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RESEARCH NOTE

A Note on $N_2O + CO$ Reaction Mechanism over Rh Surfaces

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Nitrous oxide (N_2O) is produced as a by-product during the reduction of NO_x species by CO oxidation. The kinetics of N_2O decomposition and $N_2O + CO$ reaction is the subject for numerous investigations (1–4). In one of the key studies for the reaction between N_2O and CO, McCabe and Wong (1) obtained the kinetic parameters for this reaction between 550 and 700 K and reactant partial pressures of 0.6 and 7 Torr. They measured apparent reaction orders of -1 ± 0.15 in CO partial pressure and 0.65 ± 0.1 in N_2O partial pressure under differential conversion conditions at temperatures between 564 and 583 K. They postulated a surface reaction model which involved intact adsorption of N_2O with subsequent dissociation to gas phase dinitrogen and chemisorbed oxygen which reacted with chemisorbed carbon monoxide to form carbon dioxide. The steady-state rate expression based on this model resulted in first-order kinetics with respect to N_2O partial pressures and negative first-order kinetics with respect to CO partial pressures. In the article, McCabe and Wong "speculate that the fractional N_2O pressure dependence reflects more complicated precursor adsorption kinetics for N_2O than the simple treatment afforded in this kinetic model" (1). The models postulated by Cho (2–4) for the decomposition of N_2O also proceeds with the direct decomposition pathway (i.e., the molecule adsorbs on the metal surface intact with subsequent decomposition to the gas phase di-nitrogen and chemisorbed atomic O species). In addition, mechanisms postulated by both Cho and McCabe and Wong have linear CO as the reactive intermediate (1–4).

In this note we postulated that nitrous oxide adsorption occurs on Rh surfaces dissociatively. Furthermore, we postulated that the reactive form of CO is the "bridge-bonded" CO species. A steady-state rate expression for the overall reaction was derived based on the previously mentioned postulates along with appropriate assumptions about the mechanism. The mechanism, the derivation of the rate expression and its predictions, are presented in the subsequent sections.

The model postulated in this article for $N_2O + CO$ surface reaction over supported Rh catalysts is

$$N_2O + {}^* \Leftrightarrow N_2O^*, \qquad [1]$$

$$N_2O^* + {}^* \Leftrightarrow N^* + NO^*, \qquad [2]$$

$$NO^* + {}^* \rightarrow N^* + O^*, \qquad [3]$$

$$CO + 2^* \Leftrightarrow {}^*CO^* \text{ (bridge bonded)}; \qquad [4]$$

an alternative CO adsorption model is

$$CO + {}^* \Leftrightarrow CO^*, \qquad [4a]$$

$$CO^* + {}^* \Leftrightarrow {}^*CO^* \text{ (bridge bonded)}, \qquad [4b]$$

$$2N^* \rightarrow N_2 + 2^*, \qquad [5]$$

$${}^*CO^* + O^* \rightarrow CO_2 + 3^*. \qquad [6]$$

In order to derive an analytical steady-state rate expression, the following assumptions were made:

1. All the steps that are shown to be reversible are in equilibrium.
2. The reactive form of CO is the bridge-bonded state (this point will be justified in the discussion section).
3. N_2O decomposition takes place via a two-step surface dissociation of adsorbed N_2O precursor.
4. Surface is nearly saturated with CO, and the total number of the surface sites is closely approximated by the sum of the vacant sites and CO-covered sites.
5. The rate-determining step is the dissociation of surface NO into surface N and surface O (step 3).

These assumptions along with the elementary reactions lead to such relationships as

$$k_1 P_{N_2O} \theta_v = k_{-1} \theta_{N_2O}, \qquad [7]$$

$$k_2 \theta_{N_2O} \theta_v = k_{-2} \theta_{NO} \theta_N, \qquad [8]$$

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and

$$\text{rate} = k_3\theta_{\text{NO}}\theta_v. \qquad [9]$$

From Eqs. [7] and [8], we obtain the surface coverage of NO in terms of the partial pressure of N_2O

$$\theta_{\text{NO}} = K_1 K_2 P_{\text{N}_2\text{O}}\theta_v^2/\theta_{\text{N}} \qquad [10]$$

where $K_i = k_i/k_{-i}$.

