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Au-catalyzed selective oxidation of CO: a steady-state isotopic transient kinetic study

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Abstract

Selective oxidation of CO in hydrogen, obtained from hydrocarbons, is an important reaction for producing hydrogen appropriate for use in fuel cells. This paper reports on the variations in activity and selectivity of alumina-supported Au catalysts for the selective oxidation of CO due to the presence/absence of chloride (Cl^-) species and to different Au particle sizes [dispersion, D (%)]. This study made use of elemental analysis, chemisorption, kinetic studies, and steady-state isotopic transient kinetic analysis (SSITKA) to explore these variations. A comparison of Au catalysts with different Au loadings to 5 wt% Pt/γ-Al_2O_3 is also made. Magnesium citrate was added during preparation of one of the Au catalysts [referred to as Au(Mg)], because it was found to displace Cl^- species, resulting in smaller Au particle sizes. Rapid partial deactivation was observed for all of the catalysts during the first 30 min of time-on-stream irrespective of the presence or absence of Cl^- species. A reactivation after initial rapid deactivation was observed during reaction only for the Au(Mg) catalyst. This catalyst, the Au catalyst with the smallest particle size ($D > 90\%$) and the lowest Cl^- content, was more active than the catalysts with larger particle sizes (lower $\%D$) at steady state. But all Au catalysts had similar initial activity. A decrease in the concentration of reactive intermediates ($N_{\text{I-CO}_2}$) along with a very large decrease in intrinsic site activity (k), both obtained from SSITKA, appear to have been the cause of the initial deactivation of the Au catalysts. For the Pt catalyst, the decreased concentration of reactive intermediates was the main cause of initial deactivation. Although the precise reasons for the increase in activity with time-on-stream after initial deactivation of the Au catalyst prepared with magnesium citrate are not clear, it can be hypothesized that increasing amounts of water formed during the reaction may have helped in decomposing deactivating Au carbonate species or in restructuring/reconstructing the active sites. The smaller Au particle size and/or absence of Cl^- species may have contributed to this. Although there was a slight increase in the number of active CO_2 intermediates, most of the increase in rate for the Au(Mg) catalyst was due to an increase in average site activity. There is no evidence that Mg functions as a chemical promoter.

Keywords: Selective oxidation of CO; CO oxidation; Au/γ-Al_2O_3, Pt/γ-Al_2O_3; Magnesium effect on Au catalysts; Steady-state isotopic transient kinetic analysis; Deactivation; Isotopic tracing

1. Introduction

Fuel cells are gaining interest because of their potential to replace internal combustion engines in automobiles and their use in all sorts of electric power generation off the grid. Proton exchange membrane fuel cells (PEMFCs) make use of hydrogen and oxygen as fuel and produce electricity, with water the sole byproduct. The hydrogen is usually obtained from hydrocarbons by partial oxidation or steam reforming, with CO and CO_2 as the byproducts. Unfortunately, CO is a poison for fuel cell electrodes, and the acceptable limit of CO in hydrogen for fuel cells is 10 ppm. Because the CO concentration in the H_2-rich stream obtained from hydrocarbons is around 1% (10,000 ppm), removing the CO from that stream is extremely important for efficient operation of fuel cells. Pressure swing adsorption, methanation, and selective

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CO oxidation are some of the techniques available for this purpose [1]. Of these, selective CO oxidation is the easiest and most economical method of CO removal (by formation of CO_2).

Supported metal catalysts such as Pt, Rh, and Ru on oxide supports have been shown to be useful for the selective oxidation of CO in H_2. Much research has been done on Pt catalysts, including studies of deactivation behavior [2], effect of Fe promotion [3], kinetics [4], and effects of water vapor and CO_2 on activity and selectivity [5].

Au, when present in the bulk state, is inert and hence considered a poor catalyst. But highly dispersed nanosized Au particles supported on metal oxides can be very active for the CO oxidation reaction even at very low temperatures [6–11]. Au has a greater availability and lower cost than Pt. Because of these reasons, researchers have started taking an interest in Au catalysis for selective CO oxidation.

Two important characteristics that catalysts for the selective CO oxidation must have are high activity and high selectivity toward CO_2 formation. Au catalysts have been reported to be highly active and selective for this reaction at typical fuel cell operating temperatures [7]. Kahlich et al. [8] studied the kinetics of this reaction at low temperature on Au supported on Fe_2O_3, and Grunwaldt et al. [9] conducted a comparative study of Au/TiO_2 and Au/ZrO_2 for simple CO oxidation. Other studies have investigated the effect of particle size on activity and selectivity [7], the effects of water concentration and the addition of MgO and MnO_x to the catalyst on catalyst activity [10], the nature of the active sites [12], and the effects of preparation method and O_2 and CO_2 concentration in the feed stream [13]. Kung and coworkers have studied in detail the effect of the presence of Cl^- species, which originate from the Au precursor solution, on the activity of Au catalysts for CO oxidation and selective CO oxidation [11,14].

This paper reports on a study of γ-Al_2O_3-supported Au catalysts (with varying Cl^- impurity concentrations and average Au particle sizes) and their comparison with a Pt/γ-Al_2O_3 catalyst using reaction kinetics and steady-state isotopic transient kinetic analysis (SSITKA). Initially developed by Happel [15], Bennett [16], and Biloen [17], SSITKA is a powerful technique for the in situ analysis of surface reaction on heterogeneous catalysts. The major use of SSITKA is for determining the average surface residence time (τ_p), surface concentration (N_p), and surface coverage (θ_p) of the most active reaction intermediates. In this study we used SSITKA to determine the variation of these parameters for the Au and Pt catalysts with time on stream (TOS).

2. Experimental

2.1. Catalyst preparation

Three Au catalysts were prepared by the deposition–precipitation (DP) method as described by Bethke and Kung [7]. The DP method was chosen as the catalyst preparation method because it yields hemispherical metal particles, which, according to Haruta [6], have larger turnover frequencies. Au solutions of different concentrations were used to produce catalysts with different metal dispersions. Before the catalysts were prepared, the support (Al_2O_3, Vista B) was calcined at 500 °C for 10 h to form γ-Al_2O_3.

