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Investigation of the initial rapid deactivation of platinum catalysts during the selective oxidation of carbon monoxide

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Abstract

This paper reports on a study using isotopic transient kinetics analysis (ITKA) to understand the initial rapid deactivation behavior of a 5 wt% Pt/γ-Al_2O_3 catalyst during selective CO oxidation in hydrogen. The Pt catalyst exhibited the rapid deactivation typically seen for such catalysts during the initial reaction period. Based on ITKA results, the pseudo-first-order intrinsic rate constant was found to be relatively constant with time on stream while the concentration of surface intermediates leading to CO_2 decreased significantly. It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of surface intermediates as a result of carbon deposition, not a change in the intrinsic site activity.

Keywords: Selective oxidation of CO; CO oxidation; Pt catalyst; Deactivation; Pt/Al_2O_3; Isotopic tracing; Surface coverage by intermediates

1. Introduction

Hydrogen used in fuel cells can be extracted from a variety of hydrocarbons. However, small amounts of carbon monoxide are also produced from steam reforming and/or partial oxidation of these hydrocarbons. To avoid poisoning the fuel cell electrode, it is necessary to reduce the CO level from approximately 1% to less than 10 ppm. Therefore, selective oxidation of CO in the presence of hydrogen must be included in the fuel generation process.

The selective oxidation of CO in the presence of hydrogen was first studied using a Pt/alumina catalyst in 1963 [1]. Recent studies were focused on the way to improve the activity and selectivity of the catalyst, for example, the effect of the support [2], the optimum operating temperature [3], the effect of a promoter oxide [4], and the effect of impurity [5]. Other metal-based catalysts have also been found to be active for selective CO oxidation, including Ru [6], Rh [6], and Au [7–10].

Most of the previous studies of the selective oxidation of CO have been conducted under steady-state conditions. However, although Nibbelke et al. [11] commented in their paper that Pt/γ-Al_2O_3 exhibited a higher initial activity during startup compared to the activity measured after a few hours on stream, studies of initial catalyst deactivation have not been reported. This initial rapid deactivation can result in a loss of 90% of the initial activity of a Pt catalyst before steady state is reached.

The present work focused on the significant initial loss in activity of Pt during selective CO oxidation. In order to obtain surface kinetic information about CO oxidation, isotopic-transient kinetic analysis (ITKA) was used in this study. Since it allows in situ measurement of the concentration of surface intermediates and their intrinsic reactivities while the reaction is maintained at stable reaction conditions, SSITKA (steady-state isotopic-transient kinetic analysis) or ITKA (when not at steady state) is one of the most powerful techniques for the kinetic study of heterogeneous catalysis. Extensive details about the use of (SS)ITKA are given in Refs. [12,13]. A conventional selective CO oxidation catalyst, 5% Pt/Al_2O_3, was employed, and the effect of time on stream on CO oxidation rate, selectivity, concentration of surface intermediates, and catalyst intrinsic activity was investigated. Since this catalyst possesses very high activity and selectivity during initial reaction, a better understanding of the deactivation phenomena could lead to strategies to prevent or slow down deactivation, resulting in a better catalyst design.

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2. Experimental

2.1. Catalyst preparation

A catalyst consisting of 5 wt% Pt on γ-Al_2O_3 powder was prepared by incipient wetness impregnation. The support (Al_2O_3, Vista B) was first calcined at 500 °C for 10 h before being impregnated at room temperature with an aqueous solution of chloroplatinic acid hexahydrate. The catalyst was then dried overnight at 110 °C and calcined at 500 °C for 2 h under flowing dry air.

2.2. Catalyst characterization

Measurement was performed to determine the total BET surface area of catalyst sample after calcination. Prior to the BET measurement, the catalyst sample was degassed at 300 °C for 3 h. The sample was then analyzed using N_2 adsorption at 77 K in a Micromeritics ASAP 2010.

