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Research Note

Effect of temperature and pressure on the surface kinetic parameters of $Pt/\gamma\text{-}Al_2O_3$ during selective CO oxidation

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1. Introduction

The selective oxidation of CO is required to reduce the CO concentration in H_2 derived from hydrocarbons for fuel cells. Our previous studies [1,2] revealed the change in surface reaction kinetic parameters with time on stream, feed stream composition, and Fe promotion of Pt catalysts supported on $\gamma\text{-}Al_2O_3$. Both Fe-promoted and nonpromoted Pt catalysts exhibited rapid initial partial deactivation. Site blockage was the main cause of deactivation of $Pt/\gamma\text{-}Al_2O_3$ [1], whereas both decrease in intrinsic site activity and site blockage were the causes of deactivation of $PtFe/\gamma\text{-}Al_2O_3$ [2]. Fe promotion increased the intrinsic site activity of $Pt/\gamma\text{-}Al_2O_3$, probably as a result of creating more oxygen adsorption sites/ability. However, with time on stream, the intrinsic site activity of PtFe approached that of Pt as the catalyst deactivated [2].

Temperature and pressure are important variables that can significantly affect surface kinetic parameters and consequently affect reaction rate and selectivity. Temperature has an effect on every step of reaction (surface reactions, adsorption, and desorption) whereas pressure can affect the reaction in terms of the driving force to form product. Since CO oxidation is highly exothermic, operating on an industrial scale can result in temperature gradient(s) that affect the local activity/selectivity of the catalyst. At relatively low temperatures (i.e., 90 °C), it has been shown in our previous study [1] that the Pt surface is predominantly covered with adsorbed CO and that the rate of reaction is directly proportional to oxygen partial pressure. The relationship between selectivity and temperature for this reaction on Pt catalysts is not clear based on the literature. There are reports of selectivity monotonically decreasing with temperature [3–5] or first decreasing to a minimum and then increasing to a maximum [6,7] with increasing temperature. At higher temperature, the CO conversion and selectivity are limited by the reverse water-gas-shift reaction [8].

In this study, the effects of reaction temperature and total pressure on the selective oxidation of CO on $Pt/\gamma\text{-}Al_2O_3$ were investigated. Reaction temperature was varied between 80 and 110 °C to minimize temperature gradients due to exotherming and the reverse waster–gas-shift reaction. Isotopic transient kinetic analysis (ITKA) was used to determine the average surface residence time and the surface concentration of intermediates at each reaction temperature and pressure. The rate of reaction (R_{CO_2}) is related to the surface concentration of carbon intermediates ($N_{i\text{-}CO_2}$) and the surface residence time of these intermediates ($\tau_{i\text{-}CO_2}$) by $R_{CO_2} = (1/\tau_{i\text{-}CO_2})N_{i\text{-}CO_2}$ [9,10]. The reciprocal of average surface residence time ($1/\tau_{i\text{-}CO_2} = k_{ITKA}$) is a pseudo-first-order rate constant (k_{ITKA}) representing the intrinsic site activity of the catalyst. This parameter, k_{ITKA}, for this reaction can potentially be a function of not only temperature but also the surface concentrations of oxygen and hydrogen.

2. Experimental

A 5 wt% Pt on $\gamma\text{-}Al_2O_3$ was prepared as previously reported using incipient wetness impregnation of calcined (500 °C, 10 h) boehmite with an aqueous solution of chloroplatinic acid hexahydrate [1]. The catalyst was then dried overnight at 110 °C and calcined at 500 °C for 2 h under flowing hydrocarbon-free air. The BET surface area and percentage Pt dispersion (based on irreversible H_2 chemisorption) of the reduced catalyst were 230 m^2/g_{cat} and 45%, respectively.

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The catalytic activity of the catalyst for the selective oxidation of CO in the presence of hydrogen at 1.8 atm was determined for the temperature range: 80–110 °C. The effect of total pressure was determined at 90 °C and 1.2, 1.8, and 3.6 atm. All rate data reported are at steady-state reaction after 3 h TOS. Each data point reported at different conditions was from different runs to minimize any effects at one condition affecting the results at another. The differential reaction system used in this study is described in detail elsewhere [1]. Prior to reaction, the catalyst was reduced in a stream of hydrogen at 550 °C for 1 h. After reduction, the temperature was gradually decreased over 4 h to the reaction temperature, at which time the flow was switched to a feed stream containing 45% H_2, 53% He, 1% CO, and 1% O_2. The space velocity used in this study was $\sim 152{,}000\ h^{-1}$ for reaction at 80 °C and $190{,}000\ h^{-1}$ for reaction in the temperature range 90–110 °C in order to maintain differential conversion at steady state. Arrhenius plots were used in determining the apparent activation energy of the overall reaction. As indicated above, the steady-state rates of reaction from separate runs at each temperature were used in the Arrhenius plot. The CO conversion and selectivity were determined periodically until the reaction reached steady state and were calculated using the amount of reactant consumed as described by Manasilp and Gulari [3]. %CO_2 selectivity is defined as the percentage of oxygen reacted that formed CO_2.