The Au precursor, hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, Alfa Aesar), was dissolved in water and stirred for 20 min. The aqueous solution (25 ml/g of support) was then added to the support (γ-Al_2O_3) and stirred for 2 h. The stirring was carried out at low temperature in an ice bath to prevent coagulation of Au clusters in the solution [7]. The pH of the slurry as measured was 4.5 and the temperature was 3.4 °C after 1 h. During preparation of the lowest Au-loaded catalyst, magnesium citrate (Alfa Aesar) was added to the solution after 1 h of stirring. (Magnesium citrate is believed to reduce the particle size by preventing the coagulation of Au clusters during preparation [7].) The Mg/Au ratio was 1.55. The pH of the slurry as measured was 5.97 after the addition of magnesium citrate. After stirring for 2 h, the solutions were filtered and the catalysts washed three times with water at room temperature and once with warm water. The catalysts were dried at 100 °C for 30 min and then calcined under flowing dry air (HC free) at 350 °C for 4 h. Throughout the paper, the two Au catalysts without magnesium citrate are referred to as “Au1” and “Au2” (with Au loadings of around 3 and 2%, respectively), whereas the Au catalyst with citrate is referred to as “Au(Mg)” (with an Au loading of around 0.5%). The 5 wt% Pt/γ-Al_2O_3 catalyst was prepared by incipient wetness impregnation method as described in previous work [2]. This catalyst is referred to as “Pt” throughout the paper.

2.2. Catalyst characterization

Metal and Cl^- content (wt%) were determined by Galbraith Laboratories (Knoxville, TN).

2.2.1. X-Ray diffraction

X-Ray diffraction (XRD) analysis was used to study the Au and Pt catalysts using a Philips X’Pert X-ray diffractometer with monochromatized Cu-K_α radiation and a Ni filter.

2.2.2. Pulse H_2 titration

Pulse H_2 titration was used to determine dispersion, D (%), and metal particle size in the Au catalysts. The analysis was carried out at 1 atm using an Altamira AMI-1 system. Initially, the catalyst in a U-quartz tube reactor was pretreated with 30 sccm of 5% H_2 in Ar (National Welders) at 400 °C for 1 h [18]. The temperature was increased from 25 to 400 °C with a ramp rate of 10 °C/min. After pretreatment, the catalyst was flushed with Ar (National Specialty Gases, UHP) for 30 min to desorb the hydrogen; during this step, the temperature was reduced from 400 to 300 °C

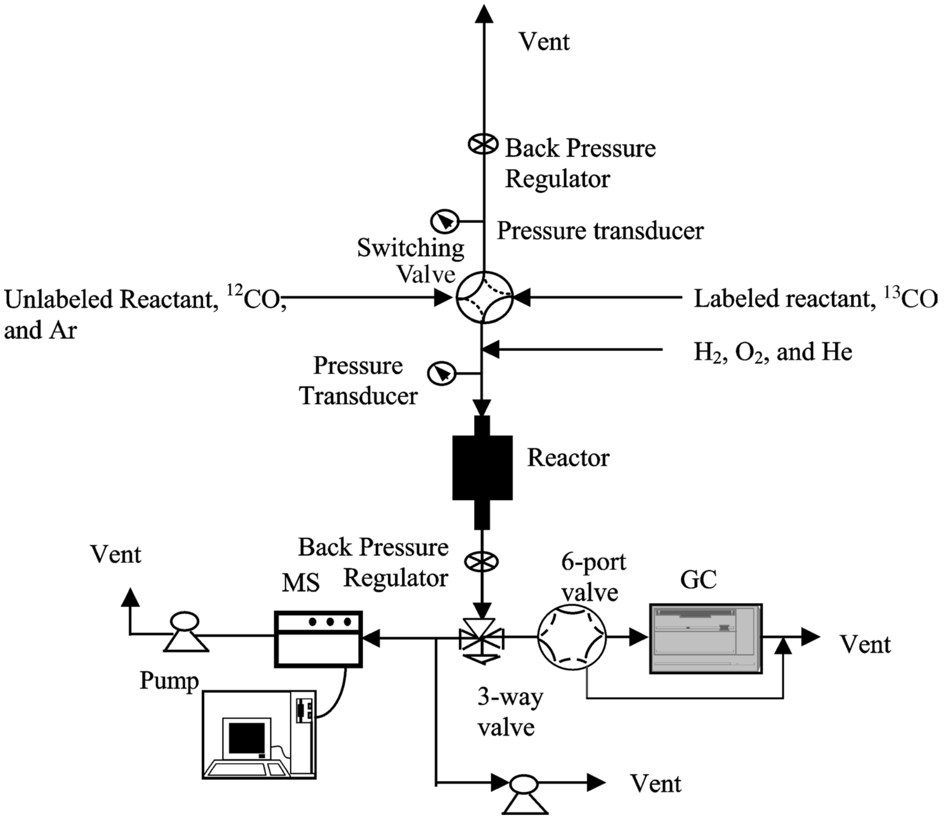

Fig. 1. Schematic diagram of the SSITKA—CO selective oxidation system.

at 10 °C/min. In the next step, 2% O_2 in He (Holox) was passed over the catalyst for 3 h at 300 °C to adsorb O_2 on the metal surface atoms. The catalyst was then flushed with Ar for 1 h to remove any weakly adsorbed oxygen. The strongly adsorbed oxygen was then titrated with pure hydrogen (National Specialty Gases, UHP) pulses. The H_2 pulses were passed over the catalyst, and unreacted hydrogen was detected using a thermal conductivity detector (TCD). A water trap was placed between the reactor and TCD to remove any water formed during the reaction. The H_2 pulses were continued until the areas under the pulses coming out of the reactor were constant. The amount of O_2 adsorbed on alumina-supported Au catalysts increases with temperature, reaching a maximum at about 340 °C followed by desorption of O_2 at higher temperatures [18]. Adsorption experiments carried out at 200 °C showed very slow adsorption of O_2. Hence 300 °C was chosen as the temperature for O_2 adsorption and pulse titration in this study.

The dispersion of the Pt catalyst was determined by static H_2 chemisorption, the details of which were given previously [2].

2.3. Reaction studies

The kinetic studies were carried out in a stainless-steel plug flow microreactor (0.3-inch id). A schematic of the reaction system used is shown in Fig. 1. About 20–25 mg of the catalyst diluted with α-Al_2O_3 was sandwiched between quartz wool and placed at center of the reactor with a thermocouple at the bottom of this catalyst bed. The reaction was carried out at 1.8 atm and 90 °C. The reactants were fed to the reactor in a ratio of $H_2/CO/O_2/He = 45/1/1/53$, with a total flow rate of 100 sccm. All Au catalysts were pretreated in a flow of hydrogen (45 sccm) at 150 °C for 1 h. The temperature was increased from 30 to 150 °C with a ramp rate of 1 °C/min. The Pt catalyst was pretreated at 550 °C for 1 h in a flow of hydrogen (45 sccm).

