinitrogen are favored for an oxygen-clean surface.

The observed shift toward the dinitrogen product on the Pt/carbon catalysts cannot be expected to be complete for the catalysts studied here. The platinum crystallites may not be sufficiently small to permit all the adsorbed oxygen atoms to migrate to the platinum–carbon interface. Thus both reaction sequences could be operating. Also, some of the adsorbed nitrogen atoms could combine with adsorbed NO to produce nitrous oxide. Finally, the presence of product CO as a potential reducing agent for NO complicates the picture. Nevertheless, the kinetic evidence for the nitrogen atom recombination sequence, when taken in its entirety, is highly suggestive of accelerated NO decomposition on an oxygen-free or -depleted platinum surface for the Pt/carbon catalysts.

The "expected" order of magnitude estimate of the preexponential factor for an elementary bimolecular desorption step is 10^{-2} cm^2 s^{-1} (*31*). Our finding of an extremely low preexponential factor for nitrogen desorption from platinum is consistent with those of other investigators as shown in Table 3. The agreement is remarkable considering the different platinum catalysts, reactions, and experimental methods used. It indicates that nitrogen desorption is an important step in both NH_3 and NO decomposition, and that the desorption rate is independent of the reaction or analysis tool. It should be noted, however, that the results summarized in Table 3 are all, with one exception, from polycrystalline platinum. Recent evidence presented by Banholzer and Masel (*40*) indicates that a special plane Pt(410) may be unusually active for NO decomposition. However, it is not expected to affect the results summarized here for polycrystalline platinum.

Finally, recall that our kinetic results for nitrogen desorption relied on the key assumption that adsorbed nitrogen is the mari in the decomposition of NO on Pt/carbon. While this assumption seemed reasonable based on (1) the shift in NO decomposition product toward N_2 rather than N_2O, (2) the apparent removal of surface oxygen from platinum by the carbon support, and (3) the good fit of the resultant rate expression to the NO decomposition data, the best argument for the mari assumption is its prediction of a preexponential factor for N_2 desorption six orders of magnitude lower than the usual value, in excellent agreement with independent results of others.

CONCLUSION

The turnover frequency for nitric oxide decomposition on platinum is an order of magnitude higher on Pt/carbon catalysts than on Pt/Al_2O_3 or than that projected from earlier work on platinum foil. Direct gasification of carbon alone by NO is negligible under the same conditions. For Pt/Al_2O_3 or platinum foil, the decomposition seems to proceed through the chemisorption of NO on platinum, with inhibition by product oxygen, the most abundant reaction intermediate in equilibrated chemisorption on the same sites as those required for NO chemisorption. On the other hand, it appears that for the case of Pt/carbon, the inhibition product oxygen is removed continuously from the platinum surface by the surrounding carbon support, producing CO and CO_2. The kinetic data indicate that the mari is now adsorbed nitrogen and not oxygen. The more important result is that the second-order rate constant for the associative desorption of nitrogen from platinum obtained from this work on carbon-supported platinum is in remarkable agreement with that extracted from published data on NH_3 decomposition or that measured directly by temperature-programmed desorption in independent studies on unsupported clean platinum surfaces.

ACKNOWLEDGMENTS

This work was supported by the Environmental Protection Agency, Grant 1 R01 AP01556-01 AHR (APC), and in its final stages by the Department of Energy, Contract DE-AT03-79ER-10502.

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