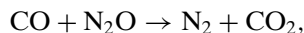
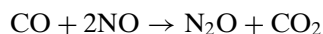


LETTER TO THE EDITOR

Does the N₂O–CO Subreaction Play an Important Role in the NO–CO Reaction on Rh?

The NO–CO reaction on Rh is of high current interest for both fundamental and applied chemistry (1, 2). This reaction contains only a few elementary steps, and one can hope to understand its mechanism in detail and then to employ the knowledge obtained in order to increase the effectiveness of reduction of nitrogen oxide to nitrogen in automotive catalytic converters (2). One of the problems which should be solved in this field is connected with the N₂O formation which accompanies the N₂ production at moderate pressures and relatively low temperatures [just after the lightoff of the reaction (1)]. N₂O produced under steady-state conditions may in principle readsorb and react farther on to make N₂. This possibility was first assessed by Hecker and Bell (3). Employing a Rh/SiO₂ catalyst (at $T = 465\text{--}525\text{ K}$), they have shown that the effect of the reactant flow rate on catalyst activity and selectivity is negligible. This observation suggests that N₂O, once formed, does not undergo further reduction. Additional confirmation of this conclusion was obtained by observing no reaction between N₂O and CO (3). More recently, the N₂O formation (on Rh/Al₂O₃ and Rh/CeO₂ catalysts) has been studied by Cho *et al.* (4). Analyzing in detail the effect of feed composition on the NO conversion, they have demonstrated that the N₂O-formation channel is significant at 450–600 K. In addition, they have observed in a separate experiment good activity of Rh/Al₂O₃ for the N₂O–CO reaction (4). From these measurements, it was not evident whether N₂O readsorption during the NO–CO reaction is important. Nevertheless, Cho *et al.* (4) have interpreted the data obtained in favor of N₂O readsorption. In particular, they have concluded that the reactions involving the latter process,

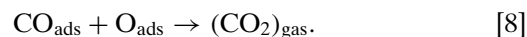
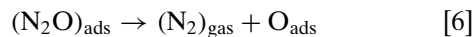
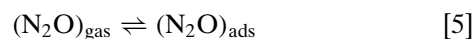
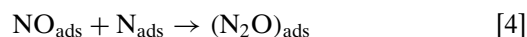


play an important role in N₂ formation. In contrast, McCabe and Wong (5) have shown (for Rh/Al₂O₃) that the N₂-formation rate in the N₂O–CO reaction is negligibly low compared to that in the NO–CO reaction. To clarify this disagreement, Cho (6) has analyzed theoretically the kinetics of the NO–CO and N₂O–CO reactions. His conclusion, repeated in the review (2), was [see Ref. (6), p. 255] as follows “The kinetic analysis . . . shows a dramatic

difference between the rate of the N₂O–CO reaction as an *intermediate* reaction and that as an *isolated* reaction. Results have revealed that the rate of the N₂O–CO reaction as an intermediate reaction in the NO–CO reaction system can be two to three orders of magnitude faster than the isolated N₂O–CO reaction, which is known to be very slow compared with the NO + CO reaction.” In addition, Cho (7) has reported experimental data indicating that the N₂O-formation rate is dependent on the reactant flow rate. The latter was also in favor of N₂ formation via N₂O readsorption.

In this letter, we show that Cho’s interpretation (6) of the results of his calculations is misleading. In fact, one can draw from his data a conclusion which is completely opposite that drawn by Cho (6).

To start, we recall that Cho (6) has assumed that the NO–CO reaction occurs via the elementary steps



Under steady-state conditions, this scheme yields the balance equation for (N₂O)_{ads} (6)

$$k_4\theta_{\text{N}}\theta_{\text{NO}} + k_5P_{\text{N}_2\text{O}}\theta_{\text{v}} = k_{-5}\theta_{\text{N}_2\text{O}} + k_6\theta_{\text{N}_2\text{O}}, \quad [9]$$

where k_4 , k_5 , k_{-5} , k_6 are the rate constants for elementary steps; θ_{N} , $\theta_{\text{N}_2\text{O}}$, θ_{v} are the coverages corresponding to N, N₂O, and vacant sites; and $P_{\text{N}_2\text{O}}$ is the N₂O pressure. Using Eq. [9] and neglecting step [7] (this approximation has been employed by Cho (6)), we can represent the rate of N₂ formation as

$$W_{\text{N}_2} = k_6\theta_{\text{N}_2\text{O}} = k_6(k_4\theta_{\text{N}}\theta_{\text{NO}} + k_5P_{\text{N}_2\text{O}}\theta_{\text{v}})/(k_{-5} + k_6). \quad [10]$$

