Microkinetic model studies of alloying effects on the CO+NO+O₂ reactions over Pt-Rh nanocatalysts

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Received 21 October 2003; revised 25 February 2004

Microkinetic model has been used to study the kinetics of CO+NO+O₂ reactions on Pt-Rh nanocatalysts. The alloy particles show an intermediate behavior for the CO+O₂ reaction. For the CO+NO reaction, the kinetic behavior of alloy particles are close to that of Rh, while for the CO+NO+O₂ reaction, it is very close to that of Pt. The rate of CO+O₂ and CO+NO+O₂ reactions is higher than that of CO+NO reaction on Pt, Rh and Pt-Rh nanocatalysts. The light-off temperature in case of CO+NO reaction is delayed in the absence of oxygen. The overall kinetics of the CO+NO+O₂ reaction on Rh is dominated by CO+NO reaction kinetics rather than by CO+O₂ reaction kinetics which has a higher inherent rate. The scenario reverses itself on Pt nanoparticles. The magnitude of the NO inhibition effect on the CO oxidation by O₂ is considerably smaller on Pt than on Rh. The simulated results are in qualitative agreement with the experimental findings.

PACS: 68.43.Mn; 82.20.Pm; 82.65.+r; 82.45.Jn; 82.20.Wt
IPC Code: Int. Cl. 7 B01J 23/42, B01J 23/36

The catalytic cleaning of vehicle exhaust gas is based on the so-called three-way catalysts (TWC), converting simultaneously CO, the uncombusted hydrocarbons (HC) and nitrogen oxides (NOₓ) into non-toxic products. In the light of the increasing stringency of vehicular emission norms, the physicochemical properties of the currently used Pt-Rh bimetallic nanocatalysts require a thorough understanding for optimum performance. The reactions of CO with O₂ and NO over Pt, Pd, Rh catalysts as well as on Pt-Rh nanocatalysts are important steps in the catalytic control of automobile exhaust emissions. In our earlier work¹, we studied the effect of alloying on the kinetics of CO+O₂ and CO+NO reaction on the Pt-Rh nanocatalysts. In this paper we examine how the rates of the CO+NO+O₂ reactions compare with those of CO+O₂ and CO+NO reactions. We have used the microkinetic model which takes into account the rates of each elementary reaction step before arriving at the overall reaction rate of CO₂ formation.

Theoretical model

We consider the microkinetic model²-⁴ in order to study the kinetics of CO+NO+O₂ reactions on Pt, Rh and the Pt - Rh nanocatalysts. The model is described below:

Kinetics of CO+NO+O₂ reaction

For the CO+NO+O₂ reaction the following elementary steps were considered⁵-⁷ in the microkinetic scheme: (i) Adsorption of CO and NO molecules onto the surface of the metal or the alloy, (ii) desorption of adsorbed CO and NO molecules from the surface, (iii) dissociation of O₂ molecule on the surface followed by adsorption of atomic oxygen, (iv) dissociation of molecularly adsorbed NO into adsorbed atomic nitrogen and oxygen atom, (v) formation of N₂ molecules through two possible steps, namely, β-N₂ and δ-N₂ steps, and finally, (vi) formation of CO₂ molecules through the combination of adsorbed CO molecule and adsorbed oxygen atom.

\[
\begin{align*}
\text{CO} & \leftrightarrow \text{CO}_a \\
\text{NO} & \leftrightarrow \text{NO}_a \\
\text{O}_2 & \rightarrow 2\text{O}_a \\
\text{NO}_a & \rightarrow \text{N}_a + \text{O}_a \\
\text{N}_a + \text{N}_a & \rightarrow \text{N}_2 (\beta - \text{N}_2) \\
\text{NO}_a + \text{N}_a & \rightarrow \text{N}_2 + \text{O}_a (\delta - \text{N}_2) \\
\text{CO}_a + \text{O}_a & \rightarrow \text{CO}_2
\end{align*}
\]