Static hydrogen and carbon monoxide chemisorption at 35 °C on the reduced platinum catalyst were used to determine the concentration of reduced surface platinum atoms. This measurement was performed in a Micromeritics ASAP 2010 using ASAP 2010C V 3.00 software. Prior to H_2 or CO chemisorption, the calcined catalyst was evacuated to 10^{-6} mm Hg at 100 °C for 15 min and then reduced in flowing hydrogen at 550 °C for 1 h after ramping up the temperature at 10 °C/min. The catalyst was evacuated to 10^{-6} mm Hg at 550 °C for 30 min to desorb any hydrogen before the temperature was lowered to 35 °C and evacuated for 30 min. After measuring the total H_2 (or CO) adsorption isotherm, the sample was evacuated to 10^{-6} mm Hg and then the adsorption procedure was repeated to determine the reversible isotherm. The concentration of exposed metal atoms on the surface was calculated by extrapolating the total and reversible adsorption isotherms to zero pressure, determining the amount of irreversible H_2 (or CO) chemisorbed from the difference, and assuming a coverage of one H atom (or CO molecule) (irreversibly adsorbed) per Pt atom exposed on the surface.

2.3. Reaction system

The system consisted of a differential flow reactor connected to a gas chromatograph and mass spectrometer, as shown elsewhere [12,14]. The catalyst was placed in a 0.3 in. (7.6 mm) i.d. stainless-steel reactor. The pressure in the reactor was kept constant at 1.8 atm (182 kPa) using a back pressure regulator. A thermocouple was placed at the bottom of the catalyst bed. A Valco two-position valve with an electric actuator was used to switch between the labeled CO (^{12}CO vs ^{13}CO). The reactor outlet was connected to a gas chromatograph (Varian CP-3380) and a quadrupole mass spectrometer (Pfeiffer Vacuum). A part of the reaction effluent was introduced into the mass spectrometer via a 1/16-inch capillary tube and differential pumping. A 6-port sampling valve was placed between the reactor outlet and the GC. In the GC, the products were separated by a 6-ft long 80/100 mesh carbosphere column (Alltech). Hydrogen, carbon monoxide, and oxygen were first separated at 35 °C and then the GC was ramped to 150 °C at 20 °C/min to determine the concentration of CO_2.

2.4. Reaction measurements

The catalytic activity of the catalyst for the selective oxidation of CO in the presence of hydrogen was determined at 90 °C and 1.8 atm. Prior to CO oxidation, approximately 50 mg of catalyst was diluted with α-alumina and 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. A gas space velocity of $\sim 190{,}000\ h^{-1}$ was used. The CO conversion and selectivity were determined periodically until the reaction reached steady state and calculated using the method described by Manasilp and Gulari [5].

2.5. Isotopic-transient kinetic analysis

Isotopic transients were taken by switching between isotopically labeled CO (^{12}CO vs ^{13}CO). A trace of argon was present in the ^{12}CO stream to measure the gas-phase holdup in the reaction system. The kinetic parameters, such as average surface residence time and concentration of surface intermediates, were calculated using the method described by Shannon and Goodwin [12]. By integrating the normalized step-decay or step-input responses, the overall mean surface residence time of all adsorbed surface intermediates could be determined. The decrease in the transient response of the old 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.

3. Results and discussion

3.1. Catalyst characterization

The BET surface area of the 5 wt% Pt/γ-Al_2O_3 after calcination was 230 m^2/g.

The amounts of H_2 and CO irreversibly chemisorbed on Pt atoms extrapolated to zero pressure were found to be 116 µmol of H atom/g_{cat} and 127 µmol of CO/g_{cat}, respectively. The metal dispersion of reduced platinum catalyst determined from the amount of H_2 chemisorption was 45.4%, corresponding to an average Pt particle size of 2.4 nm. This latter quantity was calculated based on the correlation be-

