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Effect of Fe promotion on the surface reaction parameters of Pt/γ-Al_2O_3 for the selective oxidation of CO

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Abstract

Selective oxidation of CO in hydrogen is an important reaction for producing hydrogen from hydrocarbons suitable for use in fuel cells. Pt has been shown to be very active for this reaction. This article reports on the results of an investigation into the impact of Fe promotion on Pt/γ-Al_2O_3 using isotopic transient kinetic analysis (ITKA). In this study, Fe promotion was found to have an impact on activity, selectivity, and also time-on-stream behavior of surface reaction parameters. It increased activity and selectivity, as has been also noted by others. ITKA revealed that the higher activity of PtFe is due mainly to an increase in intrinsic site activity when compared with nonpromoted Pt. Fe promotion did not affect significantly the total concentration of active surface intermediates. In a previous study, Pt/γ-Al_2O_3 was found to exhibit steady activity for selective CO oxidation after an initial rapid partial deactivation. The PtFe catalyst also showed rapid initial partial deactivation similar to Pt. The activities of both catalysts decreased with time-on-stream about the same degree in reaching a pseudo-steady state. Unlike for Pt where initial partial deactivation was due primarily to a decrease in active intermediates, the initial rapid partial deactivation for PtFe was the result of both a decrease in the concentration of surface intermediates and a decrease in the average intrinsic site activity, but was due mainly to the decrease in the intrinsic site activity. The intrinsic site activity of PtFe approached that of Pt with time-on-stream. It would appear that carbon deposition causes the initial partial deactivation on Pt and may partially do so on PtFe. However, evidence suggests that reoxidation of Fe is likely a significant cause of the loss of activity of PtFe. As partial deactivation proceeds, the effect of Fe promotion of the Pt sites decreases.

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1. Introduction

Poisoning by CO impurities of the electrode in a proton exchange membrane fuel cell is a potential problem in using hydrogen derived from hydrocarbons by reforming or partial oxidation. To reduce the amount of CO in the hydrogen stream to a tolerable level ($<$ 10 ppm) without sacrificing too much hydrogen, a suitable catalyst must be used downstream of hydrogen generation to convert the CO to CO_2. Pt/alumina has been found to be suitable for this purpose [1,2]. Unfortunately, rapid partial deactivation during the initial reaction period at desired low reaction temperatures makes the catalyst much less active and selective than it could be. Our previous work [3] showed that the adsorption of CO is more favorable on the Pt surface than either oxygen or hydrogen. We suggested that the imbalance between the amounts of CO and O_2 adsorbed on the catalyst surface under typical reaction conditions might be the main reason for carbon deposition, the apparent cause of the initial deactivation to steady-state reaction. Carbon removal by reaction with either oxygen or hydrogen in the reactant stream is not sufficient at desirable low reaction temperature ca. 90 °C to prevent carbon buildup on the initial catalyst surface.

There have been several investigations of the effects of promoters (Fe oxide, ceria) on the activity and selectivity of Pt/alumina [4–6]. Korotkikh and Farrauto [4] studied the effect of Fe oxide promotion on Pt/alumina powdered catalysts and monolith catalysts. They found that with Fe oxide promotion, CO conversion increased significantly but the selectivities remained relatively constant. In a following paper, Fe-promoted Pt/alumina catalyst was studied in detail [5]. A noncompetitive dual-site mechanism for the

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selective oxidation of CO was proposed. The promoted Pt catalyst was suggested to be more active due to Fe oxide providing adsorption sites for oxygen and Pt providing adsorption sites for carbon monoxide. The effect of ceria on a Pt/γ-Al_2O_3 catalyst was studied by Son and Lane [6]. The ceria-promoted catalyst gave higher conversion and selectivity than Pt alone at low temperature ($\sim 100\,^\circ C$). A smaller effect was obtained when the O_2-to-CO ratio was increased.

In this study, the effects of Fe promotion of Pt/alumina on the surface reaction parameters during the selective oxidation of CO were investigated using isotopic transient kinetic analysis (ITKA). From the reaction and ITKA results, the effect of Fe promotion on the apparent activity, the intrinsic “site” activity, and the concentration of active intermediates was able to be determined. The evolution of the site activity distribution with time-on-stream was also determined.

2. Experimental

2.1. Catalyst preparation

A catalyst consisting of 5 wt% Pt on γ-Al_2O_3 powder was prepared according to the procedure described in the previous study [3]. The catalyst was calcined at 500 °C for 2 h in flowing hydrocarbon-free dry air. This catalyst is referred to as the “Pt” catalyst through the paper.

To prepare 0.5 wt% Fe + 5 wt% Pt on γ-Al_2O_3 powder, a portion of the 5 wt% Pt on γ-Al_2O_3 powder after calcination was impregnated with an $Fe(NO_3)_3 \cdot 9H_2O$ solution. The catalyst was then recalcined at 300 °C for 2 h. This catalyst is referred to as “PtFe.”

A 0.5 wt% Fe on γ-Al_2O_3 catalyst was also prepared for comparison purposes. Calcined γ-Al_2O_3 was impregnated to incipient wetness with an $Fe(NO_3)_3 \cdot 9H_2O$ solution, dried, and then calcined at 300 °C for 2 h. This catalyst is referred to as “Fe.”

2.2. Catalyst characterization

BET surface area measurement and static H_2 and CO chemisorption were performed according to the procedures provided in our previous work [3]. Even though the amount of Fe by weight seems to be small compared with the amount of Pt, it is significant in terms of atomic percent. Therefore, we report percentage dispersion calculated both with and without considering Fe.

2.3. Temperature-programmed reduction

The reducibilities of the calcined Pt, PtFe, and Fe catalysts were measured by temperature-programmed reduction (TPR) using an Altamira AMI-1 system. TPR used a temperature ramp of 5 °C/min from 40 to 700 °C in a flow of 5% H_2 in Ar. H_2 consumption was measured by analyzing the effluent gas with a thermal conductivity detector. The detector output was calibrated by reduction of Ag_2O powder.

