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Structure sensitivity of selective CO oxidation over Pt/γ-Al_2O_3

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Abstract

In this study, the effect of particle size on the reaction rate and selectivity of preferential oxidation of CO (PROX) reaction was investigated on 2 wt% Pt/γ-Al_2O_3 catalysts prepared by an incipient wetness technique. The particle size of the catalysts was modified by calcination temperature and duration. CO oxidation and preferential CO oxidation reaction were studied on these catalysts at $\lambda = 2(P_{O_2}/P_{CO}) = 1$. The CO oxidation reaction activation energy decreased with increasing particle size, consistent with previous reports. CO reaction orders exhibited no systematic change with respect to particle size, but a minor but systematic decrease in the CO oxidation reaction order was seen with respect to oxygen partial pressure with decreasing particle size, indicating higher selectivity toward PROX reactions at higher λ on larger particles. On catalysts with 69 and 83% dispersions, the light-off curves were identical in hydrogen-free streams, whereas on the catalyst with higher dispersion, the light-off temperature was lower in the presence of hydrogen, indicating that the hydrogen oxidation reaction was more facile on catalysts with more defect sites.

Keywords: CO oxidation; Hydrogen; Structure sensitivity; Platinum

1. Introduction

The preferential oxidation of CO in a H_2-rich mixture (PROX) has long been of considerable technical interest for the purification of hydrogen feed gas. H_2-fueled polymer electrolyte membrane fuel cells (H_2-PEMFCs) have been proposed as an alternative technology for the current conventional internal combustion engine. The use of H_2 in vehicle applications is faced with serious problems associated with the distribution and storage of hydrogen. A promising way to overcome these problems is to produce the hydrogen feed gas on-board, in a fuel-processing unit, by converting a conventional fuel such as natural gas, gasoline, or methanol to a H_2-rich gas mixture. The resulting gas mixture contains significant amounts of CO and is further processed in a water–gas shift reactor. The effluent gas mixture from a typical water–gas shift reactor contains 0.5–1% CO [1]. Unfortunately, even this low CO concentration cannot be tolerated by the H_2-PEMFCs. The H_2-PEMFC anode uses a Pt catalyst, which is very sensitive to CO poisoning at its low operating temperatures. Thus it is crucial to purify the hydrogen feed gas further to reduce the CO concentration to <10 ppm [2].

Selective CO oxidation is the most straightforward, simple, and cost-effective method among the other techniques for CO removal from H_2-rich atmospheres unless the CO tolerance problem is solved in more innovative ways [3]. Recent studies have investigated the effects of O_2/CO ratio in the feed stream, the space-time, and Pt loading on CO conversion and selectivity. It is known that CO conversion is higher at higher oxygen/CO ratios (λ); but as λ increases, the selectivity toward CO decreases. For example, Kahlich et al. [4] obtained 80% CO conversion and 40% selectivity at around 230 °C over 0.5% Pt/Al_2O_3 with an inlet stream of 1% CO and 1% O_2 in the presence of hydrogen. Kim and Lim [5] and Marino et al. [6] found that both the maximum CO conversion and selectivity were 45–50% when stoichiometric amounts of CO and O_2 in excess hydrogen composed the inlet stream. Son and Lane [7] studied the effect of O_2/CO ratio in the feed stream and the contact time on CO conversion and the selectivity over 5% Pt/Al_2O_3 and found that maximum CO conversion increased with increasing O_2 concentration, whereas maximum CO selectivity decreased. They also observed that the CO conversion

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improved with increasing space-time. Manasilp and Gulari [1] investigated the effect of Pt loading on maximum CO conversion and selectivity over Pt/Al_2O_3 (sol–gel) in a feed stream of 1% CO, 1% O_2, and 60% H_2 and found that although the maximum CO conversion increased with increasing Pt loading, the selectivity remained constant.

The structure sensitivity of CO oxidation reaction has already been established. It is known that under ultra-high-vacuum conditions, the CO oxidation reaction is structure-sensitive [8–10]. The reaction rates on the terrace sites of single-crystal catalysts are higher with respect to the rates on the defect sites (step and kink sites). However, the structure sensitivity of CO oxidation is dependent on the experimental conditions for supported metal catalysts. McCarty et al. [11] observed that the specific rate depends on the dispersion of the $Pt/\alpha\text{-}Al_2O_3$ catalyst for low CO concentrations, but found no dependency at high CO concentrations. Recent studies on supported Pt catalysts showed that the CO oxidation is a structure-sensitive reaction, with turnover frequencies (TOFs) of the reaction increase with decreasing dispersion (increasing particle size) of the catalysts [12,13].