The suffix 'a' denotes the component in the adsorbed phase. Adsorption is the first step in the overall reaction scheme. The rate of adsorption of
species \(i\) on metal \(m\) is given by molecular collision theory \(^2\): 
\[
\sigma_{im} = \frac{(RT/2\pi M_i)^{1/2} \sigma_m (S_{im})_{im}}{C_i},
\]
where \(M_i\) is the molecular weight of the species \(i\); \(\sigma_m\) is the area occupied by 1 mole of surface atoms (cm\(^2\)/mole) of the metal \(m\); \((S_{im})_{im}\) is the initial sticking coefficient of the species \(i\) on the metal \(m\); \(C_i\) is the concentration of the component \(i\) in the gas phase and is calculated from the gas pressure through the relation 
\[
C_i = \frac{P}{RT} \text{(moles/c.c)}
\]
and \(\theta_i\) is the fraction of vacant surface sites available for adsorption and is given by 
\[
\theta_i = 1 - \theta_{CO} - \theta_{NO} - \theta_N - \theta_O;
\]
\(R\) is the universal gas constant and \(T\) is the temperature in Kelvin. \(\theta_i\) is the surface coverage of adsorbed species \(i\).

The rate of desorption of CO and NO \(^2\) is given by
\[
\tau_{\text{CO}}^{\text{des}} = A \exp \left[ -E_{\text{RT}} \right] \theta_{\text{CO}}, \quad \tau_{\text{NO}}^{\text{des}} = A \exp \left[ -E_{\text{RT}} \right] \theta_{\text{NO}}
\]
and the rates of \(N_2\) formation do not exist for this case. Here, \(A\) and \(E\) are the interaction parameters (kcal/mole) which account for the repulsive interaction between CO\(-\)CO, CO\(-\)NO and CO\(-\)N\(_2\). Here \(A\) and \(E\) denote respectively the pre-exponential factor \((s^{-1})\) and the activation energy (kcal/mole) for a particular rate of the elementary reaction step occurring on the surface. The rate of NO dissociation is given by 
\[
\tau_{\text{NO}}^{\text{diss}} = A \exp \left[ -E_{\text{RT}} \right] \theta_{\text{NO}}, \theta_{\text{CO}}\text{ and } \tau_{N_2} = A \exp \left[ -E_{\text{RT}} \right] \theta_{N_2}, \theta_{\text{O}}\theta_{\text{N}}
\]
The rate of formation of \(CO_2\) molecules is given by 
\[
\tau_{\text{CO}_2} = A \exp \left[ -E_{\text{RT}} \right] \theta_{\text{CO}}, \theta_{\text{O}}, \theta_{N}, \theta_{\text{N}_2}
\]
and step is not found to occur on Pt. \(^3\)

The steady state continuity equations for the adsorbed species \(CO, NO, N_2\), and \(O_2\) are respectively given by \(^4\)
\[
\tau_{\text{CO}}^{\text{CO}} - \tau_{\text{CO}}^{\text{C}_2} = 0 \quad \tau_{\text{NO}}^{\text{NO}} - \tau_{\text{NO}}^{\text{N}_2} = 0 \quad \tau_{\text{NO}}^{\text{NO}} - \tau_{\text{NO}}^{\text{N}_2} - 2 \tau_{\text{NO}}^{\text{O}} = 0 \quad \tau_{\text{NO}}^{\text{NO}} + 2 \tau_{\text{NO}}^{\text{CO}} + \tau_{\text{NO}}^{\text{N}_2} - \tau_{\text{CO}}^{\text{O}} = 0
\]

For studying the kinetics of the CO\(+\)NO\(+\)O\(_2\) reaction, one has to solve the set of the above four equations self-consistently for \(\theta_{\text{CO}}, \theta_{\text{NO}}, \theta_{\text{N}}, \theta_{\text{O}}\). This helps us to estimate \(\tau_{\text{CO}}\) which is a yardstick for comparing the rates of different reactions, namely, CO\(+\)O\(_2\), CO\(+\)NO and CO\(+\)NO\(+\)O\(_2\).