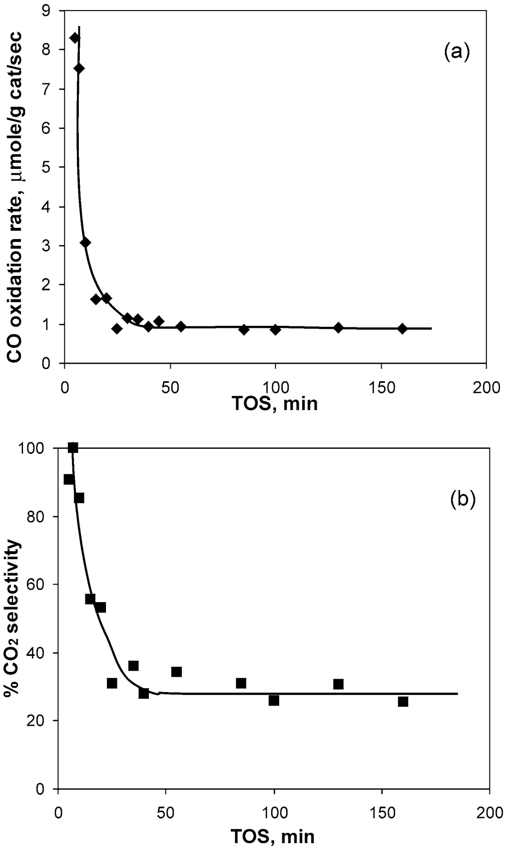

Fig. 1. Time-on-stream behavior for (a) the CO oxidation rate and (b) CO_2 selectivity at $P_{O_2} = 1.8$ kPa.

tween percentage dispersion and metal particle size as described by Anderson [15].

3.2. Catalytic oxidation of carbon monoxide in the presence of hydrogen

Time-on-stream (TOS) behavior of CO oxidation rate and CO_2 selectivity are shown in Figs. 1a and 1b, respectively. Both CO oxidation rate and CO_2 selectivity decreased rapidly with TOS. The results illustrate the rapid deactivation of Pt catalysts typically seen during the initial reaction period.

Isotopic transient kinetic analysis was used to decouple the CO oxidation rate of this Pt catalyst into the contributions from site activity and concentration of surface intermediates. The average surface residence times and concentrations of CO_2 intermediates and reversibly adsorbed CO were calculated using (SS)ITKA software. The switching was conducted at 5 min TOS and periodically afterward until steady-state reaction was reached.

The effect of oxygen partial pressure on the reaction rate and concentration of surface intermediates is shown in Fig. 2. The oxygen partial pressure was varied from 0.9 to 3.6 kPa while keeping the carbon monoxide partial pressure constant at 1.8 kPa. The reaction rate, as well as the concentration of surface CO_2 intermediates, at all partial pressures decreased rapidly with time on stream. Using a pseudo-first-order deactivation constant, k_d, to characterize the deactivation of this Pt catalyst, initial k_d's were determined to be 0.131, 0.11, and 0.057 min^{-1} for oxygen partial pressures of 0.9, 1.8, and 3.6 kPa, respectively. Based on these results, it would appear that increasing the oxygen partial pressure slightly decreased the rate of deactivation of the catalyst.

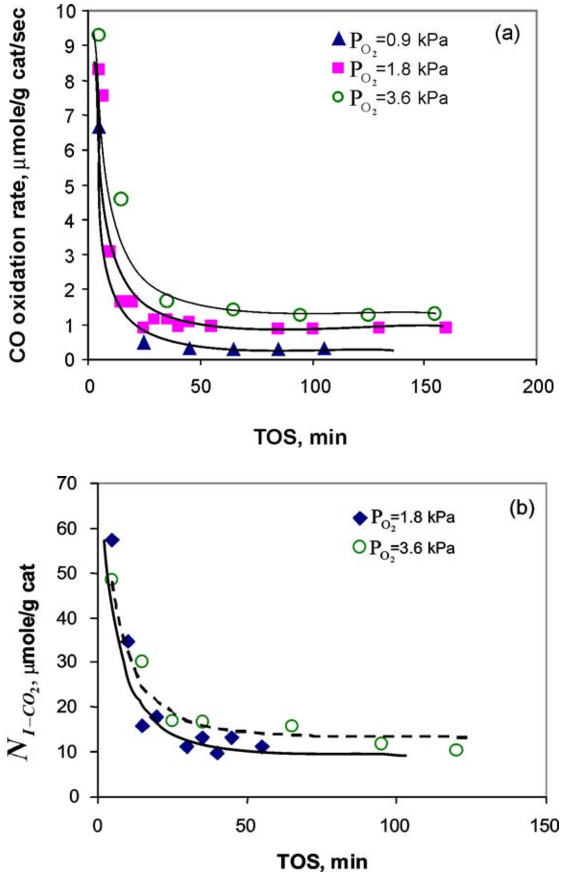

Fig. 2. Time-on-stream behavior for (a) the CO oxidation rate at different oxygen partial pressures and (b) the concentration of CO_2 surface intermediates, N_{I-CO_2}, at oxygen partial pressures of 1.8 and 3.6 kPa.