TABLE 1

Surface Coverages (6) for the Overall NO–CO Reaction at $P_{\text{NO}} = P_{\text{CO}} = P_{\text{N}_2\text{O}} = 400$ ppm and for the Isolated N₂O–CO Reaction at $P_{\text{CO}} = P_{\text{N}_2\text{O}} = 400$ ppm ($T = 583$ K)

Coverage	NO–CO	N ₂ O–CO
θ_{CO}	0.376	0.880
$\theta_{\text{N}_2\text{O}}$	5.072×10^{-7}	1.466×10^{-9}
θ_v	0.274	0.120
θ_{N}	0.344	0
θ_{NO}	5.417×10^{-3}	0

The N₂O–CO reaction was considered by Cho (6) as a subreaction of the NO–CO reaction. This means that in the absence of NO the N₂O–CO reaction occurs via steps [2], [5], [6], and [8]. Accordingly, the rate of N₂ formation is given by

$$W_{\text{N}_2} = k_6\theta_{\text{N}_2\text{O}} = k_6k_5P_{\text{N}_2\text{O}}\theta_v/(k_{-5} + k_6). \quad [11]$$

Employing a complete set of equations corresponding to reaction scheme [1]–[8] (without step [7]), Cho (6) has calculated the adsorbate coverages corresponding to the NO–CO and N₂O–CO reactions. Typical results of his calculations for the case when the CO and N₂O pressures are the same for both reactions ($P_{\text{NO}} = P_{\text{CO}} = P_{\text{N}_2\text{O}} = 400$ ppm for the overall NO–CO reaction, and $P_{\text{CO}} = P_{\text{N}_2\text{O}} = 400$ ppm for the isolated N₂O–CO reaction) are shown in Table 1. Further, Cho (6) has compared the rates of N₂ production for the overall and isolated systems. The ratio of these rates, called by Cho (6) the “enhancement factor” (η), is equal to the ratio of the respective N₂O coverages because in both cases the reaction rate is given by $W_{\text{N}_2} = k_6\theta_{\text{N}_2\text{O}}$ (cf. Eqs. [10] and [11]). According to Cho’s calculations, η is typically in the range from 10^2 to 10^3 (e.g., $\eta = 346$ for the data shown in Table 1). The fact that the “enhancement factor” is high, $\eta \simeq 10^2$ – 10^3 , has been interpreted by Cho (6) as an indication that “the rate of the N₂O–CO reaction as an intermediate reaction in the NO–CO reaction system can be two to three orders of magnitude faster than the isolated N₂O–CO reaction.” This interpretation is not correct because really he has used for comparison the *total* rate of N₂ formation in the NO–CO reaction. The total rate results from the direct NO + CO channel and from N₂O readsorption. For this reason, the fact that the total N₂-formation rate in this reaction is much higher than the N₂-formation rate in the N₂O–CO reaction does not indicate that the N₂O–CO reaction as an intermediate reaction in the NO–CO reaction system is much faster than the isolated N₂O–CO reaction. To evaluate the relative contribution of the N₂O–CO reaction to the overall NO–CO reaction, one can

note that for the reaction scheme under consideration, the N₂O readsorption does not result in the formation of N_{ads} or NO_{ads}. This means that the contributions of the direct NO + CO channel and the N₂O readsorption to the total rate (Eq. [10]) are, respectively, given by

$$W_{\text{N}_2}^{\text{dir}} = k_6k_4\theta_{\text{N}}\theta_{\text{NO}}/(k_{-5} + k_6) \quad [12]$$

and

$$W_{\text{N}_2}^{\text{rea}} = k_6k_5P_{\text{N}_2\text{O}}\theta_v/(k_{-5} + k_6). \quad [13]$$

Comparing the latter equation with Eq. [11], we obtain that the ratio of the N₂-formation rate, resulting from the N₂O–CO channel in the overall NO–CO reaction, to the N₂-formation rate in the isolated N₂O–CO reaction equals the ratio of the respective coverages corresponding to vacant sites. For example, from the data shown in Table 1, one can conclude that the contribution of the N₂O–CO reaction to the total rate of N₂ formation in the overall NO–CO reaction is only two times larger than the N₂-formation rate in the isolated N₂O–CO reaction. Thus, for the scheme under consideration, the overall NO–CO reaction occurs primarily via the direct channel.

Finally, it is reasonable to emphasize that we do not claim that Cho’s opinion (4–7) that the N₂O–CO reaction as an intermediate reaction plays an important role in the NO–CO reaction is wrong [even if we are not sure that this opinion is right (e.g., recent data (8) obtained for the NO–CO reaction on Rh(111) indicate in line with Refs. (3) and (5) that the contribution of N₂O readsorption to the overall reaction is negligible)]. Our analysis only indicates that Cho’s conclusion (4–7) about the importance of the N₂O–CO reaction is in fact not supported by his calculations (6).

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