The effluent from the reactor during reaction was analyzed by gas chromatography (GC) (Varian CP-3380). In the GC, the products were separated by a 6-ft-long 80/100 mesh carbosphere column (Alltech). At 35 °C, H_2, CO, and O_2 were first separated, and then the GC was ramped to 150 °C at 20 °C/min for separating CO_2. The CO conversion and selectivity were determined periodically using a definition given by Manasilp and Gulari [5].

Reaction on the Au2 catalyst for different reactant flow rates showed that external mass transfer did not affect reaction rate measurements. The Weisz–Prater parameter was calculated for all of the catalysts and indicated no internal mass transfer effects at the reaction conditions used.

2.4. SSITKA

The SSITKA studies were carried out by making a switch from ^{12}CO to ^{13}CO (Isotec, 99 atom% ^{13}C, 12 atom% ^{18}O). A trace of argon was present in the ^{12}CO stream to measure

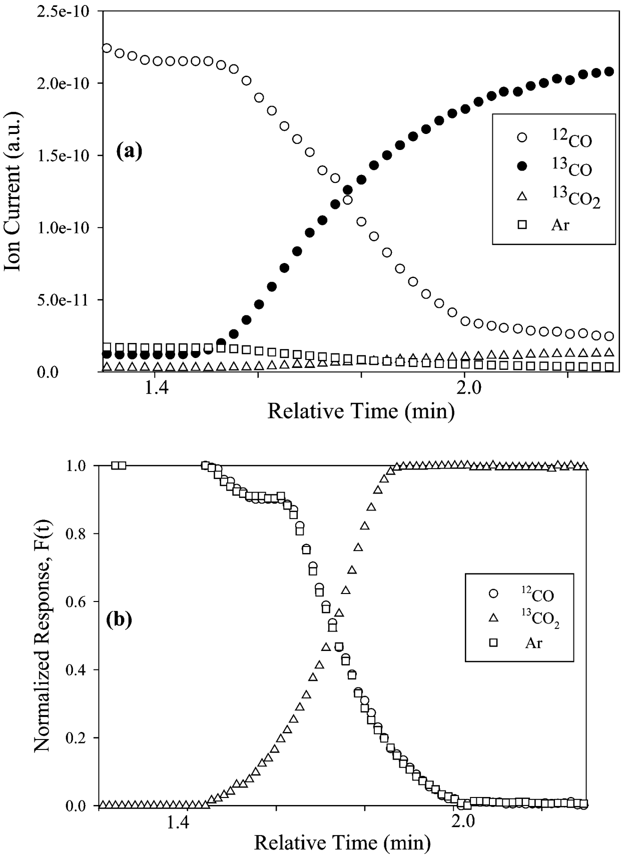

Fig. 2. Typical SSITKA transients: (a) actual transients, (b) normalized transients.

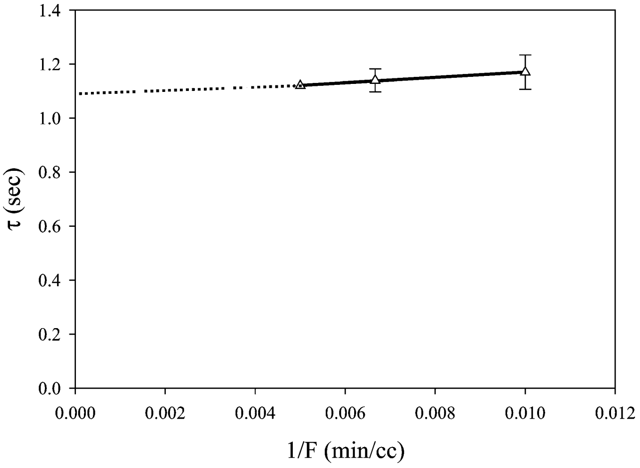

Fig. 3. Variation of $\tau_{\text{I-CO}_2}$ with inverse flow rate $(1/F)$ for the Au1 catalyst.

the gas-phase holdup in the reaction system. A quadrupole mass spectrometer (Pfeiffer Vacuum, Prisma) was used to monitor the decrease in the old label and the increase in the new label in the CO_2 along with CO coming out of the reactor, as shown in Fig. 2a. The mass spectrometer was coupled with a high-speed data acquisition system interfaced to a personal computer using Balzers Quadstar 422 v 6.0 software. The SSITKA parameters, including average surface residence time $(\tau_{\text{I-CO}_2})$, surface concentration $(N_{\text{I-CO}_2})$, and surface coverage $(\theta_{\text{I-CO}_2})$ of reactive intermediates, were calculated using the method described by Shannon and Goodwin [19]. The average residence time was determined by integrating the normalized isotopic transient (Fig. 2b) of the product relative to that of the inert tracer (Ar).

A potential problem for SSITKA measurements of CO adsorption and reaction can be readsorption of product CO_2. If this were to occur, it would cause an increase in the average surface reaction residence time $(\tau_{\text{I-CO}_2})$, resulting in overestimation of $N_{\text{I-CO}_2}$ and underestimation of k. Methods for removing readsorption effects to determine the true surface reaction residence time, taking into account both interparticle and intraparticle readsorption, have been given by Ali and Goodwin [20]. Experiments performed under the conditions of this study for different flow rates to check whether readsorption affected the average surface residence time of product CO_2 on Au1 indicated that the values of $\tau_{\text{I-CO}_2}$ (and consequently of $N_{\text{I-CO}_2}$) were essentially free from readsorption effects on the Au catalysts at these conditions (Fig. 3). The same was true for the Pt/γ-Al_2O_3 catalyst [21].

3. Results and discussion

The actual metal loadings as determined by Galbraith Laboratories for the Au and Pt catalysts are given in Table 1.

3.1. X-Ray diffraction

No peaks for metallic Au were seen in powder XRD. This was due in large part to the small particle sizes of the Au present in the catalysts. Also, the detection of Au peaks was more difficult, because of overlap with the large γ-Al_2O_3 peaks present. The XRD pattern of the Pt catalyst after calcination also showed peaks corresponding to γ-Al_2O_3. No peaks for Pt metal were seen, for the same reason they were not seen for Au.