2.4. Temperature-programmed desorption

For the temperature-programmed desorption (TPD) studies, approximately 50 mg of a calcined catalyst sample was reduced in a stream of hydrogen for 1 h at 550 °C. The catalyst was then cooled down to 300 °C where it was purged with He and further cooled down to room temperature. To measure how CO and H_2 competitively adsorb in the presence of the other, a gas mixture of 1% CO and 45% H_2 in He was used in this study. The catalyst sample was saturated with this gas mixture at room temperature for 40 min and then purged with He at the same temperature for 30 min before heating up to 700 °C at 10 °C/min ramp rate. The amounts and species of effluent gases were detected using a Pfeiffer Vacuum Prisma mass spectrometer.

2.5. Reaction system

The design of ITKA reaction systems, such as used in this study, has been shown elsewhere [7,8]. Details of the particular system used for this reaction was described in our previous study [3]. The product stream was analyzed using an on-line Varian (CP-3380) with a carbosphere column. Hydrogen, carbon monoxide, and oxygen were first separated at 50 °C, and then after 5 min the gas chromatograph was ramped to 150 °C at 15 °C/min to determine the concentration of CO_2.

2.6. 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 Pt or 25 mg of PtFe catalyst was diluted with α-alumina and reduced in situ 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, 1% O_2, 1% CO, and 53% He. Total gas space velocities of $\sim 190{,}000\ h^{-1}$ (100 cc/min) and $760{,}000\ h^{-1}$ (200 cc/min) were used for Pt and PtFe catalysts, respectively, to produce differential conversions at steady state. The CO conversion and selectivity were determined periodically until the reaction reached steady state and were calculated using the method described by Manasilp and Gulari [2]. CO_2 selectivity (%CO_2) basically represents the percentage of O_2 consumed that reacts with CO.

2.7. Isotopic transient kinetic analysis (ITKA)

Isotopic transients were measured after switching between isotopically labeled CO (^{12}CO vs ^{13}CO). A trace of argon was present in the ^{12}CO stream to determine the gas-phase holdup in the reaction system. The transient responses of the old isotopically labeled and the new labeled CO_2 and CO exiting the reactor were monitored with a

Table 1
Characterization results for the Pt and PtFe catalysts

Catalyst	BET surface area (m^2/g_{cat})	H_{irr} (μmol H atoms/g_{cat})	CO_{irr} (μmol CO/g_{cat})	Dispersion (%)
5% Pt/Al	230	116	127	45.4[a]
5%Pt/0.5%Fe/Al	233	83	77	32.3[a] (24.2[b])

[a] Calculated from the amount of irreversibly adsorbed hydrogen assuming $H_{irr}/Pt_s = 1$.

[b] Calculated considering both Pt and Fe and assuming $H_{irr}/Pt_s = 1$ and $H_{irr}/Fe_s = 1$.

mass spectrometer (Pfeiffer Vacuum Prisma) equipped with a high-speed data acquisition system interfaced to a personal computer using Balzers Quadstar 422 Version 6.0 software. The surface kinetic parameters (average surface residence time and concentration of surface intermediates) were calculated using the method described by Shannon and Goodwin [7]. By integrating the normalized decay response to the step change in isotopic concentration relative to the measured gas-phase holdup, the mean surface residence time of all carbon-containing adsorbed CO_2 surface intermediates ($\tau_{I\text{-}CO_2}$) was able to be determined. The concentration of surface intermediates was determined from $\tau_{I\text{-}CO_2} R_{CO_2}$, where R_{CO_2} is the rate of CO_2 formation. The distributions of the pseudo-first-order rate constant ($k = 1/\tau_{I\text{-}CO_2}$) were calculated from the isotopic transients for CO_2 using the method described by Hoost and Goodwin [9]. This method is based on a constrained, standard Tikhonov regularization of Fredholm integral equations of the first kind. It reveals the distribution of activity, k, for the reaction sites. This distribution is represented by $F(k)$.

3. Results

3.1. Catalyst characterization

As shown in Table 1, Fe addition did not change the BET surface area of the catalysts. It was approximately 230 m^2/g_{cat} for both Pt and PtFe catalysts.

The amounts of hydrogen and carbon monoxide irreversibly chemisorbed on the Pt and PtFe catalysts and the percentage metal dispersions are summarized in Table 1. The average metal particle sizes were ca. 4.5 nm for the PtFe catalyst and 2.4 nm for the Pt catalyst. These quantities were calculated based on the irreversible hydrogen chemisorption and the correlation between percentage dispersion and metal particle size as described by Anderson [10].

It is obvious from Table 1 that the amounts of CO and H_2 chemisorption were lower on the PtFe catalyst than on the Pt catalyst. The amount of irreversible CO chemisorbed on the PtFe catalyst was only 61% that on the Pt catalyst, while the amount of irreversible H_2 chemisorption was ca. 71%.

3.2. Temperature-programmed reduction

Reduction behaviors of alumina-supported Pt, PtFe, and Fe catalysts obtained by TPR experiments are shown in Fig. 1. The Pt catalyst showed only one reduction peak at ~ 218 °C. Two reduction peaks were observed for the PtFe catalyst, as expected. The first peak represents platinum oxide reduction and perhaps some catalytic reduction of iron. The second peak at ~ 290 °C is the catalytic reduction of iron oxide. By comparison of these results with the results for an Fe/γ-Al_2O_3 catalyst that exhibited two reduction peaks at 377 and 464 °C, it is obvious that Pt decreases the reduction temperature required for iron oxide as a result of hydrogen spillover. While Jia et al. [11] reported some higher-temperature peaks for Pt/γ-Al_2O_3, the present results are consistent with most previous works on Pt [12–14]. Based on calibration of the TCD using silver oxide reduction, the amount of hydrogen consumed indicated 100% reducibility of the Pt catalyst with negligible reduction at temperatures lower than 40 °C.