Isotopic transients were induced by switching between isotopically labeled CO (^{12}CO to ^{13}CO) after the reaction reached steady state. This had no effect on the rate of reaction. A small amount of Ar in the ^{12}CO stream was used to account for gas-phase holdup. The kinetic parameters, such as average surface residence times of CO_2 intermediates and reversibly adsorbed CO ($\tau_{i\text{-}CO_2}, \tau_{CO,rev}$) and surface concentrations of reaction intermediates, and reversibly adsorbed CO ($N_{i\text{-}CO_2}, N_{CO,rev}$), were calculated using the method described by Shannon and Goodwin [9]. The decrease in the transient response of the old carbon label and the increase in the transient response of the new label in the CO_2 and CO exiting the reactor were monitored by a mass spectrometer equipped with a high-speed data acquisition system interfaced to a personal computer using Balzers Quadstar 422 v 6.0 software. For these reaction conditions, readsorption of CO_2 was not significant and did not have to be taken into account in determining the average surface residence time for reaction ($\tau_{i\text{-}CO_2}$).

3. Results and discussion

3.1. Effect of temperature

The effect of temperature on steady-state CO oxidation rate, selectivity, pseudo-first-order rate constant ($k_{ITKA} = 1/\tau_{i\text{-}CO_2}$), and the surface concentration of CO_2 intermediates ($N_{i\text{-}CO_2}$) is reported in Table 1. As expected, at temperatures between 80 and 110 °C, CO oxidation rate increased with temperature. The apparent activation energy determined from an Arrhenius plot (Fig. 1) was 57.7 kJ/mol. The data at different temperatures were corrected to account for a variation in conversion between 5 and 16% using the power-law rate expression (Rate $= k_r P_{O_2}$) that has been found to apply for the reaction in this temperature range for this Pt catalyst [1]. By varying space velocity and by using the Weisz–Prater criterion ($\Phi < 0.15$) [11], no mass or heat transfer limitations were determined to occur under these reaction conditions. The apparent activation energies for reaction on Pt determined in other studies [3,6,12] at higher temperatures (150–250 °C) have been found to be approximately 70–80 kJ/mol. The increase in apparent activation

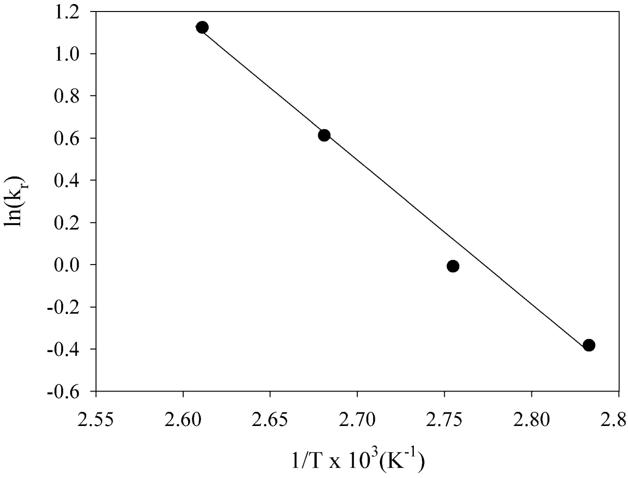

Fig. 1. Arrhenius plot for the selective oxidation of CO on Pt/γ-Al_2O_3.