3.2. Au dispersion

Dispersions and particle sizes obtained from pulse H_2 titration for the three Au catalysts are reported in Table 1,

Table 1
Physical properties of Au and Pt catalysts

Catalyst	Metal[a] (wt%)	Concentration of Au$_s$[b] (μmol/g$_{cat}$)	Dispersion[c] (%)	Avg. metal particle size[d] (nm)
Au/γ-Al_2O_3 [Au1]	2.89	13.2	9	13.9
Au/γ-Al_2O_3 [Au2]	1.54	14.1	18	6.8
Au-Mg/γ-Al_2O_3 [Au(Mg)]	0.33	15.6	93	1.3
Pt/γ-Al_2O_3 [Pt]	5	115.4	45	2.4

Maximum measured error: [a] ±5%; [b] ±10%; [c] ±3%; [d] ±10%.

Table 2
Chloride (Cl^-) content of the Au and Pt catalysts

Catalyst	Chloride (Cl^-) content[a] (%)		
	Before pretreatment, as prepared	After pretreatment[b]	After reaction[c]
Au1	0.29	0.33	–
Au2	0.22	0.22	–
Au(Mg)	0.03	0.03	0.06
Pt	0.48	–	–
Mg/Au2	0.67	–	–

[a] Maximum measured error, ±5%.

[b] Pretreatment in the presence of H_2 (45 sccm) at 150 °C for 1 h. Temperature ramp rate, 1 °C/min from 30 to 150 °C.

[c] After 230 min TOS of the reaction.

as are these parameters for $Pt/\gamma\text{-}Al_2O_3$ (determined by static H_2 chemisorption). Fukushima et al. [22] studied O_2 chemisorption on supported Au and found dissociative adsorption of O_2. The stoichiometry of Au_s:O was 2 at 200 °C and 1 at 300 °C [18]. Because the temperature chosen for titration, as discussed earlier, was 300 °C, a stoichiometry of 1 was used for calculations here. The reactions taking place on the catalyst surface can be summarized as follows:

$$Au_s + O \rightarrow Au_s\text{–}O \tag{1}$$

and

$$Au_s\text{–}O + H_2 \rightarrow Au_s + H_2O. \tag{2}$$

From the results given in Table 1, the Au(Mg) catalyst had the largest dispersion and, consequently, the smallest particle size.

During Au catalyst preparation, $HAuCl_4$ forms H^+ and $AuCl_4{}^-$ ions after dissolving in water. The chloride ligands in $AuCl_4{}^-$ are then displaced by hydroxyl groups and water molecules, resulting in a tendency to coagulate by condensation into clusters of Au complexes and hence forming larger particles. Another possible reason for formation of the larger Au clusters is the presence of residual Cl^- species from the precursor solution, which causes agglomeration of Au particles during heat treatment [14]. The greater the amount of Cl^- species present, the larger the particle size. The amounts of Cl^- present in the various catalysts prepared in this study are given in Table 2. The Mg citrate added during preparation serves a dual purpose. First, it acts as a ligand to Au^{3+} ions and competes with hydroxyl groups for attaching to Au^{3+} [7]. This results in displacement of the hydroxyl ligands, which ultimately breaks up the Au clusters. Second, it displaces the residual Cl^- species, resulting in smaller Au particle sizes. Thus magnesium citrate added during preparation plays an important role in reducing the Au particle size.

3.3. Selective CO oxidation reaction

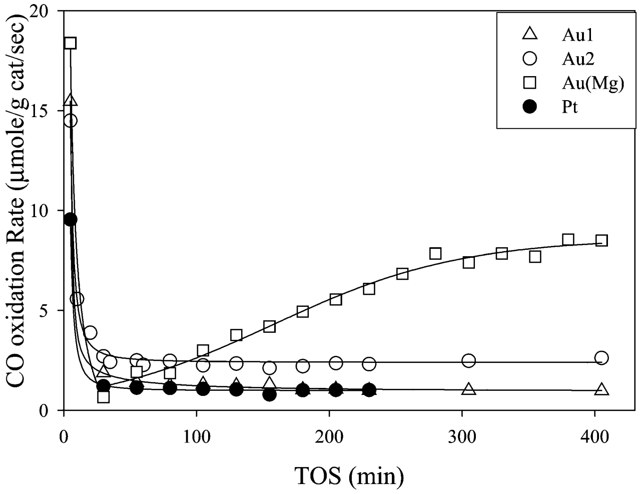

Fig. 4. Time-on-stream behavior of CO oxidation rate for Au1, Au2, Au(Mg) and Pt catalysts (maximum error measured: ±5% for Au1, Au2 catalysts and ±10% for Pt and Au(Mg) catalysts).

Fig. 4 compares the rates of selective CO oxidation with TOS for the various Au and Pt catalysts studied. A rapid initial partial deactivation was observed for the Au1, Au2, and Pt catalysts. For Au1 and Pt catalysts, the rate dropped by about 90% during the first 30 min TOS before a constant steady-state value was established. For Au2, the decrease was about 80%. Such an initial fast partial deactivation for Pt has been noted and studied in detail earlier [2]. The Au(Mg) catalyst also exhibited the same rapid initial decrease in rate, but then, surprisingly, it showed a significant increase in rate to its steady-state value—the highest rate/g_{cat} of any of the catalysts. The activity of the catalyst was almost 10 times that of the Pt catalyst at steady state. Thus an apparent reactivation occurred for this catalyst after the initial deactivation. A similar result on Au catalysts after injection of pulses of water during selective CO oxidation was reported by Grisel and Nieuwenhuys [10]. An important observation from the present study is that the initial partial deactivation behavior of the Au catalysts was independent of the amount of Cl^- species present or the Au particle size.

Fig. 5 shows the selectivity variations for the Au and Pt catalysts. The trend for selectivity was similar to the rate of the reaction. All of the catalysts showed initial rapid declines in CO_2 selectivity from initial values of 80–100%. At steady state, Au1 and Au2 catalysts showed selectivities of around 18 and 22%, respectively. The Pt catalyst exhibited a steady-state CO_2 selectivity of around 35%. Although these three catalysts showed similar behavior, Au(Mg) displayed quite different and reproducible behavior, similar to the rate of reaction. During the initial period (i.e., $\leqslant 30$ min of TOS), the CO_2 selectivity decreased to a minimum (around 10%) before increasing to a high steady-state value (around 65%).