A Langmuir–Hinshelwood single-type site mechanism is widely accepted to explain CO oxidation on Pt [3,11,16]. Adsorbed CO is assumed to react with adsorbed O on an adjacent Pt site. At low reaction temperatures, the noble metal surface is believed to be predominantly covered with adsorbed CO [3,11] and the irreversible molecular adsorption of oxygen is suggested to be the rate-determining step. Many studies have been conducted in order to determine the reaction order at particular temperatures or in temperature ranges, as reported by Kahlich et al. [3]. Since the reaction orders are dependent on the reaction temperature and, perhaps, the partial pressures of reactants [3], we conducted additional experiments to determine the reaction orders for our reaction conditions.

The approach we used to determine the reaction orders has been described by Kahlich et al. [3]. The process parameter, λ, is defined as two times the ratio of partial pressures of oxygen and carbon monoxide. The partial pressures of oxygen and carbon monoxide were varied between 0.9 and 3.6 kPa. At $\lambda = 2$ and steady-state operation, the reaction orders for the power-law form of the rate expression were found to be $+1$ and 0 for oxygen and carbon monoxide, respectively. Our results (at 90 °C) when compared to the previous work (from 100 to > 230 °C) [3] indicate that the reaction order with respect to the partial pressure of oxygen is relatively constant ($\sim +1$) with reaction temperature. On the other hand, the reaction order for carbon monoxide increases when the reaction temperature decreases.

Since the rate of reaction $R_{CO_2} = 1/\tau_{I-CO_2} * N_{I-CO_2}$, the reciprocal of the surface residence time of CO_2 intermediates ($1/\tau_{I-CO_2}$) with units of s^{-1} is equivalent to a pseudo-first-order intrinsic rate constant, k, and represents the intrinsic activity of the catalyst (a type of turnover frequency, TOF). In this study, the pseudo-first-order intrinsic rate constant, k was only weakly dependent on the oxygen partial pressure as shown in Fig. 3. This implies that only the surface concentration of CO_2 intermediates is strongly dependent on the oxygen partial pressure.

Fig. 4 shows the TOS behavior of the pseudo-first-order intrinsic rate constant, k or $1/\tau_{I-CO_2}$. It is obvious that the average intrinsic activity of the Pt sites did not vary greatly with TOS. With the exception of the first data point, k was relatively constant with TOS. On the other hand, as seen in Fig. 2b, the concentration of CO_2 surface intermediates decreased with TOS in a fashion similar to that for the reaction rate (Fig. 2a). It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of active intermediates for CO oxidation (related to the available active Pt sites), not a change in the intrinsic activity.

The concentration of surface Pt atoms calculated from the hydrogen chemisorption measurement was 116 μmol/g_{cat}. The concentration of surface CO (both reversibly adsorbed, N_{CO}, and CO_2 intermediates, N_{I-CO_2}) determined via ITKA at 5 min TOS of reaction was 88 μmol/g_{cat} (Table 1). Thus, ca. 76% of surface Pt atoms would have been occupied by CO initially. If one assumes that every site was available for reaction at 5 min TOS, this would leave only ca. 28 μmol of sites/g_{cat} available for the adsorption of hydrogen and

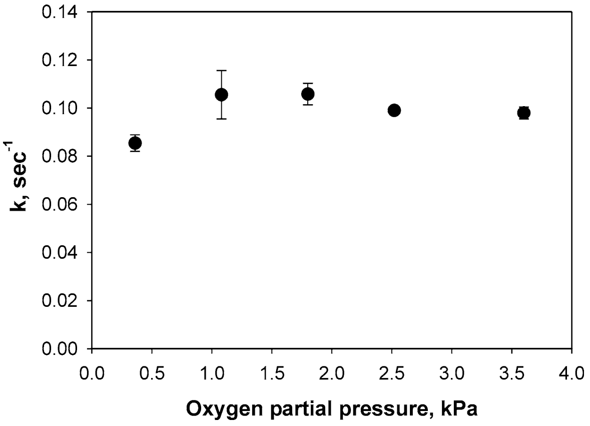

Fig. 3. Oxygen partial pressure dependency of the pseudo-first-order intrinsic rate constant, k.