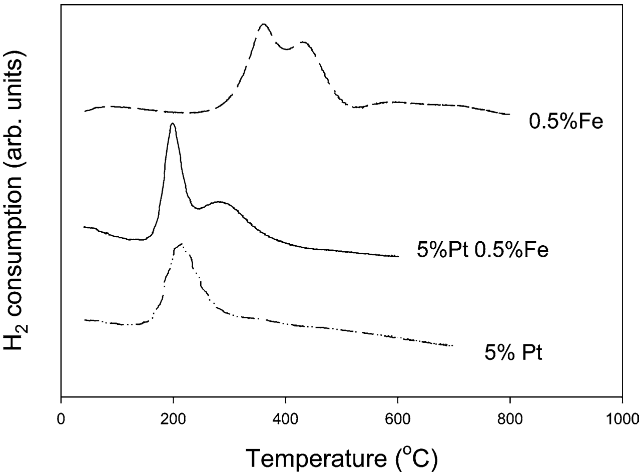

Fig. 1. Temperature-programmed reduction profiles of Pt, PtFe, and Fe catalysts.

3.3. Temperature-programmed desorption

Fig. 2 shows the TPD profiles of H_2, CH_4, CO, and CO_2 for desorption of the adsorbed gas mixture (1% CO, 45% H_2 in He), where CO_2 would have been formed by the Boudouard reaction from CO. Both Pt and PtFe had similar desorption behavior except for methane, where the peak was shifted slightly. Surprisingly, no peak for the desorption of CO was observed for any of the catalysts, but there was a peak for CO_2 desorption at ca. 320 °C for Pt and PtFe and at ca. 180 °C for Fe, indicating the higher activity of Fe for the well-known Boudouard reaction. There was a broad

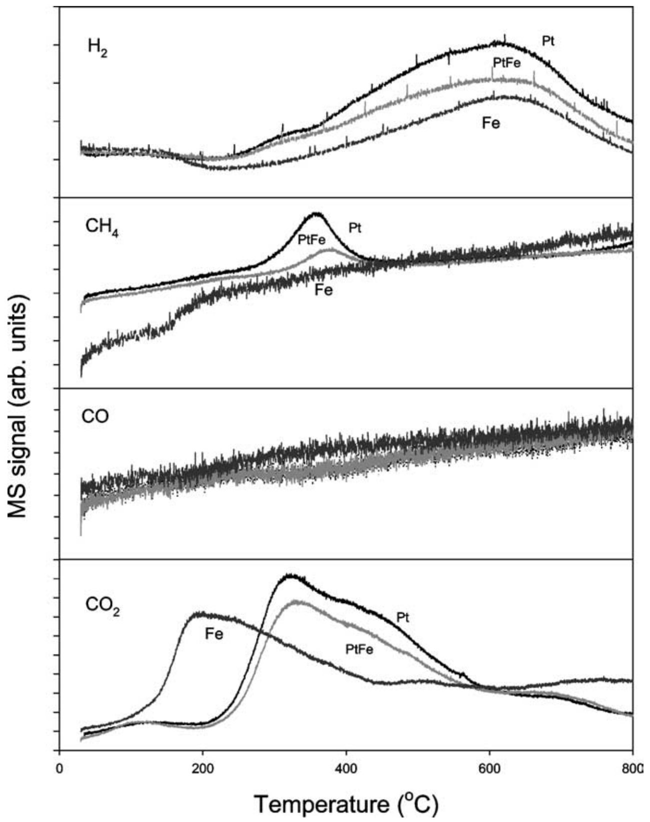

Fig. 2. Temperature-programmed desorption of gas mixture (1% CO, 45% H_2 in He) on Pt, PtFe, and Fe catalysts.

peak for H_2 desorption starting at 220 °C with a peak around 600 °C that was essentially identical for Pt, PtFe, and Fe. No low-temperature peak for H_2 desorption was observed as has been reported by Miller et al. [15] for TPD of pure hydrogen adsorbed on Pt/γ-Al_2O_3. As the H_2 peak was very broad starting at 220 °C, it is possible that some desorption occurred at lower temperature and contributed to the background.

3.4. Activity measurement

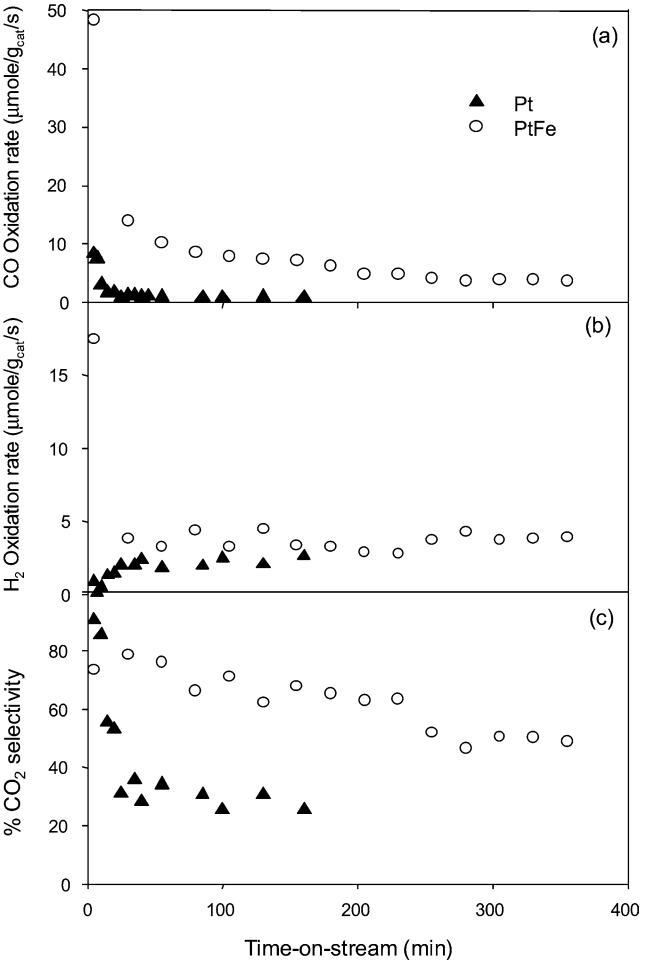

Fig. 3. (a) CO oxidation rate. (b) H_2 oxidation rate. (c) CO_2 selectivity of the Pt and PtFe catalysts (moles of O_2 reacted with CO/total moles of O_2 consumed).