A question can be raised about the effect on CO_2 selectivity of the presence of MgO in the Au(Mg) catalyst, because CO_2 can react with MgO. The concentration of MgO present on the catalyst surface was around 210 $\mu mol/g_{cat}$. Considering the maximum rate of CO_2 formation of around 18 $\mu mol/(g_{cat}\,s)$, it would have taken around 11.5 s for the MgO to be totally saturated by CO_2. The initial rapid de-

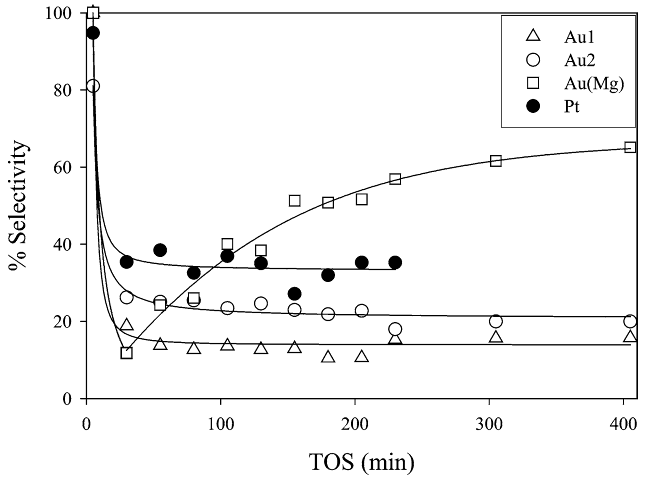

Fig. 5. Selectivity (%) as a function of time-on-stream for Au1, Au2, Au(Mg) and Pt catalysts.

activation with loss of CO_2 selectivity in the current study occurred over a period of 1800 s. Hence the possibility of a significant decrease in selectivity resulting from the formation of Mg carbonates can be ruled out, even if the process was not totally efficient.

It is obvious that two phenomena were occurring in the case of the Au(Mg) catalyst: one leading to partial deactivation and the other, a type of induction phenomenon, causing activation of new sites and/or reactivation of deactivated sites. Together, these two phenomena yielded the results shown in Figs. 4 and 5.

Fig. 6 compares the TOFs (determined based on pulse H_2 titration and static H_2 chemisorption for the Au and Pt catalysts, respectively) with the TOS of these catalysts. This figure shows that the Pt catalyst had a much lower TOF than all of the Au catalysts for all TOS. This suggests that the Pt catalyst, while having the highest metal surface area/g, had a much lower site activity or fraction of Pt surface atoms active for reaction. It is especially important to note that all of the Au catalysts had approximately similar initial TOF values as well as similar initial rates (at 5 min TOS). These results further confirm the similar concentrations of Au_s obtained from pulse H_2 titration for all the Au catalysts, as shown in Table 1.

The activities and the deactivation behaviors of these catalysts can be better explained by considering the contributions to the overall activity from the intrinsic site activity (k, s^{-1}) and the concentration of surface intermediates ($N_{\text{I-CO}_2}$), both of which can be obtained by SSITKA. Overall activity is the product of these two parameters $\{\text{Rate} = kN_{\text{I-CO}_2} = (1/\tau_{\text{I-CO}_2})N_{\text{I-CO}_2}\}$ [23]. Fig. 7 shows the variations in k with TOS for the Au and Pt catalysts. For Au1 and Au2 catalysts, the reduction in k was significant, whereas for the Pt catalyst, there was very little decrease in k. The Au(Mg) catalyst exhibited a variation in k similar to that observed for the rate.

Fig. 8a shows the variations in the concentration of reactive intermediates ($N_{\text{I-CO}_2}$) with TOS for Au1, Au2, and Au(Mg) catalysts; Fig. 8b shows the variation with TOS for the Pt catalyst. $N_{\text{I-CO}_2}$ is the concentration of intermediates on the catalyst surface leading to CO_2. There was a rapid decrease in the concentration of these intermediates during the first 30 min TOS for all catalysts. The decreases for the Au catalysts (around 50%) were significantly less than the decrease for the Pt catalyst (around 90%). Hence, considering the changes in k and $N_{\text{I-CO}_2}$, we can conclude that for the Pt catalyst, deactivation was due mainly to a decreased concentration of reactive surface intermediates. In contrast, for the Au1 and Au2 catalysts, there were decreases in both $N_{\text{I-CO}_2}$ and k, but the k decrease (around 70%) was the primary cause of deactivation. The $N_{\text{I-CO}_2}$ decrease was probably due mainly to deposition of carbon from CO on the active sites, as has been shown previously for Pt [2]. This deposition decreases adsorption of the reactants and hence increases formation of reactive intermediates. We sent a sample of the Au2 catalyst after it had reached steady state during reaction to Galbraith Laboratories for carbon analysis; the amount

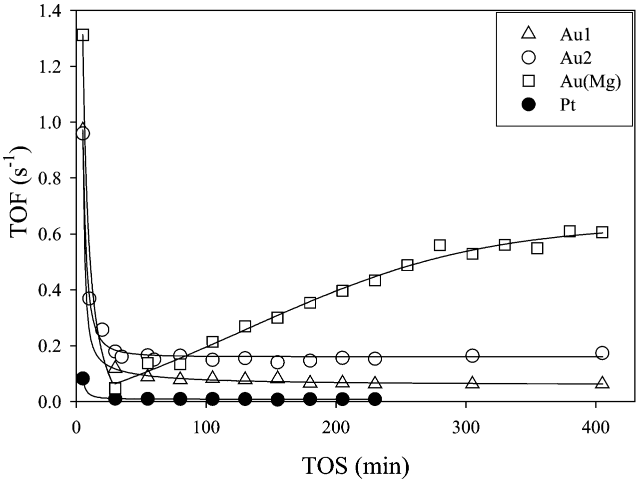

Fig. 6. Turnover frequency comparison of Au and Pt catalysts as a function of time-on-stream.

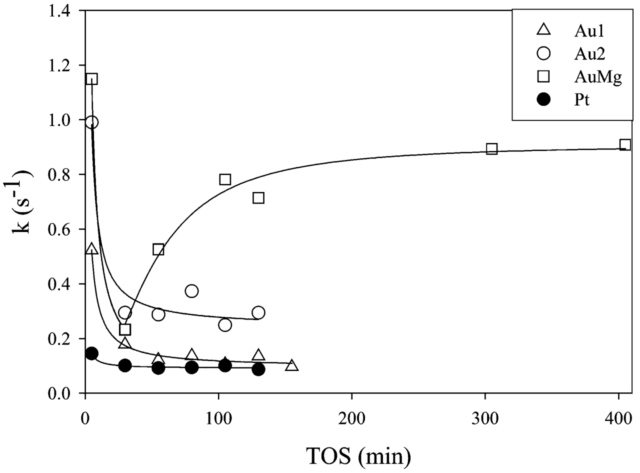

Fig. 7. Intrinsic SSITKA site activity variation with time-on-stream for Au1, Au2, Au(Mg) and Pt catalysts (maximum error measured, ±10%).