In addition to the structure sensitivity of CO oxidation reaction, the structure sensitivity of hydrogen chemisorption over precious metals also has been demonstrated [14–17]. The portal model of hydrogen chemisorption, based on strong evidence from nuclear magnetic resonance spectroscopy, indicates that low-coordination edge and corner sites serve as the adsorption portals for hydrogen. After being blocked by additives, such as alkali promoters [18–20], the adsorption desorption kinetics decrease significantly without much change in their initial adsorption heats. Furthermore, the presence of alkali promoters significantly reduces hydrogen spillover by eliminating the support hydroxyl sites [14,20]. Consequently, the working objective of this study was to eliminate high-energy, electron-deficient edge and corner sites without any other additives, to observe their contribution in the selective CO oxidation reaction.

2. Experimental

The 2% $Pt/\gamma\text{-}Al_2O_3$ catalysts were prepared using an incipient wetness technique. For this, an appropriate amount of the metal salt $Pt(NH_3)_4Cl_2{\cdot}H_2O$ (tetraamine platinum-II-chloride; Johnson Matthey) was dissolved in 2 mL of distilled water/g support to bring the samples to incipient wetness. The solution was impregnated onto the $\gamma\text{-}Al_2O_3$ (Johnson Matthey, 65 m^2/g BET surface area), and the final mixture was dried overnight at room temperature and at 25 °C for 2 h. The batch of the catalyst was divided into four portions, and each portion was calcined in air at a different temperature for 4 h unless otherwise indicated. The calcination temperatures were 410, 450, 500, and 600 °C. The calcined catalysts were reduced in the reactor at 300 °C for 2 h before the experiments. The metal dispersions of the finished catalysts were measured by a modified H_2 chemisorption experiment [21] using previously described equipment [22]. The dispersion of the Pt was calculated by assuming a 1:1 stoichiometry of H:Pt.

The CO oxidation and preferential oxidation of CO of these catalysts were tested in a fixed-bed reactor under atmospheric pressure. To do this, 50 mg of catalyst was placed in a 5-mm-i.d. Pyrex tube. The reactor was placed inside a temperature-controlled (UDC 2300 Universal Digital Controller) tubular furnace (Protherm PTF 12/70/450). The fresh catalysts were exposed to the reactive gas mixture at room temperature. The furnace temperature was increased at a rate of 5 K/min up to 250 °C and kept under the flow of the reactant gases for 2 h. This pretreatment was applied to ensure the reduction of the metal, as well as to attain the steady-state coverage of the surface intermediates under reaction conditions. The gas-phase steady state was monitored on-line with a mass spectrometer. After 2 h, the furnace was cooled (still under the flow of reactive gases) to room temperature. Finally, the temperature of the furnace was increased from room temperature to reaction temperature at a rate of 1 °C/min under the flow of feed gases. The temperature of the catalyst bed was monitored by a thermocouple placed on the Pyrex tube over the catalyst zone. The internal and external bed temperature calibrations done previously indicated that the external measurement did not cause much error [23]. The gas flow rates were adjusted using MKS type 1179A mass-flow controllers. The total flow rate of the feed stream was 200 mL/min. The gas composition during the PROX experiments was 1.6 vol% CO, 0.8 vol% O_2, 20 vol% H_2, and the balance helium. The product gases were analyzed using a quadrupole mass spectrometer (Pfeifer QMS 200) for the PROX reaction, and the gas analysis was performed with a gas chromatograph (HP 4890) equipped with a thermal conductivity detector and a Porapak Q column during the CO oxidation experiments.

Along with CO conversion data, the selectivities of the reaction over different catalysts were also determined. The selectivity was calculated as the ratio of CO consumption over the total oxygen consumption, which includes the loss due to H_2 oxidation as follows:

$$\%\text{selectivity} = \frac{0.5([\mathrm{CO}]_{\mathrm{in}} - [\mathrm{CO}]_{\mathrm{out}})}{[\mathrm{O_2}]_{\mathrm{in}} - [\mathrm{O_2}]_{\mathrm{out}}} \times 100. \tag{1}$$

3. Results and discussion

3.1. Structure sensitivity of CO oxidation

In the first part of this study, the structure sensitivity of CO oxidation was studied over well-characterized Pt/Al_2O_3 catalysts. To do this, 100 mg of catalyst was exposed to a 200-mL/min flow rate of a feed stream comprising 5% CO, 2.5% O_2, and the balance N_2. The conversions were determined from the CO_2 amounts produced. To clarify the structure sensitivity of the CO oxidation reaction, the TOFs (the ratio of the reaction rate to active site density) of catalysts with varying particle sizes are compared. The turnover plots of the catalysts as a function of reaction temperature are given in Fig. 1.

