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

INTRODUCTION

In our recent paper of the same title on the reaction of nitric oxide on carbon-supported platinum samples, Pt/C, we reported a shift in nitrogen product from approximately 90% N_2O for NO decomposition on Pt/Al_2O_3 to about 50% N_2 for the case of Pt/C (*1*). This shift in product selectivity was explained by a change in the most abundant reaction intermediate (*mari*) from adsorbed oxygen for Pt/Al_2O_3 to adsorbed nitrogen for Pt/C. Nitrogen becomes the *mari* as adsorbed oxygen is removed continuously by the carbon support, yielding CO and CO_2. While in our original paper we discussed qualitatively the reasons why the shift toward N_2 product on our Pt/C samples cannot be expected to be complete, we should have accounted quantitatively for the N_2O as well as the N_2 product in our kinetic analysis.

RESULTS AND DISCUSSION

Accordingly, we propose the following extended analysis for NO decomposition on Pt/C catalysts. There are two overall reactions with stoichiometric equations:

$$NO \Rightarrow \tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 \qquad \text{(I)}$$

$$NO \Rightarrow \tfrac{1}{2}N_2O + \tfrac{1}{4}O_2. \qquad \text{(II)}$$

In our original paper (*1*), we postulated the following elementary steps:

$$NO + * \overset{K_1}{\rightleftharpoons} NO^* \qquad (1)$$

$$NO^* + * \xrightarrow{k_2} N^* + O^* \qquad (2)$$

$$N^* + N^* \xrightarrow{k_3} N_2 + 2^*. \qquad (3)$$

In the above sequence, * represents an active site on the platinum surface. Adsorbed oxygen, which is an inhibitor to the NO decomposition reaction, reacts in subsequent, unspecified steps with the carbon support, producing CO and CO_2 and regenerating the active site. As discussed in our paper, these latter steps can be considered to be kinetically nonsignificant so long as there is sufficient carbon to remove oxygen from the platinum surface, thereby leaving N* as the *mari*.

Furthermore, we can only speculate on the elementary step(s) responsible for the formation of N_2O in the overall reaction Eq. (II), e.g., the reaction of N* with NO or the combination of NO* and NO* to form a dimer $(NO)_2^*$ that in subsequent steps leads to N_2O. In any event, we need not specify the elementary step(s) to account for N_2O formation in the rate of NO decomposition. This can be seen as follows. The rate of NO decomposition at steady state is

$$v = v_{I} + v_{II} \qquad (4)$$

or

$$v = v_{I}\left\{1 + \frac{v_{II}}{v_{I}}\right\}, \qquad (5)$$

where v_I and v_{II} are the rates of NO decomposition by reactions I and II, respectively. Using the assumptions of N* as *mari*, conservation of active surface sites, and the steady-state approximation $v_2 = 2v_3$, we obtained in our original analysis (*1*):

$$v_{I} = \frac{k_2K_1[NO]}{\{1 + [(k_2K_1/2k_3)[NO]]^{1/2}\}^2}. \qquad (6)$$

The rate expression given in our original

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TABLE 1

Effect of Temperature and Catalyst on Nitrogen Product Selectivity (P_{NO} = 13 kPa)

Temperature (K)	Catalyst[a] (D/%)	$\frac{x_{N_2O}}{x_{N_2O} + x_{N_2}}$[b]	$\frac{x_{N_2O}}{x_{N_2}}$[b]
623	1% Pt/S (3.4)	0.45	0.82
	1% Pt/S (20)	0.57	1.3
	0.9% Pt/G (8.0)	0.55	1.2
573	1% Pt/S (3.4)	0.45	0.82
	1% Pt/S (31)	0.41	0.70
	2.1% Pt/S (21)	0.40	0.67
	10% Pt/G (8.3)	0.56	1.3
523	1% Pt/S (3.4)	0.40	0.67
	5.3% Pt/NS (14)	0.35	0.54
473	5.3% Pt/NS (35)	0.4	0.7

[a] Carbon supports: S, spheron; G, graphon; NS, neo spectra (see *1*). Platinum dispersion, D is given in parentheses.

[b] x_{N_2O} and x_{N_2} are the respective mole fractions at the reactor exit.

paper had erroneously "k_3" instead of "$2k_3$" in the denominator of Eq. (6) above.