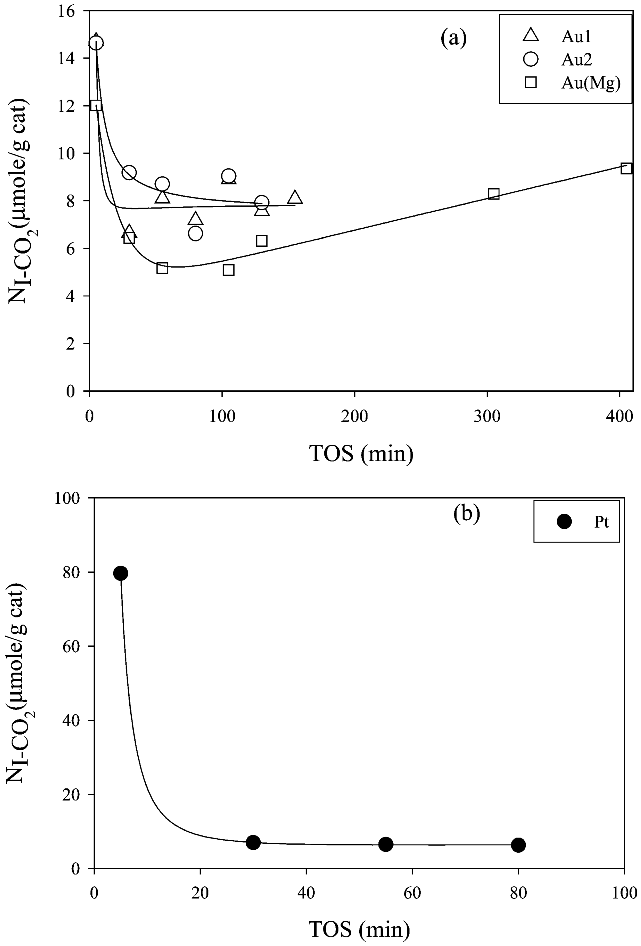

Fig. 8. Concentrations of reactive intermediates as a function of time-on-stream for (a) Au1, Au2 and Au(Mg) catalysts, (b) Pt catalyst (maximum error measured, ±10%).

of carbon found by the combustion/colorimetric titration method was around 0.5 wt%.

For the Au(Mg) catalyst, both $N_{I\text{-}CO_2}$ and k attained minimum values at 30 min TOS and then increased to their steady-state values. The decrease in $N_{I\text{-}CO_2}$ was smaller (around 50%) than the decrease in k (around 83%), suggesting that the decline in intrinsic site activity, not the decrease in the concentration of reactive intermediates, was the major cause of deactivation. There was an increase in the concentration of reactive intermediates during reactivation, as shown in Fig. 8a, but this alone is not sufficient to explain the large increase in rate. The increase in intrinsic site activity (k) after the initial rapid decrease was more significant (Fig. 7), suggesting the possible creation of sites of higher activity and/or reactivation of deactivated higher activity sites during this activation/reactivation period. This result was completely replicable.

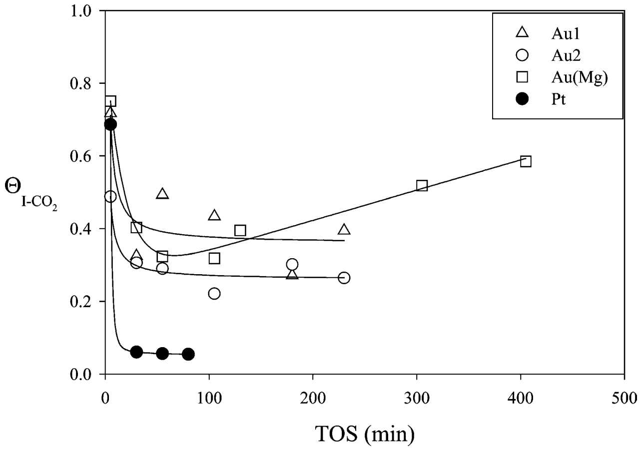

Fig. 9. Variations in surface coverage of reactive intermediates ($\theta_{I\text{-}CO_2}$) for Au1, Au2, Au(Mg) and Pt catalysts (maximum error measured, ±10%).

Another important parameter obtained from the SSITKA data was the surface coverage ($\theta_{I\text{-}CO_2}$) of the most reactive intermediates. Fig. 9 shows the variations in ($\theta_{I\text{-}CO_2}$) for all of the catalysts. The Au1, Au(Mg), and Pt catalysts showed surface coverages of active intermediates of around 70% at 5 min TOS; the value for the Au2 catalyst was around 50%. The θ values of all of the catalysts dropped during first 30 min TOS, explaining the decreases in TOF and reaction rate. The Au(Mg) catalyst showed an increase in ($\theta_{I\text{-}CO_2}$) after the initial drop, exhibiting a value of around 60% at steady state. An important fact to remember here is that k also increased with TOS after initial deactivation.

Five samples of the Au(Mg) catalyst (two at 30 min TOS and other three after 130, 230 and 330 min TOS) were sent to Galbraith for carbon analysis. The results showed a decrease in the amount of carbon between the minimum activity and steady state (2.18 ± 0.1% at 30 min vs 1.65% at steady state). Although the decrease was not substantial, this could be one of the reasons for the increased activity of the catalyst after 30 min TOS.

The selective CO oxidation reaction may be a structure-sensitive reaction on Au catalysts with strong metal–support interactions [6]. According to Haruta [6], the particle–support perimeter interface plays a very important role in the reaction. This interface is composed of Au oxide or hydroxide and is stabilized by interaction with metal oxide supports, making it more active. The reaction is purported to proceed at the perimeter interface with CO adsorbing on the edge and corner sites of the Au nanoparticles while oxygen in molecular form adsorbs at the support–metal interface. The smaller the particle size, the more perimeter per gm of Au is available for reaction, and hence the higher the activity of the catalyst. The order of average metal particle diameters of the Au catalysts used in this study was Au1 > Au2 > Au(Mg), and the activity of these catalysts at steady state was the reverse: Au(Mg) > Au2 > Au1, which is consistent with the foregoing discussion.