The PtFe catalyst was tested for its activity and selectivity and compared with the nonpromoted Pt catalyst. The space velocity used was four times that used for the nonpromoted catalyst to have differential conversion at steady state. Assuming that oxygen is consumed by either CO or H_2 oxidation, the rate of H_2 oxidation can be calculated. Rates of CO and H_2 oxidation and percentage CO_2 selectivities of the PtFe and Pt catalysts with time-on-stream (TOS) are plotted together for comparison purposes in Fig. 3. The CO oxidation rates of both catalysts dropped significantly with TOS. An increase in H_2 oxidation rate was detected for Pt, reflecting the decrease in percentage CO_2 selectivity. Although rate of H_2 oxidation increased with TOS, it was not as significant as the rapid decrease in rate of CO oxidation resulting in a rapid decrease in total oxidation rate. PtFe showed an opposite change in H_2 oxidation rate. Decrease in H_2 oxidation rate from 5 to 30 min TOS along with CO oxidation rate resulted in a slower decrease in percentage CO_2 selectivity. The Fe-promoted catalyst reached a pseudo-steady state after 300 min TOS, whereas the nonpromoted catalyst reached steady state after only 30 min. However, considering the relative change in activity to steady state, both catalysts would appear to have had the same degree (%) of deactivation. The initial CO oxidation rate on PtFe was about 5.7 times higher than that on unpromoted Pt (48.2 vs 8.3 μmol/(g_{cat} s)). At steady state, this ratio was slightly lower (~ 4). The CO_2 selectivity on PtFe was also higher than that on Pt during most of the TOS. At steady state, Pt gave 27% CO_2 selectivity whereas PtFe gave almost 50%. An initial reproducible slight increase in selectivity during 5–10 min TOS was observed for PtFe.

Additional experiments were performed to determine the effect of oxygen and carbon monoxide partial pressure on the reaction rate and selectivity as shown in Table 2. The partial pressures of oxygen and carbon monoxide were varied between 0.9 and 3.6 kPa. The process parameter, λ, is

Table 2
Activity and selectivity of Pt and PtFe at different feed compositions

Catalyst	P_O	P_{CO}	Reaction rate (µmol/(g_{cat} s))		CO_2 selectivity (%)	
	(kPa)	(kPa)	Initial	Steady state	Initial	Steady state
Pt	0.9	1.8	6.6	0.3	52	20
	1.8	1.8	8.3	0.9	91	27
	3.6	1.8	9.3	1.3	61	17
	0.9	0.9	5.1	0.6	39	20
	3.6	3.6	8.6	2.0	42	25
PtFe	0.9	1.8	25.7	4.2	88	64
	1.8	1.8	48.2	4.3	73	50
	3.6	1.8	50.2	4.3	25	40
	0.9	0.9	14.6	4.1	50	56
	3.6	3.6	53.6	5.6	59	60

defined as two times the ratio of partial pressures of oxygen and carbon monoxide. For $\lambda = 2$ ($P_{CO} = P_O$), partial pressure of CO had a positive effect on the CO oxidation rate (both initial and steady state) for both Pt and PtFe. A surprising result is the effect of oxygen partial pressure. It affected the initial reaction rate for both Pt and PtFe; however, with TOS its effect became greater for Pt but less and less for PtFe, being negligible at steady state. Selectivity was also affected by changing the partial pressures of the reactants. For Pt, even though there was no clear direct dependence of the initial selectivity on CO partial pressure, the steady-state selectivity may have increased slightly with P_{CO}. For PtFe, both initial and steady-state selectivity increased with P_{CO}. There was no clear evidence of selectivity dependence on oxygen partial pressure for either Pt or PtFe.

The power law expression for CO oxidation on both catalysts was determined. The approach we used has been described by Kahlich et al. [16]. At $\lambda = 2$ and steady-state operation, the reaction orders for the power law form of the rate expression for Pt were found to be +1 and 0 for O_2 and CO, respectively. The PtFe catalyst had reaction orders of 0 and 0.2 for O_2 and CO, respectively. This change in reaction order for O_2 indicates the impact of Fe promotion on the mechanism or at least the surface adsorption parameters.

To better understand the cause of catalyst deactivation, additional experiments were performed by preexposing the reduced catalyst to a stream of O_2/He (Pt_PreO$_2$ and PtFe_PreO$_2$) or CO/He (Pt_PreCO and PtFe_PreCO) at reaction temperature (90 °C) for 1 h before starting the reaction. Pt_PreH$_2$ and PtFe_PreH$_2$ indicate pretreatment in H_2, the standard reaction. The results are shown in Fig. 4. Initial reaction rate for PtFe after switching from O_2/He to the reactant stream was 44% lower than that for normal reaction, and the reaction rate continued to be lower for the remaining TOS. On the other hand, contacting PtFe with CO/He before reaction had only a slight effect on the reaction rate. In contrast to PtFe, exposure of Pt to O_2/He before reaction did not have any effect on the reaction rate, but exposure to CO/He, on the other hand, decreased the initial reaction rate to the same value as at steady state. The results from this investigation suggest that contacting PtFe with O_2 effectively deactivated it. Preoxidation of Pt has little impact because Pt is quickly reduced under reaction conditions where there is a large excess of H_2. Fe in PtFe, on the other hand, is more difficult to reduce. The low activity of PtFe after preoxidation of the surface suggests that deactivation during reaction may