In order to determine the coverage of surface N, the steady-state condition between the two products must be used. In other words, the rate of CO_2 production must be equal to the rate of the N_2 production, such that

$$k_5\,\theta_{\text{N}}^2 = k_6\theta_{\text{CO}}\theta_{\text{O}}. \qquad [11]$$

As a result of assumption 4, the surface coverage of carbon monoxide is taken as 1, and the resulting expression for the surface coverage of atomic nitrogen is obtained as

$$\theta_{\text{N}} = (k_6\theta_{\text{O}}/k_5)^{1/2}. \qquad [12]$$

A steady-state balance for the surface oxygen species results in the following expression

$$\theta_{\text{O}} = k_3\theta_{\text{NO}}\theta_v/k_6\theta_{\text{CO}} \cong k_3\theta_{\text{NO}}\theta_v/k_6 \qquad [13]$$

for surface oxygen coverage. Substituting Eq. [13] into Eq. [12], we get

$$\theta_{\text{N}} = (k_3\theta_{\text{NO}}\theta_v/k_5)^{1/2}. \qquad [14]$$

In order to determine the vacant site concentration, we will use assumptions 2 and 4 (i.e., the surface is nearly saturated with CO and the reactive form of CO is bridge bonded). If we assume that the adsorption of CO takes place via step [4] in the mechanism, the CO coverages can be predicted from

$$K_4 P_{\text{CO}}\theta_v^2 = \theta_{\text{CO}}. \qquad [15]$$

On the other hand, we may choose steps [4a] and [4b] as CO adsorption pathways to bridge-bonded species. In such a case, the coverage of CO can be determined from

$$K_{4\text{a}}K_{4\text{b}}P_{\text{CO}}\theta_v^2 = \theta_{\text{CO}}. \qquad [15\text{a}]$$

Equations [15] and [15a] are equivalent in terms of the coverage and partial pressure functionality. Therefore, the simpler form (i.e., Eq. [15]) will be used in the analysis. The vacant site concentration can be determined from Eq. [15] and the site balance equation

$$\theta_v + \theta_{\text{CO}} = 1. \qquad [16]$$

The following second-order polynomial can be obtained in terms of the vacant site concentration

$$\theta_v^2 + (K_4 P_{\text{CO}})^{-1}\theta_v - (K_4 P_{\text{CO}})^{-1} = 0. \qquad [17]$$

TABLE 1

The Activation Energy Data for the Proposed Model

Step	E_{af} (kcal/mol)	Ref.	E_{ar} (kcal/mol)	Ref.
1	0	1	5	1
2	0	8	21	8
3	19	8	—	—
4	0	1	18–31	9, 13
	Bridge bonded		41.5 ± 1.0	15
5	31	10	—	—
6	24–27	7	—	—

The physically meaningful root of Eq. [17] is

$$\theta_v = \{-1 + (1 + 4K_4 P_{\text{CO}})^{1/2}\}/(2K_4 P_{\text{CO}}). \qquad [18]$$

The value of K_4 was estimated in the orders of 10^2–10^3 Torr^{-1} from the adsorption rate data (1–4) and desorption activation energy of CO given in Table 1. Therefore, $(4K_4P_{\text{CO}})^{1/2} \gg 1$, which simplifies Eq. [18] to

$$\theta_v = (K_4 P_{\text{CO}})^{-1/2}. \qquad [19]$$

Substituting Eqs. [14] and [19] in Eq. [10] yields the coverage of NO as

$$\theta_{\text{NO}} = [K_1 K_2 P_{\text{N}_2\text{O}}/(k_3/k_5)^{1/2}]^{2/3}/(K_4 P_{\text{CO}})^{1/2}, \qquad [20]$$

and the rate of nitrous oxide decomposition is obtained as

$$\text{rate} = \left(k_3 k_5^{1/2} K_1 K_2\right)^{2/3} K_4^{-1} P_{\text{N}_2\text{O}}^{2/3}/P_{\text{CO}}. \qquad [21]$$

The effective rate constant as a result of this analysis is

$$k_{\text{eff}} = \left(k_3 k_5^{1/2} K_1 K_2\right)^{2/3} K_4^{-1}. \qquad [22]$$

According to Eq. [22], the effective activation energy of the reaction must have the form

$$E_{\text{a,eff}} = 2/3(E_{\text{a},3} + E_{\text{a},5}/2 + \Delta H_1 + \Delta H_2) - \Delta H_4, \qquad [23]$$

where $E_{\text{a},i}$ is the activation energy for the ith step in the mechanism and ΔH_i are the heats of reaction of ith step.

DISCUSSION

In this article, an $N_2O + CO$ reaction mechanism was postulated. This mechanism involved stepwise dissociation of N_2O on the metal surface and the bridge-bonded form as the reactive chemisorbed CO species. With these postulates, and appropriate assumptions about kinetics, the mechanism resulted in rate expressions consistent with the experimental data of McCabe and Wong (1).

The dissociation of N_2O on metal surfaces is usually modeled as a single-step mechanism where a surface species decompose into a gas phase N_2 and chemisorbed oxygen (1, 8). Such a mechanism may be valid for clean surfaces. However, when the surface is predominantly covered by CO—evident from the negative reaction orders—the interaction of metal surface with chemisorbed N_2O may be substantially different. In this note, the postulated mechanism involves steps that are generally accepted as valid in NO_x–CO reactions. N_2O undergoes a two-step dissociation forming surface intermediates common to the intermediates that were involved in forming N_2O during a de-NO_x reaction.