There is increasing support in the literature for the fact that moisture plays a very important role in enhancing the activity of supported Au catalysts for CO oxidation [24–27] and selective CO oxidation [10,28]. In the present study, the water formed from the oxidation of H_2 during the reaction may have played an important role in increasing the activity of the Au(Mg) catalyst with TOS. Fig. 10 shows

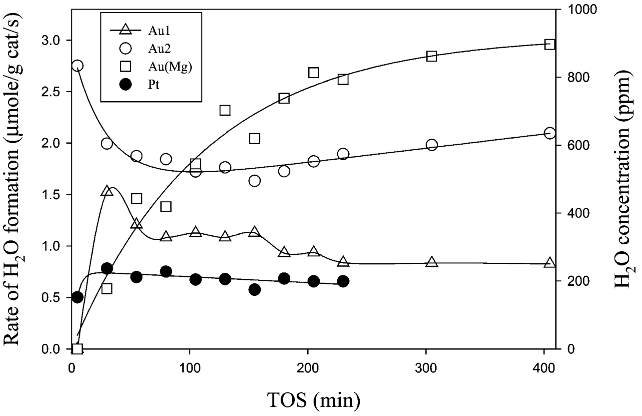

Fig. 10. Rate of water formation and concentration of water (ppm) as a function of TOS for Au and Pt catalysts.

the rate of water formation during the selective CO oxidation reaction on the Au and Pt catalysts as a function of TOS. It can be speculated that the water formed on the Au(Mg) catalyst is able to reactivate deactivated Au sites and/or create additional sites through reconstruction of the Au particles. This reconstruction may increase the perimeter interface and/or change its structure, resulting in increased activity. Grisel and Nieuwenhuys [10] have confirmed the fact that for some Au catalysts, adding water has a positive effect on the activity of the catalyst. They injected a 50-μl pulse of water during the selective CO oxidation reaction and found an increase in conversion on Au/MnO_x/MgO/Al_2O_3, Au/MgO/Al_2O_3, and Au/Al_2O_3 catalysts. In the present case, the water formed during the reaction (which is significant after the initial deactivation period), not added water, would have been the cause of the increased activity for the Au(Mg) catalyst.

Kung et al. [11] recently addressed the issue of the deactivation mechanism of Au and the role of water in regeneration of the active sites. According to these authors, the deactivation may result from formation of inactive carbonate intermediates through dehydration of bicarbonate intermediates. The reaction occurring at the surface can be written as

$$\text{Au–}(CO_3H) + \text{Al–OH} \Longleftrightarrow \text{Au–}(CO_3)\text{–Al} + H_2O_{ads}. \quad (3)$$

The concentration of the reactive intermediates obtained from SSITKA confirms that a decrease in active intermediates (presumably bicarbonates, in accordance with the foregoing equation) occurred after 30 min TOS for the Au1 and Au2 catalysts. Both of these catalysts were not very active, and hence water formed during the reaction was much less (around 250 ppm for Au1 and 600 ppm for Au2, at steady state). During the first 5 min TOS, the Au(Mg) catalyst was very active, and the selectivity toward CO_2 was 100% (Fig. 5); hence all of the O_2 was used in producing CO_2. But as the reaction proceeded, the selectivity toward CO_2 dropped, and more water molecules were formed, as shown in Fig. 10 (0 ppm at 5 min TOS vs around 900 ppm at 405 min TOS), which were adsorbed in part on the support surface. As seen in Eq. (3), equilibrium would have shifted towards the left, producing the original active bicarbonate intermediate species in place of a deactivated site. Thus active sites may have been "regenerated" as the reaction proceeded, resulting in increased activity of the catalyst. Hence regeneration could be another reason, along with reconstruction of sites, for the increase in activity. Further research is needed to address this issue in detail.

A question can be raised as to why the water produced during the reaction reactivated only the Au(Mg) catalyst and not the Au1 and Au2 catalysts. Daté et al. [25] recently studied the effect of moisture on the activity of supported Au catalysts for the CO oxidation reaction. According to these authors, the moisture activates the oxygen and aids decomposition of carbonate (as discussed earlier), resulting in enhanced catalytic activity. Another observation from their study is that for the Au/γ-Al_2O_3 catalyst, the enhancement in the activity is significant only above 200 ppm of water. The mean diameter of the supported Au nanoparticles in that study was 3.9 nm, and the reaction temperature was around 273 K. In the present study, for Au1, the concentration of water initially increased but then rapidly decreased to a steady-state value of around 250 ppm (which is very close to 200 ppm). Au2 had a higher water concentration than Au1 (also $>$ 200 ppm). It would seem highly likely that Au particle size and/or the presence of Cl^- species may play an important role in determining the effect of water on catalyst activity. The Au particles in Au1 and Au2 were 3.5 and 1.7 times larger, respectively, than the particles in the study of Daté et al. [25] and 10.7 and 5.2 times larger on average, respectively, than those of Au(Mg). Another noteworthy parameter that may have an impact is the reaction temperature, which differs between the present study (363 K) and the study of Daté et al. (273 K) [25].

It is important to consider the relationship of the SSITKA parameters to the concentrations of the intermediates for the selective CO oxidation reaction. $N_{\text{I-CO}_2}$ is related only to the carbon intermediates leading to formation of CO_2. The intrinsic site activity (k) value is related to the rate constant in a pseudo-first-order power law rate expression and potentially includes the partial pressure of O_2. If new sites were created that increased the amount of O_2 able to adsorb, then it would be likely that: (i) k would increase; (ii) more carbon would be removed from the catalyst, possibly reactivating sites; (iii) the number of CO reacting sites would increase; and (iv) the rate of CO_2 formation would increase.