Although the reaction rate for unit amount of catalysts were similar for three catalysts with dispersions of 0.63, 0.29, and 0.20, the TOFs of these catalysts increased with increasing particle size; that is, the activity per surface platinum atom in-

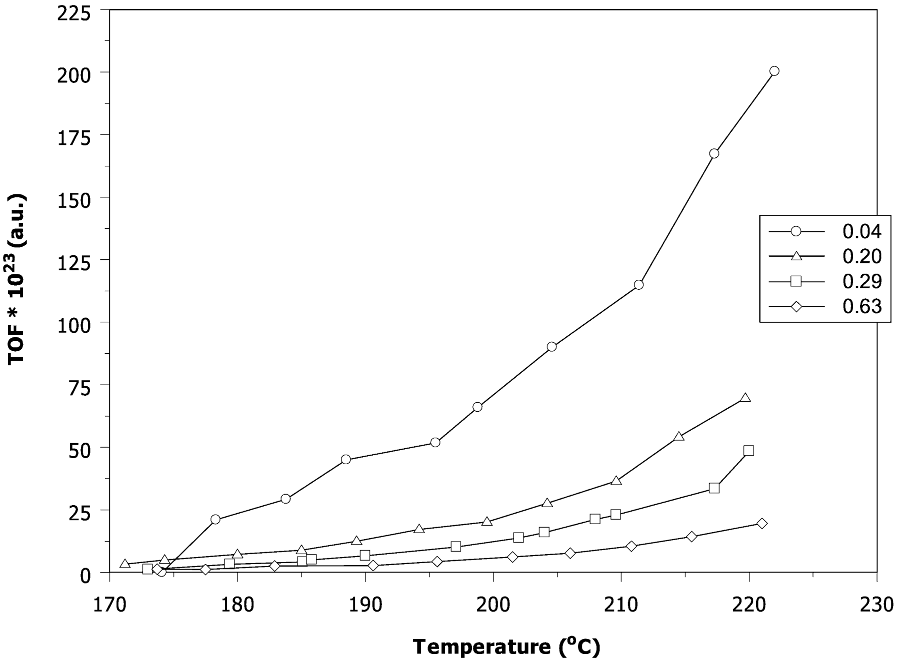

Fig. 1. The effect of the particle size on the turnover frequencies of CO oxidation reaction as a function of temperature.

Table 1
The kinetic parameters measured for CO oxidation reaction as a function of metal particle size

Calcination temperature (°C)	Dispersion	CO reaction order measurement temperature (°C)	The reaction order with respect to CO	O_2 reaction order measurement temperature (°C)	The reaction order with respect to O_2	Activation energy determination temperature range (°C)	Activation energy (kJ/mol)
600	0.04	130	-0.36 ± 0.04	173	1.15 ± 0.05	170–220	96 ± 2
500	0.20	155	-0.50 ± 0.06	188	1.15 ± 0.06	170–220	107 ± 5
450	0.29	158	-0.41 ± 0.05	170	1.04 ± 0.02	170–220	115 ± 3
410	0.63	164	-0.52 ± 0.06	190	0.95 ± 0.05	170–220	120 ± 3

creased with increasing particle size, as shown in Fig. 1. The catalyst with a dispersion of 0.04 had the highest TOF. A similar trend was reported by Gracia et al. [13]. In their study, the TOFs of four catalysts (with dispersions of 0.29, 0.51, 0.63, and 0.76) increased with decreasing dispersion values. They also observed an approximate three-fold increase in TOF as dispersion decreased from 0.63 to 0.29. That increase was nearly the same for our catalysts. Zafiris and Gorte [12] found that a catalyst with a particle size of 14 nm had a nearly 10-fold greater TOF than a catalyst with a particle size of 1.7 nm. As mentioned above, relative fractions of Pt atoms at low-coordination sites (i.e., edges and corners) decreased and the fraction of atoms on planar faces increased with increasing crystallite size [24]. The fact that the fraction of planar faces increased with increasing particle size indicates that flat surfaces have a significantly higher CO oxidation activity per surface site compared with low-coordination edge and corner atoms. This observation is also supported by studies performed on different single-crystal platinum surfaces revealing that CO adsorbed on planar surfaces was more reactive than CO adsorbed at step sites [8–10]. Oxygen molecules adsorbed at step edges are more facile in interaction with CO adsorbed on planar surfaces.

Table 2
The activation energies as a function of metal particle size reported in the literature

Pt particle size (nm)	Dispersion	E_A (kJ/mol)	References
14	–	125 ± 12	[12]
1.7	–	172 ± 17	
5	0.29	55 ± 1	[13]
2	0.63	72 ± 3	
<2	0.76	92 ± 3	

Table 1 presents the apparent activation energies measured in this study, the reaction orders with respect to CO and O_2, and the temperatures at which the order measurements were performed. The apparent activation energy data were extracted from the light-off curves by taking the conversion versus temperature data up to 10% conversion, to ensure the validity of a differential reactor assumption. The reaction orders were obtained isothermally at the temperatures indicated in Table 1; the concentration of the species was varied around the typical reaction conditions, whereas the other species concentration was maintained in excess to avoid any variation in reaction rate with respect to the concentration of that species. Table 2 gives the