The activities of Pt and Rh for the CO\(+\)O\(_2\) and CO\(+\)NO reactions are known and we resort to the first order approximation for the supported Pt\(_{50}\)Rh\(_{50}\) alloy particles by which the rate of adsorption of CO (say) for the alloy may be expressed as
\[
\tau_{\text{CO}}^{\text{CO}} = (x_{\text{Pt}}^7 \tau_{\text{CO}}^{\text{CO}})_{\text{Pt}} + [1 - (x_{\text{Pt}})_{\text{Pt}}] \tau_{\text{CO}}^{\text{CO}}_{\text{Rh}}
\]

Here, \((x_{\text{Pt}})_{\text{Pt}}\) is the surface concentration of Pt atoms on the surface of the supported Pt-Rh nanoparticles. The other elementary reaction steps were also treated on the same footing. The values of the surface concentration of Pt atoms, \((x_{\text{Pt}})_{\text{Pt}}\) were taken from our earlier Monte Carlo calculations \(^8\).

### Kinetics of CO\(+\)O\(_2\) reaction

For the CO\(+\)O\(_2\) reaction, steps represented by Eqs 1, 3 and 7 are the only relevant elementary reaction steps and the rate Eqs 8 and 11 would only require attention. One has to consider only the second and the last term of Eq. 11 which represent the rate of adsorption of O\(_2\) and the rate of CO\(_2\) formation respectively. The rates related to NO dissociation and \(N_2\) formation do not exist for this case. Here, \(0, = 1 - \theta_{\text{CO}}\) and \(\alpha_N = 0\) for the CO desorption step.

### Kinetics of CO\(+\)NO reaction

For the CO\(+\)NO reaction, all the elementary reaction steps barring the step represented by Eq. 3 are relevant. Therefore, all the rate equations need to be considered here. However, the second term in the rate Eq. 11 (i.e. the one for the rate of adsorption of O\(_2\)) would not appear here for obvious reasons. Here, \(0, = 1 - \theta_{\text{CO}}\) and \(\alpha_N = 0\).

The \(N_2O\) formation is significant only in Ultra High Vacuum (UHV) conditions \(^9\). Therefore, \(N_2O\) formation step has been ignored in our model studies on higher pressures.

### Results and Discussion

The parameters used in our studies are given in Table I. The Monte Carlo simulated values of surface concentration of Pt, \((x_{\text{Pt}})_{\text{Pt}}\) values are 0.548, 0.551, 0.559, 0.553, 0.538, 0.564, 0.528, 0.554, 0.572 and 0.523 at 450, 475, 500, 525, 550, 575, 600, 625, 650 and 675 K respectively. The kinetics of CO\(+\)O\(_2\) and CO\(+\)NO reactions were investigated separately as a function of both temperature and pressure for obtaining a deeper insight into the reactivity of both NO and O\(_2\) towards CO. A comparative study of the kinetics of the CO\(+\)O\(_2\) reaction on three different systems is depicted in Fig. 1. The turnover number is nothing but the number of CO\(_2\) molecules that are released per site per second. The rate of formation of CO\(_2\) molecules is found to be higher on Pt than on Rh which is quite obvious. It is quite evident from the
rate constants (i.e. pre-exponential factor and activation energy) and the expression for the rate of formation of CO$_2$ molecules ($r_{CO_2}$) that Pt is a better catalyst for CO oxidation than Rh. The Pt$_{30}$Rh$_{50}$ alloy particles show an intermediate behavior.