Table 1
Effect of reaction temperature on steady-state CO oxidation rate, %CO_2 selectivity, and surface kinetic parameters determined by ITKA

Temperature (°C)	CO oxidation[a] (μmol/(g_{cat} s))	CO_2[a] (%)	k_{ITKA}[b] (s^{-1})	$N_{i\text{-}CO_2}$ (μmol/g_{cat})	$\tau_{CO,rev}$[c] (s)	$N_{CO,rev}$ (μmol/g_{cat})	Total N_{CO} (μmol/g_{cat})	$\theta_{i\text{-}CO_2}$[d]	θ_{totCO}[d]
80	0.64	45	0.0845	7.6	8.4	93.7	101.3	0.065	0.866
90	0.89	30	0.0870	10.2	7.1	99.0	109.2	0.087	0.933
100	1.55	34	0.0871	17.8	7.0	93.4	111.2	0.152	0.950
110	2.40	38	0.0878	27.3	6.8	85.0	112.4	0.234	0.960

[a] Rate and CO_2 selectivity at 1.8 atm; 45% H_2, 1% O_2, 1% CO by vol with balance He. Max error was measured to be ±7 and ±10%, respectively.

[b] $k_{ITKA} = 1/\tau_{i\text{-}CO_2}$, pseudo-first-order rate constant determined by ITKA. Max error was measured to be ±5%.

[c] $\tau_{CO,rev}$, surface residence time of reversibly adsorbed CO. Max error was measured to be ±5%.

[d] $\theta_i = N_i$/(irreversibly chemisorbed H atoms), the surface coverage of species i. Max error was estimated to be ±10%.

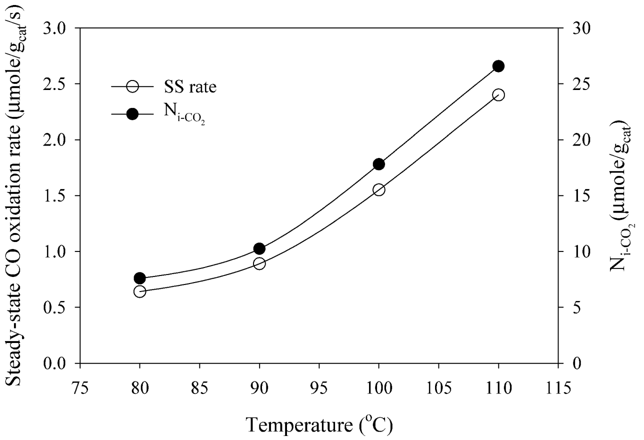

Fig. 2. Temperature dependency of steady-state CO oxidation rate and the surface concentration of CO_2 intermediates.

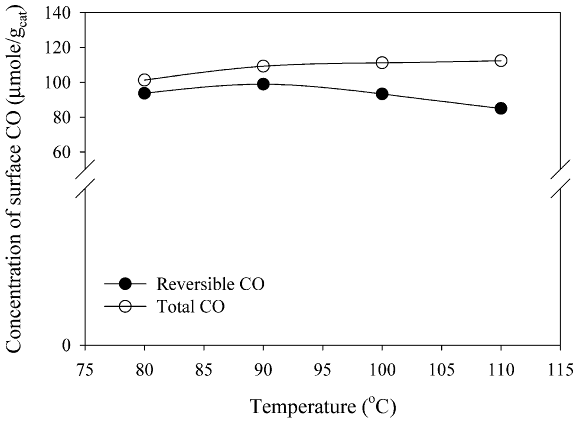

Fig. 3. Temperature dependency of the surface concentration of reversibly adsorbed CO and the total surface concentration of CO including CO_2 intermediates.

energy with temperature indicates a possible change in reaction mechanism or rate-determining step.

The effect of temperature on selectivity was not significant. However, with increasing reaction temperature, the $\%CO_2$ selectivity did appear to first decrease somewhat and then level off or slightly increase.

Isotopic transient kinetic analysis results showed a significant effect of temperature on the surface concentration of CO_2 intermediates ($N_{i\text{-}CO_2}$). At temperatures between 80 and 110 °C, this concentration increased with temperature in the same fashion as the CO oxidation rate as shown in Fig. 2. While $N_{i\text{-}CO_2}$ increased with temperature, the concentration of reversibly adsorbed CO (i.e., CO that adsorbed and desorbed without reacting) decreased slightly as shown in Fig. 3. The total surface concentration of adsorbed CO (reversibly adsorbed CO and CO_2 intermediates) remained essentially constant with temperature. Comparing the total surface concentration of adsorbed CO with the number of surface Pt atoms (116 μmol/g$_{cat}$), the CO surface coverage was very high (~90%) at these temperatures. This suggests that only a small fraction of the Pt surface was covered by adsorbed oxygen.