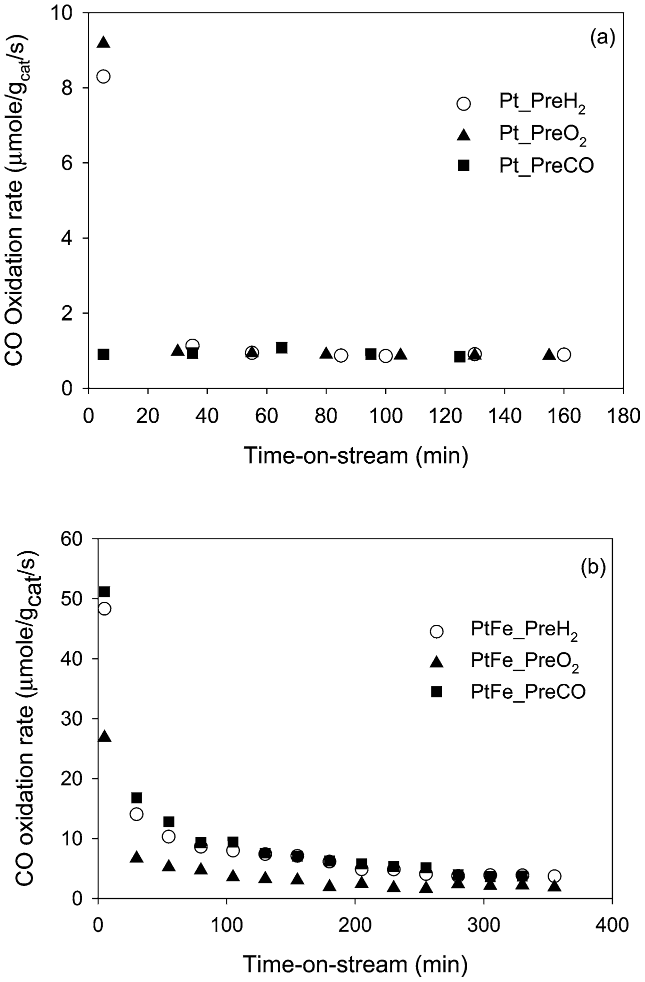

Fig. 4. Effect of preexposure to a stream of O_2/He or CO/He on (a) Pt and (b) PtFe catalysts.

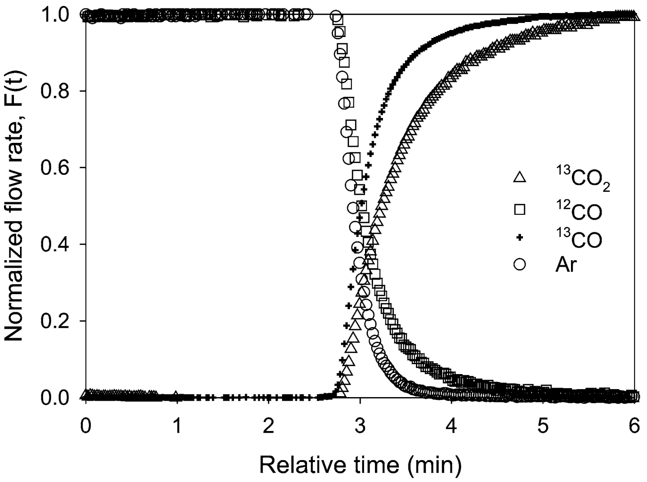

Fig. 5. Typical normalized transient response.

be due, at least in part, to oxidation of the Fe. The results also indicate the combination effect of oxidation and carbon deposition on the deactivation of PtFe. H_2-assisted dissociation of CO on a metal surface has been suggested by Wang et al. [17] and has been shown theoretically by Blyholder and Lawless [18]. The amount of carbon deposition after exposure of the PtFe catalyst to a flow of CO/He for 1 h was 23 $\mu mol/g_{cat}$, compared with 85 $\mu mol/g_{cat}$ after 1 h of reaction in the mixture (H_2, O_2, CO, He) following pretreatment in H_2.

3.5. Isotopic transient kinetic analysis

A typical normalized transient response detected after switching from ^{12}CO to ^{13}CO is given in Fig. 5. Results from the ITKA study (Fig. 6) show decreases for both Pt and PtFe in the pseudo-first-order intrinsic rate constant ($k = 1/\tau_{I\text{-}CO_2}$) and concentration of surface CO_2 intermediates ($N_{I\text{-}CO_2}$) with TOS. As rate $= (1/\tau_{I\text{-}CO_2})N_{I\text{-}CO_2} = kN_{I\text{-}CO_2}$ and $k = \text{rate}/N_{I\text{-}CO_2}$, k (or $1/\tau_{I\text{-}CO_2}$), the pseudo-first-order rate constant with units of reciprocal seconds, represents a measure of site TOF. At the beginning of reaction on Pt, k was 0.15 s^{-1}, decreasing slightly to ~ 0.1 s^{-1} after 10 min TOS and then remaining essentially constant. Fe promotion of Pt resulted in very high initial (5 min TOS) activity ($k \sim 0.7$ s^{-1}) but decreased by ca. 30% by 10 min TOS and continued to gradually decrease after that. The pseudo-steady-state k was 0.2 s^{-1} for PtFe, double that for Pt. The concentrations of surface intermediates also monotonically decreased with TOS for both catalysts. For the Pt catalyst, $N_{I\text{-}CO_2}$ decreased from 57 $\mu mol/g_{cat}$ down to ca. 10 $\mu mol/g_{cat}$; whereas $N_{I\text{-}CO_2}$ for PtFe decreased from 70 $\mu mol/g_{cat}$ at 5 min TOS to ~ 20 $\mu mol/g_{cat}$ at steady state. The maximum values of $N_{I\text{-}CO_2}$ for both catalysts were essentially the same (57–70 $\mu mol/g_{cat}$).