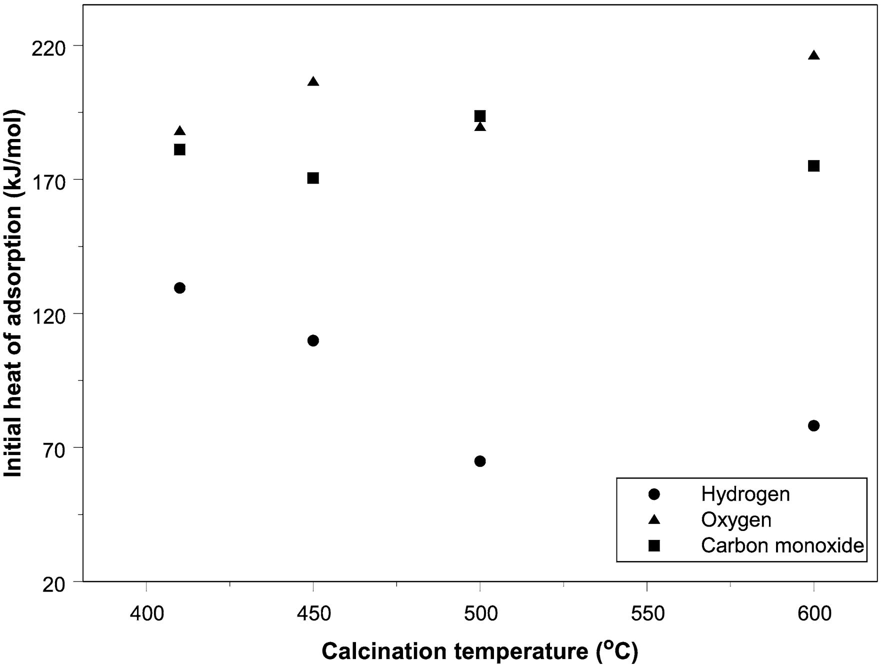

Fig. 2. Initial heats of hydrogen, carbon monoxide and oxygen adsorption as a function of calcination temperature (data from Ref. [25]).

variation of the activation energies with respect to the particle size as reported in the literature for comparison. As it can be seen from Tables 1 and 2, the activation energy decreased with increasing particle size. The values of the activation energies measured in this work were closer to those measured by Zafiris and Gorte [12]. The orders and activation energies of CO oxidation reaction in the literature compiled in a previous study [23] indicated a large variation in activation energies in the 55–170 kJ/mol range. The variation in the reported activation energies depends largely on the measurement conditions and the temperature range at which the activation energies are measured. The important point here is that our data captured the trend in activation energy variation with respect to particle size as reported in similar studies [12,13]. However, there was no specific pattern of variation of the reaction order with respect to CO. On the other hand, the reaction order with respect to O_2 showed a slight variation with particle size, similar to the activation energies. There was a minor but systematic decrease in the oxygen reaction orders with decreasing particle size, indicating that the CO oxidation reaction on smaller particles depended less on the oxygen partial pressure. In other words, an increase in oxygen partial pressure increased the rate of CO oxidation reaction faster on larger particles than on smaller particles. The initial heats of adsorption of CO, O_2, and H_2 on the same catalysts measured previously by adsorption calorimetry [25] are given in Fig. 2. By examining the initial and integral heats of adsorption measured on these catalysts, Uner and Uner [25] concluded that O_2 and CO adsorption processes are not structure-sensitive. When the reaction activation energies measured on these catalysts are consolidated with the heat of adsorption data of Uner and Uner [25], minor but apparent decreases in effective activation energy with increasing particle size can be attributed only to a variation of pre-exponential factors of the elementary reaction steps of the CO oxidation reaction due to the variation in metal particle size.

3.2. *Structure sensitivity of the preferential CO oxidation reaction*

The oxygen conversions, CO conversions, and selectivities with respect to temperature were obtained for four catalysts with different particle sizes for the preferential oxidation of CO in the presence of hydrogen. For these studies, a different set of catalysts was prepared with slightly different dispersion values than those used in the CO oxidation studies discussed earlier. The gas analysis was performed using a quadrupolar mass spectrometer to allow for continuous probing of the reaction and to facilitate simultaneous analysis of oxygen, carbon monoxide, carbon dioxide, hydrogen, and water content. The CO oxidation reaction was studied in the presence and absence of hydrogen. The results are presented in terms of oxygen conversion values in Fig. 3. Both feed streams were composed of 1.6% CO, 0.8% O_2, and the balance helium. For hydrogen-containing streams, 20% H_2 was also added to the feed. The concentration of oxygen within the catalyst bed dropped to zero at a certain temperature for four catalysts for both feed streams. The T_{50} (the temperature at which conversion of oxygen reaches 50%) of the reaction increased with decreasing dispersion, as was observed during CO oxidation in the absence of hydrogen. The T_{50} of the reaction over various catalysts shifted to lower temperatures in the presence of hydrogen (Table 3). A decreased ignition temperature in the presence of hydrogen was also observed by Kahlich et al. [4] and Oh and Sinkevitch [26]. It is interesting to note that under the reaction conditions imposed in this set of experiments, the catalysts with 69 and 83% dispersions had nearly the same oxygen consumption rates in the absence of hydrogen. But when hydrogen was introduced into