The variation of the kinetics of the CO+O$_2$ reaction with the partial pressure of the adsorbates (P$_{CO}$ and P$_{O_2}$) at constant temperature is depicted in Figs 2 and 3. Figures 2 and 3 reveal an intermediate kinetic behavior for the supported alloy particles. Figure 2 shows that the turnover number (TON) decreases with the increase in the partial pressure of CO at constant partial pressure of O$_2$. The sudden drop in TON by 2 orders of magnitude at low CO pressures as shown in Fig. 2 is a direct consequence of the inhibition of oxygen adsorption caused by a high concentration of CO$_2$. This is also corroborated by the findings of Oh$^3$ on Rh. In the limit of high $\theta_{CO}$, the CO$_2$ formation step, despite its low activation energy, would be kinetically hindered due to very low $\theta_{O}$. Again, the pathway for CO desorption is intrinsically constricted due to its high activation energy. Therefore, we observe that in the regime of high CO pressure, the CO+O$_2$ reaction gets poisoned by the accumulation of CO$_2$. On the contrary, in Fig. 3, we observe that the rate of CO+O$_2$ reaction increases with the increase in partial pressure of O$_2$. This is because of the fact that the rate of CO adsorption and consequently $\theta_{CO}$ increases significantly with the increase in P$_{CO}$ due to the high sticking co-efficient of CO. Again, the sticking co-efficient of O$_2$ being sufficiently smaller than that of CO, the rate of O$_2$ adsorption and consequently $\theta_{O}$ does not increase substantially with the increase in P$_{O_2}$ so as to inhibit the adsorption of CO. However, an increase in $\theta_{O}$ with the increase in
P03 promotes the CO oxidation by O2, as the expression for \( r_{\text{CO}_2} \) shows a first order dependence on \( \theta_0 \).

Figure 4 compares the rate of the CO+NO reaction on three different systems. It may be noticed that the turnover number for the formation of CO2 molecules is appreciably higher on Rh. However, the kinetic behavior of the supported alloy particles is an intermediate between the 2 metals but is closer to that of Rh. The low turnover number for formation of CO2 molecules on supported Pt can be attributed to its low NO dissociation capability. The NO dissociation step is the most important step in CO+NO reaction because it furnishes the adsorbed oxygen atom with which molecularly adsorbed CO can unite to form CO2 molecule. This means that for the CO+NO reaction the rate of formation of CO2 molecules is controlled by the rate of NO dissociation. The activation energy for NO dissociation is much higher on Pt than on Rh. In other words, the rate of NO dissociation on Pt is very small. Thus, the rate of formation of CO2 molecules suffers a sharp decline on Pt.

Figures 5 and 6 delineate how the kinetics of the CO+NO reaction vary with the partial pressure of the adsorbates, P_{CO} and P_{NO}, at a constant temperature. It is evident from these Figs 5 and 6 that the kinetics of the CO+NO reaction have a weak dependence on the partial pressure of the adsorbates and also that the supported alloy particles closely resemble the kinetic behavior of supported Rh. The kinetics of the CO+NO reaction have much stronger dependence on temperature as may be noticed in Figs 4, 5 and 6. The reaction pathways for the CO+NO reaction are much more complicated than that for the CO+O2 reaction. The number of adsorbed species is higher for the CO+NO reaction than for the CO+O2 reaction. Therefore, after the CO+NO reaction has progressed sufficiently, the adsorption of CO or NO would always be inhibited to some extent by the presence of other adsorbed species. Hence, the rate of CO+NO reaction shows a weak dependence on the partial pressure of the adsorbates. From Fig. 5 it is evident
that the kinetics of the CO+NO reaction varies weakly with the partial pressure of CO. So, in comparison with the CO+O2 reaction, the inhibiting role of CO in the rate of CO+NO reaction is almost absent for Rh (111) and is much less pronounced for the rest of the systems. In Fig. 3 we have already found that the rate of CO+O2 reaction increases with the partial pressure of O2. In Fig. 6 it may be noticed that the rate of CO+NO reaction on Rh (111) increases very sluggishly with the partial pressure of NO, whereas it diminishes slightly with the partial pressure of NO for the rest of the three systems. Thus, a comparison of Figs 3 and 6 would show that the increase in pressure of NO marginally affects the rate of the CO+NO reaction unlike O2 which appreciably promotes the rate of CO+O2 reaction.