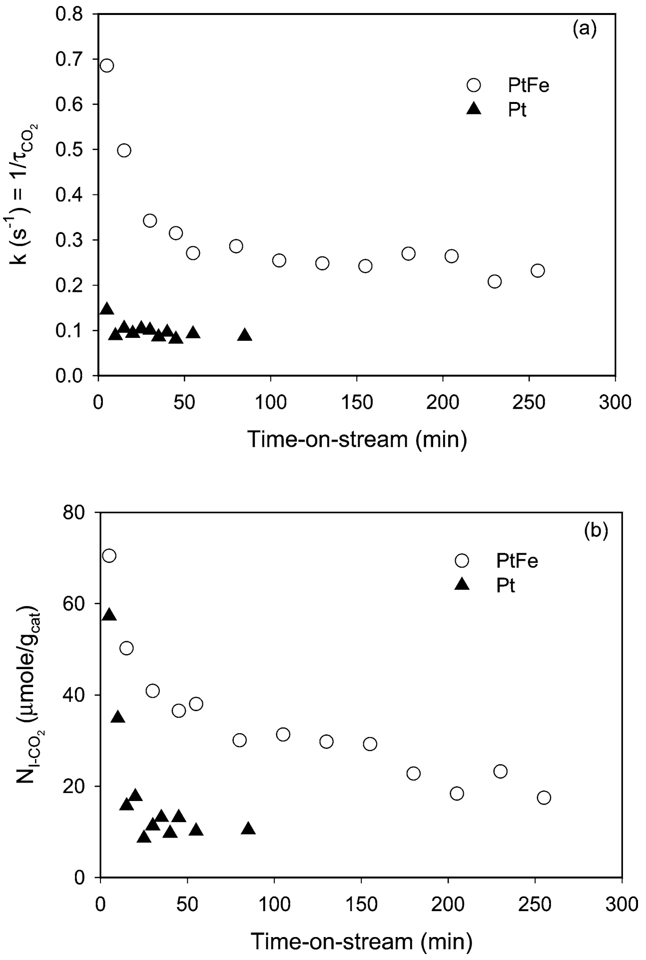

Fig. 6. Time-on-stream behavior of (a) the pseudo-first-order intrinsic rate constant and (b) concentration of surface CO_2 intermediates of Pt and PtFe for $P_{O_2} = 1.8$ kPa.

3.6. Carbon deposited on the catalyst surface during reaction

A stream of 50% hydrogen in helium was fed through the bed of the partially deactivated catalyst after it 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 composition of the effluent from the reactor. The amounts of carbon calculated from the amount of methane formed were found to be 125 and 103 $\mu mol/g_{cat}$ for Pt and PtFe, respectively. It is worth noting that this amount is very small compared with the total flow of CO during 5 min of reaction (4200–17,400 µmol C/g_{cat}); therefore, not accounting for this carbon deposition had little effect on the reported CO oxidation rate. This measurement of deposited carbon has been found to replicate that obtained by elemental analysis for carbon [3]. Fig. 7 shows how the carbon or coke deposition on the Pt and PtFe catalysts changed with TOS. It was found to increase significantly during the first 5 min of reaction, with only a small increase over the following period.

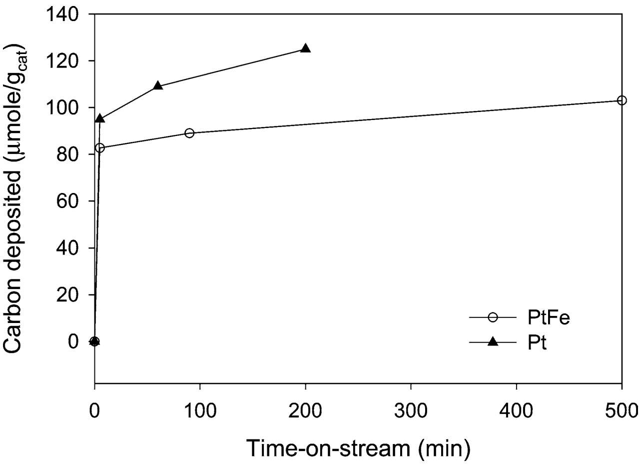

Fig. 7. Amount of carbon deposited on PtFe with time-on-stream.

4. Discussion

4.1. Chemisorption and TPD results

The chemisorption results are in agreement with the DRIFTS results for H_2 and CO adsorption obtained by Liu et al. [5]. The H_2 and CO uptakes decreased on Fe promotion in both cases. Liu et al. concluded that partial blockage of Pt as a result of Fe decoration caused this decrease.

Considering the TPD profiles of Pt, PtFe, and Fe (Fig. 2), all desorption peaks for Pt and PtFe were essentially identical. However, although PtFe showed a desorption pattern similar to that of Fe for H_2, the desorption of CO_2 occurred at a much higher temperature. It is clear from the TPD results that PtFe behaved essentially like the Pt catalyst and seemed to exhibit few characteristics of an Fe surface. Fe may associate strongly with Pt or form an intermetallic compound. Considering the composition of this PtFe catalyst and the phase diagram of PtFe [19], it is likely that the intermetallic compound $FePt_3$ formed at this composition (74 at.% Pt), at least to some degree. Because in the calcined catalyst, Pt and Fe would exist as their separate oxides, Pt can be expected to reduce first, followed by hydrogen-spillover assisted reduction of the Fe. The intermetallic compound should form only on reduction of the two metals. Even though the formation of the intermetallic compound is likely, during deactivation $FePt_3$ may have been destroyed as a result of oxidation of the Fe.

4.2. Effect of Fe promotion on overall activity

It is obvious that the PtFe catalyst had superior activity and selectivity for selective CO oxidation compared with Pt. As has previously been shown [4], PtFe is five to seven times more active than Pt at 90 °C depending on the O_2/CO ratio. However, although Korotkikh and Farrauto [4] found no change in selectivity on Fe promotion of Pt, we found significant improvement. Farrauto and co-workers [4,5] hypothesized that the promoted catalyst is more active for CO oxidation, because iron oxide provides more favorable sites for oxygen adsorption than Pt itself and is located in close contact with surface Pt. Thus, oxygen would have a greater probability for adsorption on PtFe than on Pt. Initial high oxidation rates for CO and H_2 on PtFe compared with that on Pt (Fig. 3), thus, are consistent with such an increase in oxygen activation on Fe addition. This idea also fits the results from ITKA as shown in Fig. 6a. An increase in site turn over frequency (TOF) ($k = 1/\tau$) for PtFe means that reactants spend less time on the PtFe surface to produce CO_2. If molecular adsorption of oxygen is the rate-determining step in CO oxidation as previously suggested [19,20], increasing the number of oxygen adsorption sites and possibly its rate would increase the overall rate of reaction and, perhaps, change the rate-determining step.

With Fe promotion, there is a significant change in reaction order in the power law rate expressions (Pt: 1 and 0, PtFe: 0 and 0.2 for O_2 and CO, respectively). On the Pt catalyst surface, it would appear that oxygen adsorption may be rate controlling as previously suggested. Reaction rate depends on oxygen adsorption because it has to compete with CO for the adsorption sites. For the case of PtFe, on the other hand, oxygen has more preferable adsorption sites on Fe. Consequently, rate has little or no dependence on oxygen partial pressures. We speculate that even at low partial pressures of oxygen and CO (i.e., ca. 0.9 kPa) surface Fe is saturated with oxygen while surface Pt is almost saturated with CO. The power rate law for PtFe depends somewhat (0.2 power) on the partial pressure of CO, suggesting a shift in the rate-determining step.