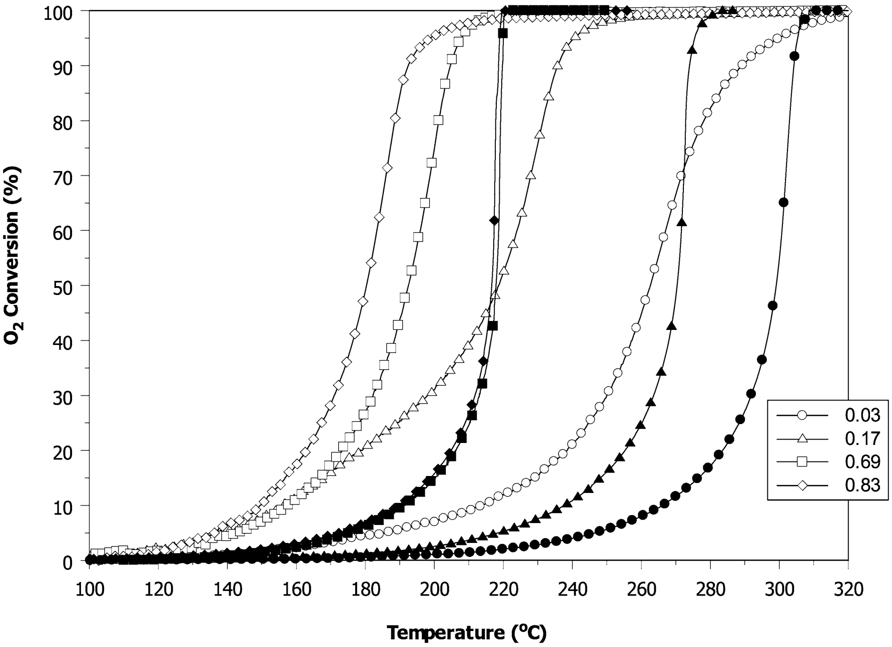

Fig. 3. The oxygen light off curves of CO oxidation (open symbols) and selective CO oxidation (filled symbols) reactions. (Total flow rate: 200 mL/min, catalyst bed: 0.05 g of catalyst.)

Table 3

Temperature required to achieve 50% conversion of CO during oxidation reactions over 2% Pt/γ-Al_2O_3 catalysts in the presence and in the absence of hydrogen

Dispersion	T_{50} (°C)		Difference between the T_{50}'s
	Without H_2	With H_2	
0.83	217	180	37
0.69	218	192	26
0.17	270	219	51
0.03	299	263	36

the flow stream, the 50% conversion temperature of the 83% dispersion catalyst was 12 K lower than that of the 69% dispersion catalyst. This is a clear indication of more facile hydrogen oxidation on metals with higher dispersion, confirming that the low-coordination sites indeed increased the rate of hydrogen adsorption and relevant subsequent processes during a chemical reaction [14,15,17].

The CO conversions and oxygen selectivities for various catalysts in the presence of hydrogen are given in Fig. 4. The CO conversions increased with increasing temperature, reaching a maximum at a certain temperature. The maximum CO conversion was around 40% for the entire set of catalysts with varying dispersions. After the peak point, it decreased to about 25–30% at 350 °C due to the reverse water–gas shift reaction between carbon dioxide and hydrogen in the gas phase. This behavior was observed for all catalysts of varying particle sizes and did not change with the repeat experiments, indicating that particle size was not affected during the reaction.

A nearly identical trend was observed for the selectivity of the CO oxidation reaction (Fig. 4b). Below 100 °C, selectivity was <5%. With increasing temperature it increased, reaching a maximum of 35–45% for four different catalysts. As in CO conversion, it decreased to approximately 25–35% when the temperature was increased to 350 °C, due to the reverse water–gas shift reaction. The temperature for the maximum CO conversion coincided with the minimum temperature for complete conversion of oxygen.

The same trend has generally been reported in the literature [1,4,5,27,28], with CO conversion increasing with increasing reaction temperature, reaching a maximum, and finally decreasing. The selectivity has also been found to show a similar trend with temperature. The selectivity and CO conversion depend mainly on the O_2/CO ratio ($\lambda = 2P_{O_2}/P_{CO}$). CO conversion increases with increasing λ, reaching 100% when λ is >1.5. On the other hand, the selectivity of CO oxidation decreases with increasing λ. For instance, Woostch et al. [27] reported that the maximum selectivity decreased from 76 to 50% when λ was increased from 0.8 to 2. In addition, T_{max} (the temperature at which maximum selectivity is reached) was changing in all studies.