The rate of NO decomposition becomes, according to Eqs. (5) and (6):

$$v = \frac{k_2K_1[\mathrm{NO}]\{1 + (v_{\mathrm{II}}/v_{\mathrm{I}})\}}{\{1 + [(k_2K_1/2k_3)[\mathrm{NO}]]^{1/2}\}^2}. \tag{7}$$

Thus the rate expression for the extended analysis is identical to that for the original analysis (v_{I} above or Eq. (2) in (*1*)) except for the expression between the brackets in the numerator:

$$\left\{1 + \frac{v_{\mathrm{II}}}{v_{\mathrm{I}}}\right\} \tag{8}$$

But, with the differential reactor conditions under which the data were obtained,

$$\frac{v_{\mathrm{II}}}{v_{\mathrm{I}}} = \frac{\text{amount of } \mathrm{N_2O} \text{ produced}}{\text{amount of } \mathrm{N_2} \text{ produced}}. \tag{9}$$

According to the data presented in Table 2 of our paper (*1*) and Tables 1 and 2 of this note (*2*), the amounts of N_2O and N_2 observed are approximately equal. Indeed, for the limited range of conditions of this study, this ratio appears to be independent of the Pt/C catalyst studied, reactor space time, temperature, and NO concentration. Thus, if N_2O does not decompose any further under the conditions of these experiments, as suggested by data presented in (*1*), the ratio of Eq. (9) is approximately equal to unity. For simplicity, we shall assume it is unity so that we obtain simply from Eq. (7):

$$v = \frac{2k_2K_1[\mathrm{NO}]}{\{1 + [(k_2K_1/2k_3)[\mathrm{NO}]]^{1/2}\}^2} \tag{10}$$

which can be rearranged as

$$\left\{\frac{[\mathrm{NO}]}{v}\right\}^{1/2} = \frac{1}{(4k_3)^{1/2}}[\mathrm{NO}]^{1/2} + \frac{1}{(2k_2K_1)^{1/2}}. \tag{11}$$

A plot of $([\mathrm{NO}]/v)^{1/2}$ vs $[\mathrm{NO}]^{1/2}$ now gives a slope equal to $(4k_3)^{-1/2}$ as compared to $(2k_3)^{-1/2}$ for the original analysis, and hence k_3 is reduced merely by a constant factor of $\sim\frac{1}{2}$. As demonstrated in our paper (*1*), the excellent fit of the data to Eq. (11) and the resultant Arrhenius plot for the nitrogen desorption rate constant k_3 over a wide range of platinum particle size and platinum loading with different carbon supports, and most significantly the prediction of a value for k_3 in agreement with other reported work, all lend support to our analysis of the data.

TABLE 2

Effect of NO Concentration on Nitrogen Product Selectivity

[NO]/%	$\frac{x_{N_2O}}{x_{N_2O} + x_{N_2}}$[a]	$\frac{x_{N_2O}}{x_{N_2}}$[a]
10.2	0.45	0.82
7.5	0.46	0.85
5.0	0.53	1.1
2.9	0.55	1.2

Note. Catalyst: 1% Pt/Spheron, D = 3.4%. Reaction conditions: T = 573 K; NO in He mixtures, total pressure 128 kPa.

[a] x_{N_2O} and x_{N_2} are the respective mole fractions at the reactor exit.

CONCLUSION

The extended analysis presented here changes none of the conclusions of the original paper, viz., the acceleration of the rate of NO decomposition on Pt/C by an order of magnitude as compared to that of Pt/Al_2O_3 and the apparent removal on inhibiting oxygen from the platinum surface by the carbon support, leaving N* as the most abundant reaction intermediate. More importantly, the value of k_3, the second-order rate constant for the associative desorption of nitrogen from platinum, extracted from our work remains in good agreement with other values reported in the literature, as listed in Table 3 of (*1*). More recently, Vajo *et al.* have reported a value of k_3 obtained from the kinetics of ammonia decomposition on Pt(110)–(1 × 2) (*3*). Their value for k_3 at 623 K is equal to 1×10^{-16} cm^2 s^{-1}, in agreement with our own result obtained from Eq. (11), namely, 0.6×10^{-16} cm^2 s^{-1}. It is remarkable that almost the same value of a rate constant for an elementary surface step can be extracted from kinetic data for different reactions on platinum consisting of a large single crystal and supported metal particles, respectively.

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