Another postulate made in this note is that the bridge-bonded carbon monoxide was the reactive form. Models based on linear CO–Rh species did not result in the fractional orders with respect to N_2O partial pressures (1). Therefore, the bridge-bonded CO species is postulated. It is important to note here that on supported Rh surfaces, the bridge-bonded species may constitute as high as 61% of total CO coverage as determined from Magic Angle Spinning (MAS) ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy of chemisorbed CO (11). This postulate is further supported by an Infrared (IR) study on the reactivity of chemisorbed CO on Rh/SiO_2 catalysts. Zhong observed that upon introduction of NO in an IR cell which contained a Rh/SiO_2 sample with pre-adsorbed CO, among the three forms of chemisorbed CO on Rh (i.e., gem dicarbonyl, linear and bridged forms) bridge-bonded CO and Rh dicarbonyl species had disappeared. Zhong commented that linearly adsorbed CO could not react with gaseous NO but that gem di-carbonyl, linear and bridged forms can exchange with NO (5).

With these pieces of supporting evidence for bridge-bonded CO as the reactive form, a rate expression was sought for the $N_2O + CO$ reaction. The pseudo equilibrium assumption was invoked for CO adsorption, N_2O adsorption, and first dissociation to surface NO and surface N steps. The rate-determining step was selected as the dissociation of surface NO into surface N and surface O species in accordance with the de-NO_x literature (12). Studies on adsorption kinetics of CO on Rh do not reveal the second-order kinetics in terms of vacant site concentrations as required for a bridge-bonded species. However, a bridge-bonded species can form from a linear CO by interacting with a nearest-neighbor vacant site. In such a case, steps [4a] and [4b] in the mechanism become relevant. When those steps in the mechanism are used to predict the coverages of bridge-bonded CO, the CO partial pressure and vacant site dependencies of the rate law take mathematically equivalent forms. The only mathematical difference between a single-step adsorption to a bridge-bonded state and a two-step mechanism is in the definition of the adsorption equilibrium constant. Therefore, in order to keep the mathematical analysis simple, the single-step adsorption into a bridge-bonded species was preferred.

McCabe and Wong suggested that the overall rate of CO–N_2O reaction could not be limited by the rate of reaction between the adsorbed species because N_2O–CO reaction proceeds much slower than CO–O_2 and CO–NO reactions on the same catalyst. However, one of the assumptions made in this note is that the reactive form of CO is the bridge-bonded one. Under certain operating conditions, a mechanism with the linearly bound CO as a reactive from for a typical NO–CO reaction can give meaningful orders in terms of NO and CO partial pressures which is in agreement with the experimental data (12). However, in the case of N_2O–CO reaction, the bridge-bonded species was necessary to maintain the fractional orders with respect to N_2O and negative first-order with respect to CO partial pressures. In addition to this mathematical necessity, the bridge-bonded species is the most abundant one as indicated by ^{13}C NMR of CO on Rh (11), and it is the reactive species in NO exchange reactions (5).

The reaction rate expression derived based on this mechanism and aforementioned postulates and assumptions yielded reaction orders of -1 in CO and 2/3 in N_2O partial pressures. These values are in excellent agreement with the experimental results of McCabe and Wong who measured apparent reaction orders of -1 ± 0.15 in CO partial pressure and 0.65 ± 0.1 in N_2O partial pressure (1).

We can calculate the effective activation energy of the overall reaction by using Eq. [23] based on the activation energy data available in the literature. The activation energies found from literature were presented in Table 1. The desorption activation energies of NO and CO available in the literature were generally obtained from Temperature Programmed Desorption (TPD) data (9, 13, 14). In a study of transient and steady-state microkinetic models of catalytic reactions on nonuniform surfaces, Broadbelt and Rekoske (15) observed that the activation energy data obtained from the Redhead analysis of TPD spectrum were always lower than their true values even on uniform surfaces. Therefore, in addition to TPD results, a desorption activation energy of the bridge-bonded CO measured via a modulated beam technique was included (14). The different values of the heats of adsorption for CO along with the rest of the activation energy data in Table 1 was used to estimate the effective activation energy of the reaction. The effective activation energy of the reaction was estimated as 36.7 and 47.2 kcal/mol for the low and high values of the heat of adsorption of CO (31 and 41.5 kcal/mol, respectively). These predicted effective activation energy values compare well with McCabe and Wong's experimental value of 40 ± 2 kcal/mol (1).

In summary, a model for nitrous oxide reduction with bridge-bonded CO is postulated. The kinetic analysis with the assumptions that the nitrous oxide goes through a stepwise decomposition on the surface, the active form of adsorbed carbon monoxide is the bridge-bonded one, and the rate-determining step is the surface NO decomposition step yielded the CO and N_2O partial pressure dependencies in very good agreement with the experimental data of McCabe and Wong (1). The apparent activation energies determined from the model strongly depend on the heat of adsorption of bridge-bonded CO.

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