At this point, it is useful to define an instantaneous selectivity,

$$S = \frac{r_{CO}}{r_{CO} + r_{H_2}} = \frac{1}{1 + (r_{H_2}/r_{CO})}, \tag{2}$$

where

$$r_{CO} = k_{CO} e^{-(E_{A_{CO}}/RT)} P_{CO}^{a} P_{O_2}^{b} \tag{3}$$

and

$$r_{H_2} = k_{H_2} e^{-(E_{A_{H_2}}/RT)} P_{H_2}^{c} P_{O_2}^{d}. \tag{4}$$

Examining Eq. (2) along with Eqs. (3) and (4) leads to some general conclusions. First, at very low conversions, where rates are nearly zero, selectivity must be very close to 1. Furthermore, depending on the relative magnitudes of the rates of

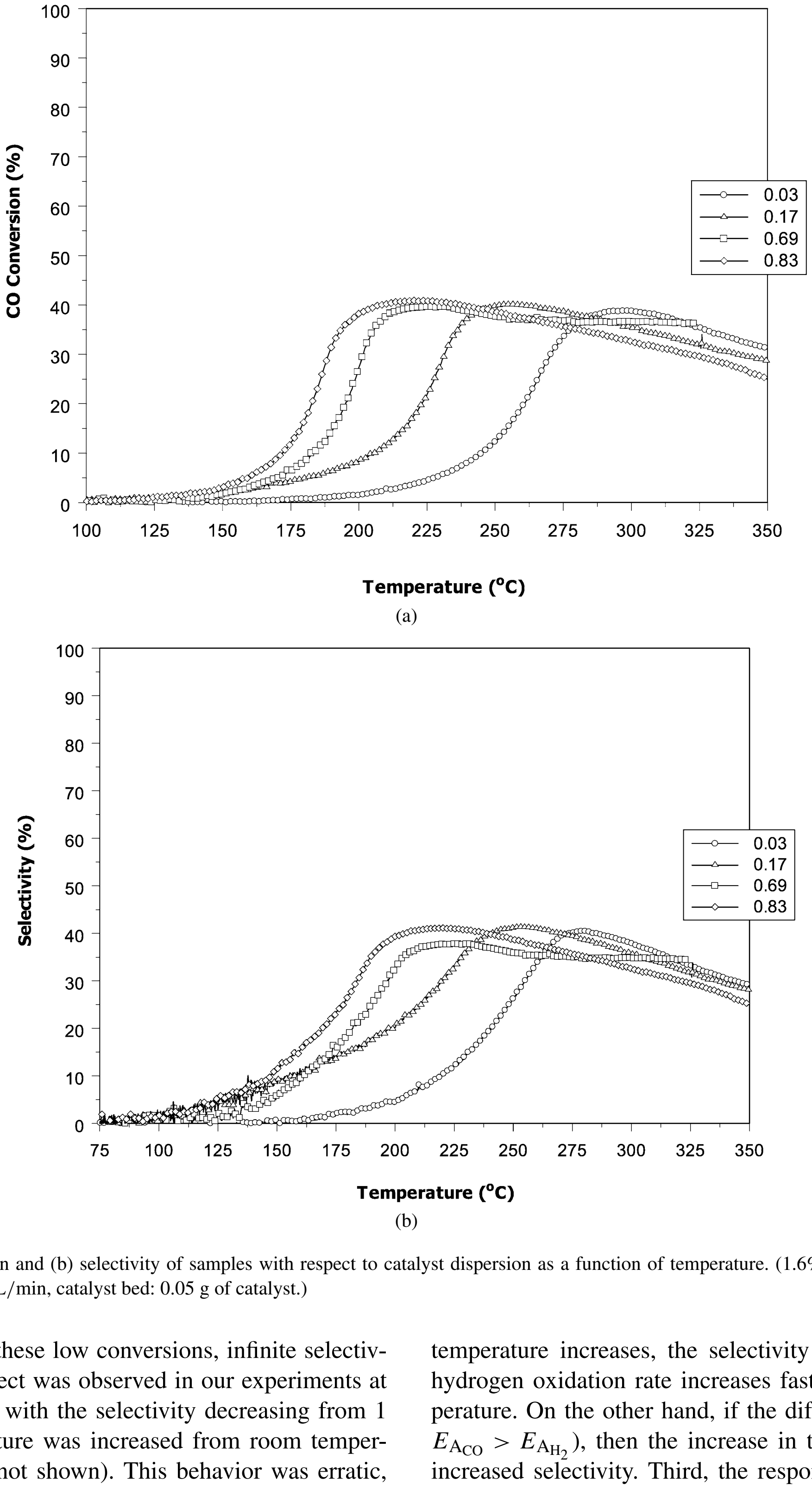

Fig. 4. (a) The CO conversion and (b) selectivity of samples with respect to catalyst dispersion as a function of temperature. (1.6% CO, 0.8% O_2, 20% H_2 and balance He; flow rate: 200 mL/min, catalyst bed: 0.05 g of catalyst.)