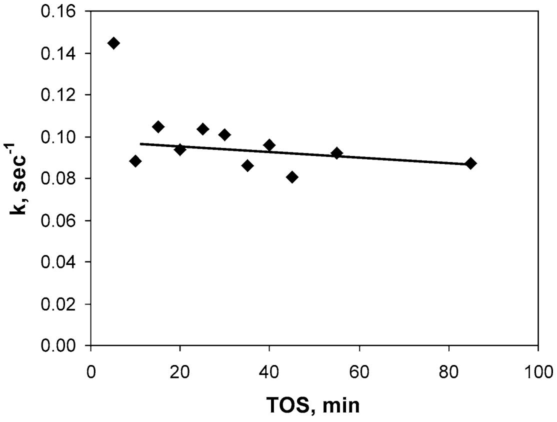

Fig. 4. Time-on-stream behavior of the pseudo-first-order intrinsic rate constant for $P_{O_2} = 1.8$ kPa.

Table 1
Isotopic transient kinetic analysis results

TOS (min)	CO conversion (%)	Rate[a] (μmol/(g_{cat} s))	τ_{I-CO_2}[b] (s)	τ_{CO}[b] (s)	N_{I-CO_2} (μmol/g_{cat})	N_{CO} (μmol/g_{cat})	k[c] (s^{-1})	$N_{[I-CO_2]+CO}$ (μmol/g_{cat})	θ_{I-CO_2}[d]	θ_{CO}[d]	$\theta_{[I-CO_2]+CO}$[d]
5	57.68	8.30	6.9	5.1	57	31	0.145	88	0.49	0.27	0.76
10	21.43	3.08	11.3	5.0	35	56	0.088	91	0.30	0.49	0.79
15	11.44	1.65	9.5	5.4	16	69	0.105	85	0.14	0.59	0.73
20	11.52	1.66	10.7	6.2	18	79	0.094	96	0.15	0.68	0.83
30	7.95	1.14	9.9	6.1	11	80	0.101	92	0.10	0.69	0.79
35	7.90	1.13	11.6	6.8	13	90	0.086	104	0.11	0.78	0.89
40	6.46	0.93	10.4	6.6	10	89	0.096	99	0.08	0.77	0.85
55	6.53	0.94	10.8	6.1	11	82	0.092	93	0.10	0.71	0.81
160	6.19	0.89	11.5	6.7	10	91	0.087	101	0.09	0.78	0.87

[a] Rate, micromoles of CO consumed per gram of catalyst per second at 90 °C; 1.8 atm; 45% H_2, 1% O_2, 1% CO by vol with balance He. Max error measured to be ±10%.

[b] τ_i, surface residence time of species I. Max error measured to be ±5%.

[c] $k = 1/\tau_{CO_2}$, pseudo-first-order intrinsic rate constant. Max error measured to be ±5%.

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

oxygen, suggesting the reason for the early high selectivity for CO_2 formation. Considering the concentration of surface CO_2 intermediates, N_{I-CO_2}, it would appear that the surface coverage by intermediates, calculated by dividing N_{I-CO_2} by the concentration of surface Pt atoms, was 0.49 at 5 min TOS. At steady state, the coverage of potential sites by active CO_2 intermediates decreased to about 9%. This decrease is reflected in the decrease in CO oxidation rate and CO_2 selectivity. Although the surface coverage of CO_2 intermediates decreased about 80% and the surface coverage of reversibly adsorbed CO significantly increased ca. 200%, the total surface CO (reversibly adsorbed CO and CO_2 intermediates) concentration remained relatively constant. This suggests that even though deactivated sites were not active for CO_2 formation, CO was able to reversibly adsorb. The results showed an oscillation in the surface coverage by CO that may have been due to the well-known phenomenon for CO oxidation called auto-oscillation [17–20].