To confirm the fact that H_2O plays an important role in the recovery of catalyst activity, several experiments were carried out in the absence of H_2 (non-selective CO oxidation), with the other conditions kept the same as for selective CO oxidation. Fig. 11 shows the TOFs as a function of TOS for the nonselective and selective CO oxidation on the Au(Mg) catalyst. It was observed that in the absence of H_2, there was also an initial partial deactivation of the catalyst during the first 30 min TOS; this occurred for the same reason as for the other Au catalysts, that is, deposition of carbon on active sites. But after that, the activity of the catalyst was

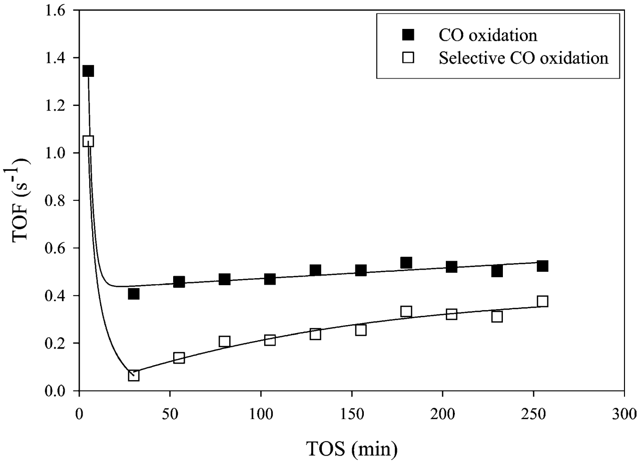

Fig. 11. Turnover frequency for non-selective and selective CO oxidation on the Au(Mg) catalyst.

almost constant (around 0.5 s^{-1}). No significant increase in the TOF for non-selective CO oxidation on Au(Mg) was observed, and the catalyst behaved like other Au catalysts (Au1 and Au2 catalysts for selective CO oxidation from this work).

Many studies of CO oxidation [12,24,25,27] have reported a regain of original activity after the introduction of water vapor in the CO oxidation feed. These results also support the fact that water may play an important role in recovering the catalytic activity during the selective oxidation of CO in H_2.

The steady-state value of TOF for nonselective CO oxidation was higher than that for selective CO oxidation. There is evidence in the literature that the effect of H_2 on Au-catalyzed CO oxidation activity can be either negative [10] or positive [29], depending on the reaction conditions, method of catalyst preparation, and other factors. Clearly, in the present study, at 90 °C, the CO oxidation activity of a Au catalyst without significant amounts of chloride was greater than that for the selective oxidation of CO in the presence of H_2. In the absence of H_2, only CO and O_2 adsorb on the active sites. But with the addition of H_2, there is a competitive adsorption between H_2 and CO and a competition for reaction with O_2. This may reduce the number of active sites available for CO adsorption as compared to that under non-selective CO oxidation.

3.4. Role of magnesium in the activity of the catalyst

The kinetic experiments showed that the Au(Mg) catalyst was more active than the Au1 and Au2 catalysts at steady state because of reactivation/modification of the catalyst. Because the presence of Mg is the only difference between Au1, Au2, and Au(Mg) other than Au particle size, the question can be asked as to whether Mg is important only during initial preparation as a structural promoter. Could it be possible that Mg acts as a chemical promoter for Au, much like Fe for Pt, in this reaction [3]? To determine whether or not this is true, a Au catalyst was prepared by adding an aqueous solution of magnesium citrate to the Au2 catalyst using the incipient wetness impregnation method. The catalyst was dried for 1 h in static air and then calcined at 350 °C for 4 h under flowing dry air (HC free). This catalyst is referred to as “Mg/Au2.”

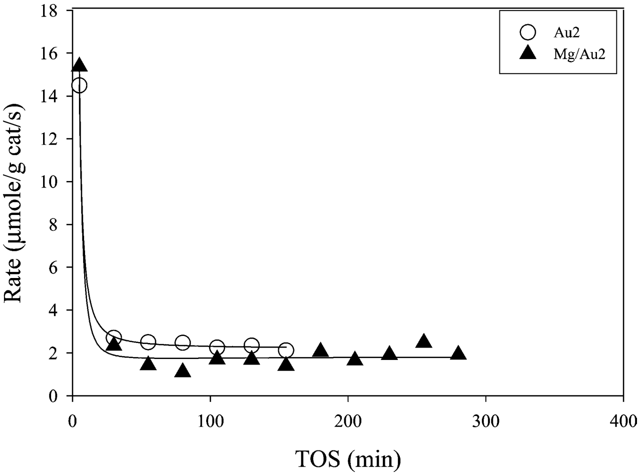

Fig. 12. Effect of the addition of magnesium citrate to the Au2 catalyst (Mg/Au2) on the rate of CO oxidation with TOS. For comparison, the rate for the Au2 catalyst without Mg is also shown.

The selective oxidation reaction was carried out on Mg/Au2 in the same way as for the other catalysts. Fig. 12 shows the variations in the rate of reaction with TOS for the Mg/Au2 and Au2 catalysts. The Mg/Au2 catalyst displayed similar deactivation characteristics as the original Au2 catalyst. No increase in the activity of Mg/Au2 was observed after the initial partial deactivation, suggesting that Mg promotion alone may not cause the increased catalyst activity. Because the activity of the Mg/Au2 catalyst was similar to that of Au2, it would appear that Mg does not have a chemical-promoting effect on Au-catalyzed reaction, assuming that there is no need for the Au and Mg to be contacted in a specific way that is possible only during preparation.

4. Conclusions

Alumina-supported Au catalysts catalyze the selective oxidation of CO at 90 °C with activities (TOF, site activity) greater than that of Pt/γ-Al_2O_3. The important conclusions of this study can be summarized as follows:

- All of the Au and Pt catalysts studied showed high initial activities and selectivities, which decreased rapidly during the first 30 min TOS. The activities of the Au catalysts with lower dispersions and higher Cl^- content (Au1 and Au2) and the Pt catalyst remained constant after the initial significant partial deactivation.
- Presence or absence of Cl^- species had little effect on the initial high activities and initial partial deactivation of the Au catalysts.

- SSITKA data showed that the decline in the concentration of reactive intermediates ($N_{\text{I-CO}_2}$) and a drop in the intrinsic site activity (k) were two major reasons for the loss of activity for the Au1 and Au2 catalysts. For the Pt catalyst, only a drop in $N_{\text{I-CO}_2}$ was the major cause of deactivation.
- The Au(Mg) catalyst, which had much smaller Au particles and the least Cl^- content, showed reactivation with TOS after the initial rapid partial deactivation. It can be speculated that this modification of the Au(Mg) catalyst was due to activation/reactivation and regeneration of active sites because of the water formed during the reaction (which was significant at steady state compared with that for the Au1 and Au2 catalysts), leading to increased activity.
- Finally, it can be suggested that Mg, which was present in the Au(Mg) catalyst, may not act as a chemical promoter. Its main role may be only to help reduce Au particle size and Cl^- content during preparation.

The results also provide further insight into the impact of Au particle size and/or Cl^- content (difficult to separate because they are intertwined) on catalyst behavior. It is highly likely that the presence of small Au particles and/or low Cl^- content in a Au catalyst, produced in the presence of Mg citrate during preparation, will cause that catalyst to be significantly affected by the formation of water, resulting in reactivation of the catalyst as the rate of water formation increases with TOS.

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