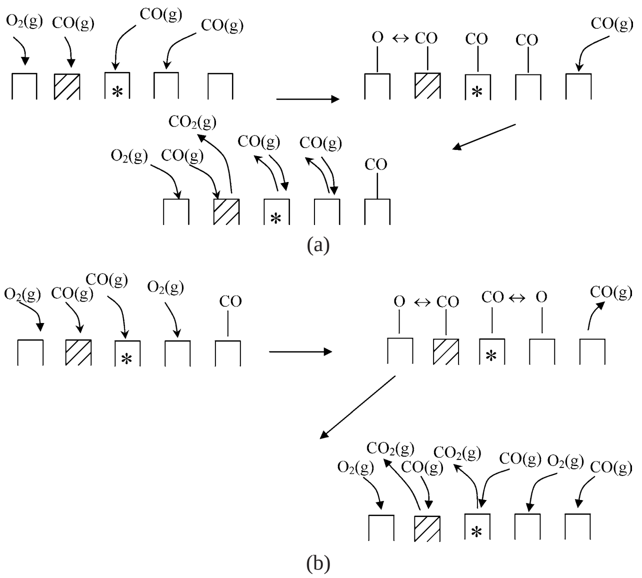

Fig. 4. Illustration of how sites not active at lower temperature may become active in forming CO_2 at higher temperature and pressure. (a) Lower temperature or pressure. Less adsorbed oxygen adjacent to adsorbed CO: CO adsorbs and then desorbs without reaction leading to site (*) not counted as active by ITKA. (b) Higher temperature or pressure. More adsorbed oxygen adjacent to adsorbed CO: reaction can occur and site (*) is detected by ITKA.

At the relatively low temperatures used in this study, the rate of CO oxidation was limited by the rate of oxygen adsorption (hence the direct dependence of rate on P_{O_2} and not P_{CO} [1]) and thus, the surface concentration of CO_2 intermediates was limited by the amount of adsorbed oxygen. The increase in temperature must have increased the adsorption competitiveness of oxygen and thus populated the surface with adsorbed oxygen as illustrated in Fig. 4. Whereas the actual distribution of active sites on the catalyst surface could be quite complicated (e.g., formation of adsorbed CO islands), the simplified picture shown in Fig. 4 is to help the reader develop an understanding of why the number of active CO_2 intermediates may depend directly on oxygen adsorption. Consider a particular site (*) shown in Fig. 4a representing the condition at low temperatures. Under this condition, even though there was a CO molecule adsorbed on that site, it was not reacted prior to desorption since there is no oxygen adsorbed on any adjacent sites. In contrast, at higher temperatures (Fig. 4b) (or pressure, see below), oxygen was more competitively adsorbed and was able to adsorb on more sites adjacent to adsorbed CO. Consequently, at higher temperatures more adsorbed CO had the possibility of reacting with adsorbed oxygen resulting in an increase in the surface concentration of CO_2 intermediates. Thus, sites not active at lower temperatures became active enough to be detected by ITKA. Since the reaction is limited by the amount of adsorbed oxygen, the surface concentration of CO_2 intermediates is a function of the surface concentration of adsorbed oxygen.

ITKA is an averaging technique and determines the average number of active intermediates (or active sites) at a given

Table 2
Effect of total pressure on steady-state CO oxidation rate, %CO_2 selectivity, and surface kinetic parameters (ratio of partial pressures kept the same)

Total pressure (atm)	CO oxidation rate[a] (μmol/(g_{cat} s))	CO_2 selectivity[a] (%)	k_{ITKA}[b] (s^{-1})	$N_{i\text{-}CO_2}$ (μmol/g_{cat})	$\tau_{CO,rev}$[c] (s)	$N_{CO,rev}$ (μmol/g_{cat})	Total N_{CO} (μmol/g_{cat})	$\theta_{i\text{-}CO_2}$[d]	θ_{totCO}[d]
1.2	0.72	40	0.0941	7.7	7.45	105.1	112.8	0.065	0.964
1.8	0.89	30	0.0870	10.2	7.10	99.0	109.2	0.087	0.933
3	1.34	38	0.0914	14.7	7.42	100.1	114.8	0.125	0.981

[a] Rate and CO_2 selectivity at 90 °C; 45% H_2, 1% O_2, 1% CO by vol with balance He. Max error was measured to be ±7 and ±10%, respectively.
[b] $k_{ITKA} = 1/\tau_{i\text{-}CO_2}$, pseudo-first-order rate constant determined by ITKA. Max error was measured to be ±5%.
[c] $\tau_{CO,rev}$, surface residence time of reversibly adsorbed CO. Max error was measured to be ±5%.
[d] $\theta_i = N_i$/(irreversibly chemisorbed H atoms), the surface coverage of species i. Max error was estimated to be ±10%.