CO or H_2 reactions at these low conversions, infinite selectivity is possible. This effect was observed in our experiments at very low temperatures, with the selectivity decreasing from 1 to zero as the temperature was increased from room temperature to ∼70 °C (data not shown). This behavior was erratic, with low-temperature selectivity values fluctuating in a manner similar to the fluctuations of the CO oxidation reaction. Second, the response of the selectivity to temperature is dictated by the sign and the magnitude of the difference between the activation energy of the hydrogen oxidation reaction and the activation energy of the CO oxidation reaction, $E_{A_{H_2}} - E_{A_{CO}}$. If this difference is positive (i.e., $E_{A_{H_2}} > E_{A_{CO}}$), then, as the temperature increases, the selectivity decreases, because the hydrogen oxidation rate increases faster with increasing temperature. On the other hand, if the difference is negative (i.e., $E_{A_{CO}} > E_{A_{H_2}}$), then the increase in temperature will lead to increased selectivity. Third, the response of the selectivity to λ is a strong function of the relative orders of the CO oxidation and hydrogen oxidation reactions with respect to oxygen, b–d. It can be deduced from Eq. (3) that if the oxygen order in hydrogen reaction is greater than the oxygen order in the CO reaction, then as the oxygen partial pressure increases, the selectivity decreases, which indeed was observed in many of the studies.

In this study, λ was used as 1; that is, a stoichiometric amount of CO and O_2 were fed into the reactor. Under these conditions, Son and Lane [7] observed that the CO conversion and selectivity changed between 40–55% and 42–58%, respectively, between 150 and 250 °C. In that study, both CO conversion and selectivity were greater than the values obtained in the present study. Kim and Lim [5] found a maximum CO conversion of 45% and a maximum selectivity of 48%. Marino et al. [6] found that the CO conversion and selectivity showed similar trends and were nearly the same after a certain temperature; both values increased from 35 to 50% with a temperature increase from 200 to 300 °C. Their findings are in excellent agreement with our results.

Although the hydrogen oxidation occurs even at room temperature in the absence of CO, the reaction is ignited at much higher temperatures in the presence of CO over a platinum catalyst, due to the poisoning effect of CO. Higher temperatures favor CO desorption and thus decrease the poisoning effect of CO [29]. The CO-TPD data of Kahlich et al. [4] demonstrate that only ∼10% of the initial CO coverage remained on the surface at 250 °C. After $T_{\max}$, oxygen was depleted completely, and water vapor in the gas phase entered the reverse water–gas shift reaction, thus decreasing both CO conversion and the selectivity.

In the low-temperature region, the selectivity increased and reached a maximum. Kahlich et al. [4] explained this increase by the decreased hydrogen coverage with increasing temperature. They proposed that H_2 and CO are coadsorbed on the surface, so that the selectivity should depend only on the ratio of the H_2 and CO coverages. The increased selectivity at low temperature is caused by the difference between the heats of adsorption of H_2 and CO. The lower adsorption energy of hydrogen (∼80 kJ/mol on Pt(111) [30] and data in Fig. 2) compared with that of CO (∼140 kJ/mol on Pt(111) [31] and data in Fig. 2) leads to reduced hydrogen coverage with increasing temperature, whereas CO coverage remains close to saturation. This causes a decrease in Θ_{H_2}/Θ_{CO}, and thus increased selectivity occurs with increasing temperature.

The fractions of high- and low-coordination atoms change with varying catalyst dispersion. The fraction of planar atoms increases with increasing particle size, whereas the fractions of corner and edge atoms decrease [24]. According to Zafiris and Gorte [12] and Gracia et al. [13], the CO oxidation reaction is faster on planar sites of the Pt metal surface because the TOFs of the reaction increases with increasing particle diameter. Thus, the selective CO oxidation reaction is expected to be a structure-sensitive reaction. Because the CO oxidation reaction is faster on planar sites, the selectivity of low-dispersed catalysts (with greater particle size) is expected to be greater compared with that of high-dispersed catalysts.

Not many studies in the literature have investigated the structure sensitivity of the selective CO oxidation reaction. Only Son et al. [32] have examined the activity and selectivity of this reaction with varying particle sizes. They prepared two types of $Pt/\gamma\text{-}Al_2O_3$ catalysts with two different pretreatment methods, and found that water-pretreated catalyst showed higher CO conversion and selectivity over a temperature range of 27–200 °C. In addition, according to XRD and TEM analysis, they found small metallic Pt particles (∼2 nm) on the water-pretreated catalyst and larger metallic Pt particles (∼16 nm) on the standard pretreatment catalyst. Therefore, they argued that the higher activity and selectivity were caused by the smaller particles on the water-pretreated catalyst below 200 °C. The selectivity of the water-pretreated catalyst decreased from 100% to ∼40% as the temperature increased. On the catalysts prepared via a standard technique, the selectivity started from a relatively low value and again reached 40% at 250 °C. The discrepancy between our selectivity values and those reported by Son et al. [32] on highly dispersed catalysts may be due to a number of factors, including the differences in space-times, the differences in gas composition, and the fact that the water-pretreated catalysts could have a finite coverage of the surface hydroxyl groups, which are known to dramatically alter the CO oxidation kinetics and mechanism [33].