Even though, as seen in Fig. 6b, PtFe had a higher concentration of surface intermediates during most TOS, the maximum concentration, which shows the largest possible number of active sites, was about the same as that for Pt. Despite the fact that $N_{\text{I-CO}_2}$ of PtFe decreased with TOS at a remarkably slower rate, we can conclude that Fe promotion does not increase the maximum concentration of active sites adsorbing CO for CO_2 formation. It is important to note that $N_{\text{I-CO}_2}$ includes only intermediates containing carbon, as the isotopic tracing is done with $^{12}C/^{13}C$. Thus, these results suggest that Fe does not promote the catalyst by providing more sites for adsorption and reaction of CO.

From a typical normalized transient response as shown in Fig. 5, the distribution of the pseudo-first-order rate constant ($k = 1/\tau_{\text{I-CO}_2}$) can be calculated [9]. The evolution of the distribution of the pseudo-first-order rate constant, representing the site activity of PtFe, with TOS is shown in Fig. 8. $F(k)$ is the activity distribution for the active CO_2 intermediates on the catalyst surface. The area under the curve area integrated from 0 to ∞ ($\int_0^\infty F(k)\,dk$) is equal to 1 in all cases. Fig. 8a shows that the amounts of less active sites relative to more active sites increased as the reaction progressed, causing the mean value for the distribution to shift to a lower value of k. This suggests that deactivation occurred preferentially for the more active sites of PtFe. Note that “active site” does not necessarily mean a single metal

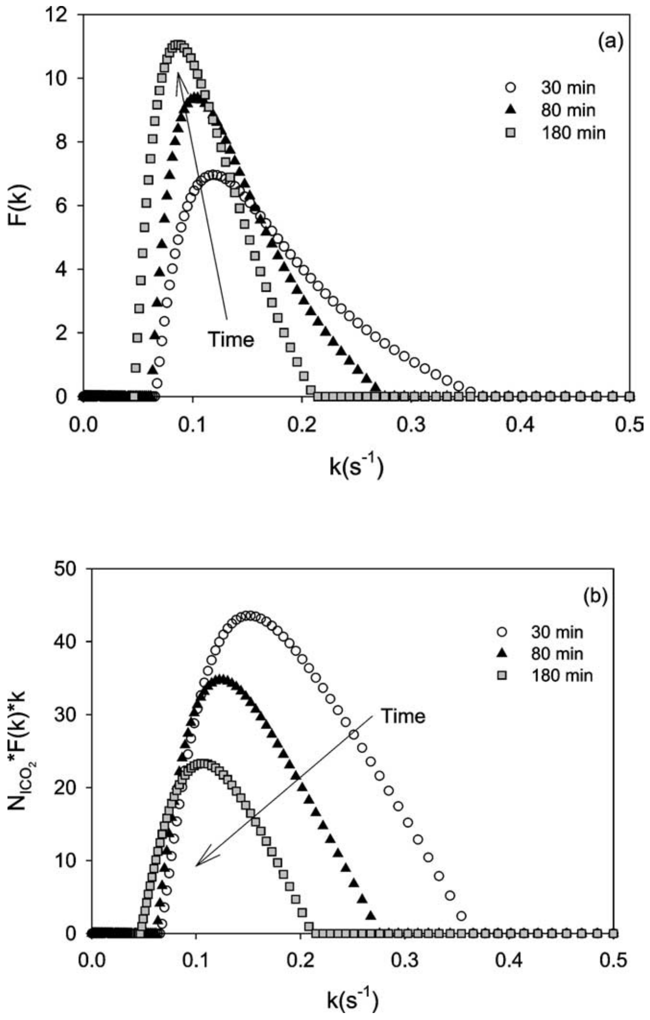

Fig. 8. (a) Rate constant distribution. (b) Shift of total CO_2 intermediates of the PtFe catalyst at different times-on-stream.

atom but may be a Pt–Fe pair. In Fig. 8b the same data were replotted after rescaling to reflect the total number of surface CO_2 intermediates and the activity of each site. The area under a curve from k_1 to k_2 corresponds to the fraction of the rate of reaction catalyzed by the active sites having activities between k_1 and k_2. Total area for a curve corresponds to the reaction rate at that TOS. It is obvious that at 30 min TOS, active sites with activities up to 0.35 s^{-1} contributed to the reaction. As time increased, highly active sites participated less and less in the reaction. Fig. 9 shows the distributions of the pseudo-first-order rate constant for PtFe and for Pt compared at 5 min TOS (Fig. 9a) and at steady state (Fig. 9b). As shown in Fig. 9a, initially there were a significant number of PtFe active sites that were more active than those of Pt. This portion decreased as TOS increased, as seen in Fig. 9b. The average site activity of the PtFe catalyst and the site activity distribution would appear to have asymptotically approached that of the Pt catalyst with TOS.