time. However, more sites may be potentially active, but not counted, since reaction is not occurring on them at that particular time (short period during the isotopic transient event). The same effect has been seen in our earlier work [1] when varying the O_2 partial pressure at constant partial pressure of CO and total pressure. By increasing O_2 partial pressure, $N_{i\text{-}CO_2}$ was found to increase without any significant change in k_{ITKA}. Increased oxygen accessibility on adsorption sites was suggested to be the main cause of this increase. Since oxygen is more competitively adsorbed at higher temperatures, one might expect $N_{i\text{-}CO_2}$ to go through a maximum with increasing temperature and then decrease as it becomes limited by the amount of adsorbed CO.

The pseudo-first-order rate constant (k_{ITKA}) determined using ITKA measurement of reaction residence time of intermediates in this temperature range (80–110 °C) remained essentially constant (Table 1). Readsorption of product CO_2 was not detected in this reaction temperature range and, therefore, did not have to be accounted for. It is worth noting that k_{ITKA} reported in Table 1 is the average value from all sites that have sufficient activity to be detected by isotopic transient kinetic analysis.

It might be initially surprising that k_{ITKA} was not a function of temperature. Let us explore why this is the case for its average value. The site activity distribution of k_{ITKA} can be calculated using the method described by Hoost and Goodwin [13]. The quantity $f(k_{ITKA})$ is the reactivity distribution for the active CO_2 intermediates on the catalyst surface. The area under the curve integrated from 0 to $\infty(\int_0^\infty f(k_{ITKA})\,\mathrm{d}k_{ITKA})$ is equal to 1 in all cases. Since correction for the gas-phase holdup cannot be directly done mathematically prior to distribution analysis, the distribution was calculated from the normalized product isotopic transient and then shifted to have the average value calculated from the figure equal to the average value obtained directly by ITKA. From the activity distributions shown in Fig. 5a, the relative homogeneity (peak width) of the site activity was essentially independent of reaction temperature. Thus, while an increase in temperature generated more sites, these new sites had activities apparently in the same range as the sites active at the lower temperature, thus giving similar average values at the different temperatures. In Fig. 5b, we illustrate how the temperature actually affected site activity based on the concentration of active sites. In this figure, $f(k_{ITKA})N_{i\text{-}CO_2}$ is plotted vs k_{ITKA} giving the distribution of the concentration of sites with different values of k_{ITKA}. Whereas $f(k_{ITKA})$ is normalized by the total concentration of active sites, $f(k_{ITKA})N_{i\text{-}CO_2}$ as shown in Fig. 5b is the distribution of the total number of active intermediates/sites having activity k_{ITKA}. The concentration of sites active at 80 °C (7.6 μmol/g_{cat}) is represented by the area under the curve with open circles in Fig. 5b. These sites (originally active at 80 °C) constituted only 28% of the total sites active at 110 °C and would appear as the upper tail of the 110 °C distribution since they would have been the most active. The