Kahlich et al. [4] and Han et al. [34] have demonstrated that the reaction kinetics and orders of CO oxidation do not change in the presence of hydrogen. If this argument were taken as correct, then it could be further argued, based on the reaction orders measured in hydrogen-free streams in this work, that a slight increase in oxygen partial pressures would have improved the selectivity and improved CO conversion values faster on larger particles than on smaller particles given that the oxygen orders are larger on larger particles. The support of this argument comes from a study by Pedrero et al. [35] who demonstrated through very well-designed experiments that the loss of selectivity was due to the reaction of spilled-over hydrogen on the support sites. Given that alkali promoters can titrate the OH groups on the support surface [20] and can inhibit hydrogen spillover [36], they demonstrated that in the presence of alkali metals, the PROX reaction can have selectivities as high as 90% when $\lambda = 2$. Pedrero et al. [35] further determined that the turnover rates on alkali-promoted catalysts were higher than those on the unpromoted ones, similar to the results obtained in this work and in previous studies of CO oxidation [12,13]. Higher turnover rates on alkali-promoted catalysts indicate that the defect-like edge and corner sites could have been blocked by the alkali promoters, even though the preparation method used by Pedrero et al. [35] required that alkali promoters be deposited on the support and metals be loaded onto the alkali-promoted support surface. In a previous study, we observed that alkali promoters present in the $\gamma\text{-}Al_2O_3$ migrated to the metal surface and blocked the defect-like sites of Pt particles [37]. Furthermore, it must be noted that hydrogen spillover is also a structure-sensitive reaction found to be more facile on highly dispersed metals [14].

We make one final comment to clarify concerns about the influence of the residual chlorine originating from the catalyst precursor. We can rule out the possibility that the effects that we observed are due to chlorine poisoning for several reasons, as follows:

(i) The effect of the calcination temperature on chlorine removal is expected to be in the direction of removal of more chlorine for the catalysts calcined at higher temperatures. Therefore, the catalysts calcined at lower temperatures should have had less activity than those calcined at higher temperatures under chlorine poisoning conditions. However, the opposite trend was observed.

(ii) The effect of chlorine on the oxygen and hydrogen chemisorption characteristics of 0.5% Pt/TiO_2 and of the CO oxidation reaction on 1% Pt/CeO_2 were monitored previously in our group by carefully conducted experiments [22,23,38]. We observed that calcination was sufficient to remove the chlorine contamination over 0.5% Pt/TiO_2, but subsequent hot water elutriation did not improve either the dispersion measured by hydrogen chemisorption or the oxygen chemisorption characteristics of the catalyst. Similar tendencies were observed for the dispersion and CO oxidation rate on 1% Pt/Al_2O_3 [23]; however, significant activity loss occurred on 1% Pt/CeO_2 when CeO_2 was prepared from a chlorine precursor requiring hot water elutriation for chlorine removal [23].

(iii) The electronic effect of chlorine contaminant would be reflected in the initial heats of adsorption of oxygen and CO measured by adsorption microcalorimetry. We did not measure such variations on the same catalysts (Fig. 2), ensuring that the effects are due to variation of the catalyst structure, not to chlorine contamination.

Therefore, we propose that the structure sensitivity of the CO oxidation reaction and of the hydrogen chemisorption processes previously reported in the literature can be successfully combined to tailor catalysts that are selective in preferential CO oxidation.

4. Conclusion

In this work, 2% Pt/γ-Al_2O_3 catalysts were prepared, and catalysts with different particle sizes were obtained by changing the calcination temperature during preparation. The catalytic properties of the catalysts were compared for the CO oxidation and PROX reactions. During the CO oxidation reaction, the turnover rates were higher on larger particles. The CO oxidation reaction orders with respect to oxygen partial pressures increased with increasing particle size, indicating higher dependency of the reaction kinetics on the oxygen partial pressure on larger particles. The light-off temperatures and T_{50} of the CO oxidation reaction decreased when hydrogen was added to the feed stream. On catalysts with 69 and 83% dispersion, the light-off curves were identical in hydrogen-free streams and the light-off temperature of the catalyst with higher dispersion was lower, indicating that hydrogen oxidation reaction was more facile on catalysts with more defect sites. No difference was seen in the maximum selectivity values of the catalysts with different dispersions. However, the maximum selectivity temperature increased with increasing particle size.

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