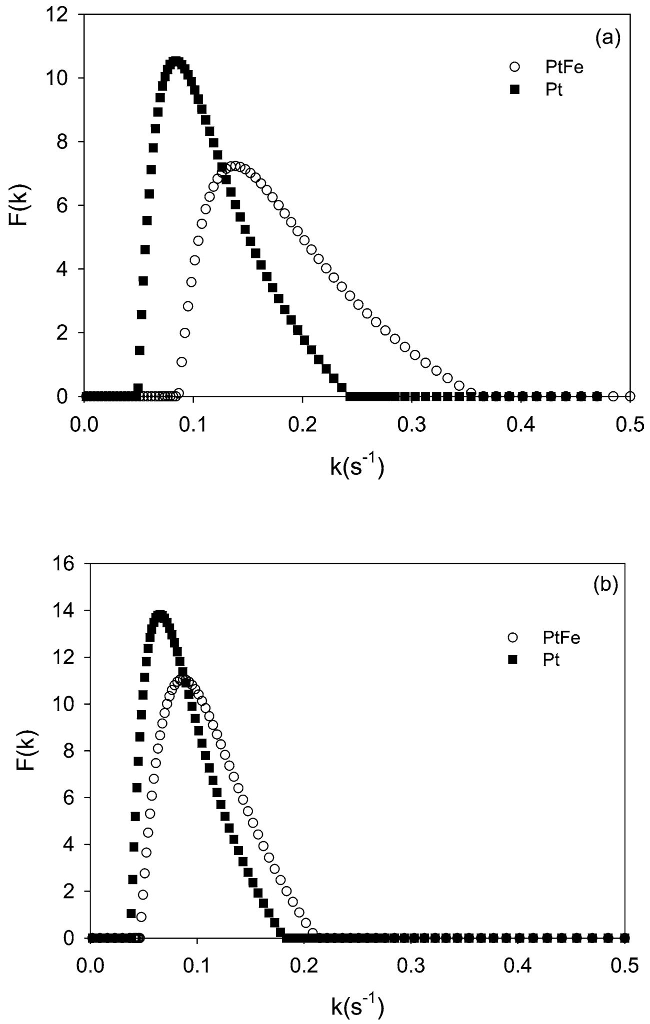

Fig. 9. Rate constant distribution of the Pt and PtFe catalysts at (a) 5 min TOS and (b) steady state.

4.3. Selectivity

The CO_2 selectivity with TOS on both Pt and PtFe followed the same trend as $N_{\text{I-CO}_2}$ except for the first PtFe data point at 5 min TOS. For Pt, it monotonically decreased, whereas for PtFe it monotonically decreased after a small initial increase with TOS. For Pt, the large decrease in CO oxidation rate and the smaller increase in H_2 oxidation rate (Fig. 3) with TOS resulted in a rapid decrease in percentage CO_2 selectivity. These results suggest a change in adsorption ability of CO relative to H_2 with TOS in addition to a decrease in oxidation ability with deactivation. On the other hand, for PtFe, the decrease in both CO and H_2 oxidation rates implies that the oxidation ability of the catalyst for both reactions decreased rapidly with TOS.

4.4. Deactivation behavior

Pt and PtFe showed different deactivation behavior considering the intrinsic site activity, k, and the concentration of active intermediates, $N_{\text{I-CO}_2}$. As deactivation progressed, the intrinsic site activity of Pt remained relatively constant, whereas, for PtFe, it decreased significantly. On the other hand, the concentration of active intermediates for Pt decreased more rapidly with TOS compared with that for PtFe. With TOS, the site activity of PtFe appeared to asymptotically approach that of Pt, indicating that its surface was becoming more like that of Pt with significant deactivation.

For both Pt and PtFe the number of active intermediates, $N_{\text{I-CO}_2}$, decreased significantly with TOS, although much more slowly for PtFe. It is likely that deactivation of Pt is due simply to carbon deposition on the surface, resulting in site blockage [3]. On the other hand, deactivation of PtFe is due to both site blockage by carbon and some other mechanism causing a decrease in site activity, most probably related to a change in oxygen adsorption ability. As the site activity of PtFe approached that of Pt with TOS, we suggest that deactivation decreased the promoting effect of Fe. There are many possible causes such as carbon deposition, reoxidation of Fe, and permanent deactivation such as phase separation and sintering. As the catalysts could be regenerated by reducing in a H_2 stream, it is highly unlikely that phase separation or sintering occurred. Given the deactivation effect of preexposure of the PtFe catalyst to O_2, oxidation of Fe during reaction is suggested to be a significant cause of deactivation.

On the Pt catalyst the amount of carbon deposition (Fig. 7) increased significantly during the first 5 min TOS and continued to increase but at a much slower rate until it exceeded the equivalent of ca. 100% surface coverage at about 200 min TOS. Because Pt still had some activity at this TOS, it is impossible to have had 100% surface coverage of Pt by carbon. Multilayer coverage of carbon and/or carbon deposition on the support are likely to have occurred. Even though most of the carbon deposition occurred during the first 5 min TOS on both Pt and PtFe, the carbon deposited later caused different effects on Pt and PtFe. The concentration of surface intermediates, $N_{\text{I-CO}_2}$, for Pt decreased rapidly, whereas that for PtFe gradually decreased. Although the amounts of carbon deposited at steady state were not significantly different (125 $\mu\text{mol/g}_{\text{cat}}$ for Pt and 103 $\mu\text{mol/g}_{\text{cat}}$ for PtFe), it would appear that CO adsorbed on the sites of PtFe still had more oxygen available for reaction for a longer period. This idea follows from the results of Lee and Gavriilidis [20] for Au/γ-Al_2O_3 catalysts and Bulushev et al. [21] for Fe-promoted Au/C catalysts where deactivation was decreased either by injecting excess oxygen [21] or by promoting the catalyst with more preferable oxygen adsorption sites [22]. This idea is also consistent with the ITKA results showing that the concentration of surface intermediates on PtFe decreased at a much slower rate than that on Pt.

5. Conclusions

Effects of Fe promotion of Pt for the selective oxidation of CO can be summarized as follows:

- Overall reaction rate increases because of an increase in intrinsic site activity, possibly as a result of more oxygen adsorption sites and/or an increase in oxygen adsorption ability. The ITKA results support the hypothesis about an increase in oxygen adsorption ability on Fe addition.
- With TOS, site activity of PtFe appears to asymptotically approach that of Pt, indicating that the surface becomes more like Pt as deactivation occurs.
- Even though the amount of carbon deposition during the initial deactivation period is similar for both catalysts, the concentration of surface intermediates on PtFe decreases at a slower rate perhaps due to Fe providing oxygen adsorption sites and increasing oxygen accessibility to adsorbed CO.
- Fe promotion does not increase the number of active sites. The maximum concentrations of active intermediates were approximately the same for both Pt and PtFe catalysts.

Although the deactivation of the Pt catalyst appears to be the result of mainly a decrease in the concentration of surface intermediates, for the PtFe catalyst, it is the result of both a decrease in the average intrinsic site activity and a decrease in the concentration of surface intermediates, with the decrease in average intrinsic site activity having the biggest effect. The decrease in the concentration of carbon surface intermediates with TOS for both catalysts is probably due to carbon deposition. In the case of PtFe, the intrinsic site activity decreased most likely because of a reoxidation of Fe which decreased the oxygen adsorption ability. The intrinsic site activity of PtFe approached that of Pt with TOS as the Fe promotion effect was diminished.

Acknowledgment

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