The inherent rate of CO+O2 reaction is much higher than that of CO+NO reaction on Rh, Pt and Pt-Rh nanocatalysts. We have included the results for Rh(111) surface (Fig. 7) as it is a standard system on which immense work has been done. It may be noticed that the onset of the CO+O2 reaction takes place at a much lower temperature than that of the CO+NO reaction. In other words, the light-off temperature for the CO+NO reaction is higher than that of CO+O2 reaction. It may be recalled here that the light-off temperature for a particular reaction is the minimum temperature at which it is fired. This observation is in agreement with experimental findings for Rh/Al2O3. It is also evident from Fig. 7 that the kinetics of CO+NO+O2 reaction on Rh(111) is closer to that of CO+NO reaction rather than that of CO+O2. Thus, the kinetic behavior of the CO+NO+O2 system on Rh(111) is dominated by the CO+NO reaction kinetics rather than by the CO+O2 reaction kinetics. Here, the overall kinetics of the CO+NO+O2 system is found to be controlled by the CO+NO reaction which has a lower inherent rate. From this observation one can at once infer that the presence of NO in the gas mixture inhibits the formation of CO2 on Rh. In other words, the rate of CO+O2 reaction on Rh(111) is strongly suppressed when NO is present in the reacting gas, whereas the CO+NO reaction is only mildly affected by the presence of oxygen. This finding is also corroborated by experimental results for Rh/Al2O3.

The overall kinetics of the CO+NO+O2 reaction on supported Pt is governed by the CO+O2 reaction kinetics. Therefore, the kinetics of the CO+NO+O2 reaction on supported Pt has more of CO+O2 character and less of CO+NO character. It is quite obvious that the rate of CO oxidation by O2 is much less impeded by the presence of NO. This observation agrees well with the experimental findings.

Now, Pt-N bond strength being much less than Rh-N bond strength, N2 is instantaneously released from the surface of Pt through the combination of 2 N2's as soon as N2 is formed from the dissociation of NO2. The role of inhibition of NO in the oxidation of CO by O2 on Rh can thus be explained in terms of blocking of sites by N2 as N2 binds to Rh-sites more strongly. The kinetics of the CO+NO+O2 on
supported Pt is very close to that of supported alloy particles.

The rate of CO+NO+O\(_2\) reaction on Rh, Pt and Pt-Rh systems is higher than that of CO+NO reaction and the light-off temperature for the CO+NO reaction is higher than that of CO+NO+O\(_2\) reaction on all these 3 systems. Therefore, it can be inferred here that the light-off is delayed in the absence of O\(_2\). From this observation on the light-off behavior one may arrive at the conclusion that it is the presence of oxygen that is of crucial importance in three-way catalysts.

Conclusion

Microkinetic model has been used to study the effect of alloying on the kinetics of CO+NO+O\(_2\) reactions on Pt-Rh nanocatalysts. The following results have been found:

(i) The supported alloy particles show an intermediate kinetic behavior for the CO+O\(_2\) reaction and the kinetic behavior of the supported alloy particles is close to that of Rh for the CO+NO reaction, while for the CO+NO+O\(_2\) reaction it is very close to that of Pt;
(ii) the inherent rate of CO+O\(_2\) and CO+NO+O\(_2\) reaction is higher than that of the CO+NO reaction on all the systems studied in this work; (iii) the light-off temperature of the CO+O\(_2\) and CO+NO+O\(_2\) reaction is higher than that of CO+NO reaction on the systems studied; and (iv) the kinetics of the CO+NO+O\(_2\) reaction on Rh show more of CO+NO character and less of CO+O\(_2\) character. The situation is just the opposite for Pt. Though the model used here is very simple, it can account for many experimentally observed facts. The present findings may be gainfully exploited in three-way catalysis.

References