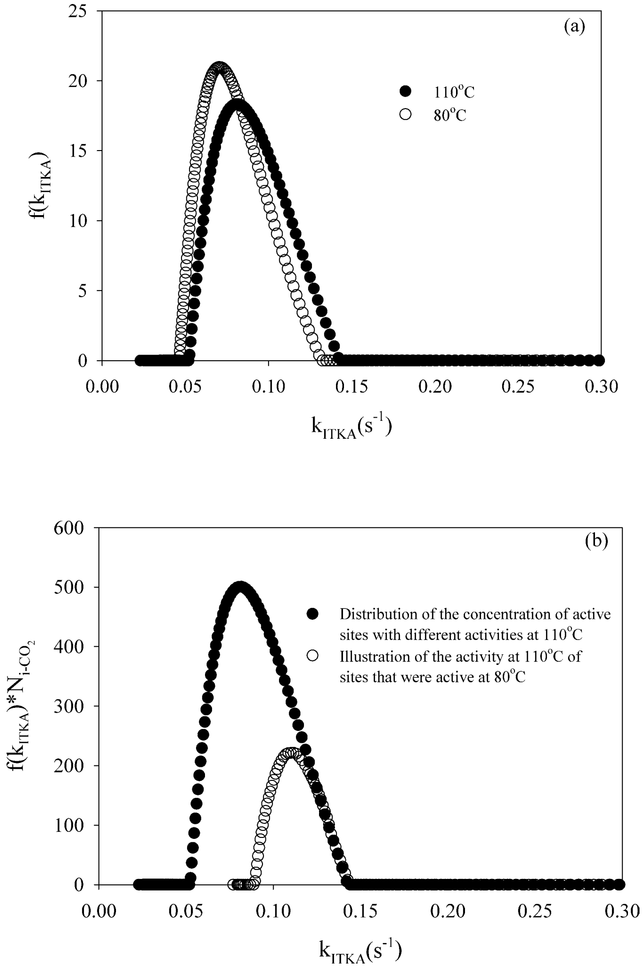

Fig. 5. (a) Steady-state reactivity distribution at 80 and 110 °C. (b) Illustration of the activities at 110 °C of sites that were active at 80 °C.

Table 3
Oxygen partial pressure dependency of rate, k_{ITKA}, and the surface concentration of intermediates [1]

P_{O_2} (kPa)	CO oxidation rate[a] (μmol/(g_{cat} s))	k_{ITKA}[b] (s^{-1})	$N_{i\text{-}CO_2}$ (μmol/g_{cat})
0.9	0.30	0.106	2.8
1.8	0.89	0.106	8.8
3.6	1.30	0.098	13.3

[a] Rate and CO_2 selectivity at 90 °C; 45% H_2, 1% O_2, 1% CO by vol with balance He. Max error was measured to be ±7 and ±10%, respectively.

[b] $k_{\mathrm{ITKA}} = 1/\tau_{i\text{-}CO_2}$, pseudo-first-order rate constant determined by ITKA. Max error was measured to be ±5%.

new sites active at 110 °C would have had activities that were less than those of sites active at 80 °C. However, the average value of k_{ITKA} for all active sites (new sites that had lower activities and low temperature active sites with higher activity) would appear to have a value similar to that at 80 °C.

3.2. *Effect of total pressure*

The effects of total pressure on CO oxidation rate, %CO_2 selectivity, and surface kinetic parameters are summarized in Table 2. The CO oxidation rate and $N_{i\text{-}CO_2}$ at steady state increased with total pressure whereas k_{ITKA} was essentially constant. The increase in $N_{i\text{-}CO_2}$ with pressure is suggested to be due to the increase in oxygen partial pressure, consistent with the results of our previous study [1] as shown in Table 3. The power-law rate expression for Pt/γ-Al_2O_3 was found to be Rate $= k_r P_{O_2}$. Increasing the oxygen partial pressure increases the driving force for oxygen adsorption. Since the CO surface coverage was very high (∼ 96%) under these reaction conditions, the surface reaction was limited by the amount of adsorbed oxygen. Increasing the total pressure and consequently the oxygen partial pressure would appear to have increased the amount of oxygen adsorption as illustrated in Fig. 4. This resulted in an increase in the concentration of intermediates and consequently the rate of reaction. Total concentration of surface CO was relatively constant as total pressure increased.

4. Summary

The results of this investigation showed that under this reaction condition, increasing reaction temperature and total pressure had similar effects on the overall activity and surface kinetic parameters of the Pt catalyst for the selective oxidation of CO. The effects of temperature and total pressure can be summarized as follows:

– Increasing temperature from 80 to 110 °C or total pressure from 1.2 to 3 atm increased the rate of reaction significantly, but had only a slight effect on the selectivity.

– As shown by ITKA, reaction temperature or total pressure affects the surface concentration of CO_2 intermediates, but not average site activity (average pseudo-first-order rate constant).

– Since $N_{i\text{-}CO_2}$ seemed to be limited by the amount of adsorbed oxygen at low temperatures (80–110 °C), the increase in $N_{i\text{-}CO_2}$ while total concentration of surface CO remained essentially constant suggests that increasing temperature or total pressure plays a significant role in activating nonactive or less active sites by increasing the probability of oxygen adsorption.

We conclude that, for the selective oxidation of CO on Pt/γ-Al_2O_3 at relatively low temperatures, one can increase the rate of CO oxidation without significantly affecting selectivity by changing the operating conditions (total pressure, temperature) and thus the surface concentration of intermediates. Since the reaction appears to be limited by the amount of adsorbed oxygen, increasing oxygen adsorption by either increasing temperature or total pressure increases the overall rate of reaction. Loss of hydrogen (nonselective oxidation) and the amount of oxygen consumed can be minimized by using higher operating pressures instead of an increased O_2/CO ratio to get higher CO conversion.

Acknowledgments

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