In addition to the deactivation of the Pt catalyst for CO oxidation, a change in selectivity was also observed. While the CO oxidation rate decreased, the H_2 oxidation rate increased from ca. 0.86 $\mu mol/(g_{cat}\,s)$ at 5 min TOS to ca. 2.6 $\mu mol/(g_{cat}\,s)$ at steady state. This suggests that hydrogen is better able to compete for oxygen because of the decrease in activated CO intermediates. The increase in H_2 oxidation rate, however, did not fully compensate for the decrease in the rate of CO oxidation. The decrease in CO_2 selectivity is, thus, the result of a decrease in CO oxidation rate and a concomitant increase in H_2 oxidation rate. The TOF_{chem} based on hydrogen chemisorption calculated ($\approx 0.008\ s^{-1}$) was about 11 times lower than that based on ITKA ($TOF_{ITKA} \approx 0.09\ s^{-1}$) at steady state.

All results reported in this study were reproducible with a measured error as shown in Table 1.

3.3. Characteristics of the catalyst surface at steady state

In order to confirm the cause of deactivation, additional experiments were conducted to try to determine the surface composition of the catalyst after reaction.

The deactivated catalyst was regenerated at different temperatures in a stream of hydrogen for 1 h. As shown in Fig. 5, some initial activity was recovered using regeneration temperatures lower than 300 °C. On the other hand, regeneration at temperatures higher than or equal to 300 °C resulted in a complete recovery of the initial activity.

The catalyst bed was flushed with the reactant stream excluding oxygen for 1 h before adding oxygen and starting CO oxidation reaction. At 5 min TOS (after oxygen was fed), the CO oxidation rate was found to be approximately the same as the rate at steady state (after deactivation) in the normal run. This result suggests that CO is the source of the species that deactivates the catalyst.

A stream of 50% hydrogen in helium was fed through the bed of the partially deactivated catalyst after it had reached steady-state reaction while the temperature in the reactor was raised from the reaction temperature to 550 °C. A mass spectrometer was used to detect the gas outlet composition from the reactor. Approximately 125 μmol of methane/g_{cat} was detected in the temperature range of 230 to 280 °C.

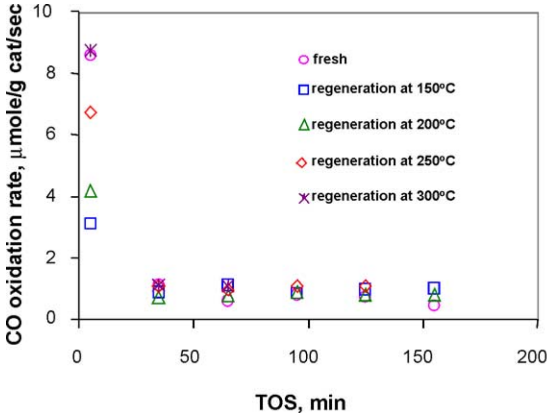

Fig. 5. Time-on-stream behavior of the CO oxidation rate after regeneration at different temperatures.

After reaching steady-state reaction, a sample of the partially deactivated catalyst was removed and sent to Galbraith, Inc., for carbon determination. The amount of carbon determined by the combustion/coulometric titration was 167 $\mu mol/g_{cat}$, 117 $\mu mol/g_{cat}$ more than the reduced catalyst had before reaction, thus confirming the results from the reaction of hydrogen with the partially deactivated catalyst. A 117–125 $\mu mol/g_{cat}$ of carbon is equivalent to a Pt surface coverage of 100%. However, since the catalyst still had significant activity for CO and H_2 oxidation, the Pt surface cannot have been fully blocked.

4. Conclusions

The selective oxidation of CO in the presence of hydrogen using 5% $Pt/\gamma\text{-}Al_2O_3$ exhibited high initial partial deactivation before reaching steady state. The observed rate and CO_2 selectivity were very high during the initial reaction period, but decreased significantly with time on stream. By using isotopic transient kinetic analysis, the pseudo-first-order intrinsic rate constant was found to be relatively constant, whereas the concentration of active intermediates decreased significantly with time on stream. It can be concluded that the deactivation of this Pt catalyst is mainly the result of a decrease in the concentration of surface CO_2 intermediates, not the intrinsic activity. Regeneration of the catalyst in a stream of hydrogen at temperatures higher than or equal to 300 °C was able to completely recover the initial activity and selectivity of the deactivated catalyst. We suggest that the deactivation of Pt is due to carbon deposition on the Pt surface and that this carbon deposition causes a significant decrease in CO_2 selectivity. The decrease in CO_2 selectivity appears to be due to CO adsorption leading to CO_2 intermediates being affected more than H_2 and O_2 adsorption.

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