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The study of the active surface for CO oxidation over supported Pd catalysts

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CO oxidation was investigated on various powder oxide supported Pd catalysts by temperature-programmed reaction. The pre-reduced catalysts show significantly higher activities than the pre-oxidized ones. Model studies were performed to better understand the oxidation state, reactivities and stabilities of partially oxidized Pd surfaces under CO oxidation reaction conditions using an *in situ* infrared reflection absorption spectrometer (IRAS). Three O/Pd(100) model surfaces, chemisorbed oxygen covered surface, surface oxide and bulk-like surface oxide, were prepared and characterized by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The present work demonstrates that the oxidized palladium surface is less active for CO oxidation than the metallic surface, and is unstable under the reaction conditions with sufficient CO.

CO oxidation, *in-situ* IRAS, temperature-programmed reaction, palladium, catalytically active surface

1 Introduction

Carbon monoxide, as a toxic gas to human beings and other creatures, is one of the major polluting gases from automobile exhausts as well as industrial gas emissions. Efforts have been made for years to develop better catalytic systems for catalytic oxidation of CO, among which platinum group metal based catalysts exhibit excellent performance toward CO oxidation in an oxidizing condition similar to that of the automobile exhausts. Meanwhile, as a probe and model reaction, the catalytic oxidation of CO on Pt-group metals serves as a prototype catalytic reaction in catalysis and surface chemistry fields, particularly in characterizing and identifying different chemisorbed species and intermediates. Catalytic oxidation of CO by Pd catalysts has been intensively investigated, both by using UHV-based surface science and by traditional heterogeneous catalytic studies. However, arguments still exist about some fundamental questions in the catalytic process, especially the active phase and structure details of catalytically active Pd species.

Goodman and co-workers [1,2], using UHV apparatus combined with high pressure *in-situ* reaction cell, concluded that there is no so-called pressure gap between CO oxidation reactions under low and relatively high pressures, that is to say, the Langmuir-Hinshelwood kinetic process governs a wide pressure range. Metallic Pd surface rich of chemisorbed oxygen has been found to be the most catalytically active surface under both the low and high pressure conditions, although the highly active state is relatively shorter under the high pressure condition than that under the low pressure one limited by the mass transfer. However, Frenken *et al*. [3,4] observed the formation of metal oxides under the reaction conditions and purposed oxides as the higher active surfaces. Zemlyanov *et al*. [5] and Zorn *et al*. [6] proposed that reduced Pd metal surface (Pd^0) as well as partially charged $Pd^{\delta+}$ correspond to a much higher activity toward CO oxidation compared with palladium oxide. They found that $Pd^{\delta+}$ can be easily reduced by CO and that a reduced Pd metal surface covered by chemisorbed oxygen is

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*Corresponding author (email: chenms@xmu.edu.cn) the active phase responsible for the high catalytic activity of CO oxidation. Based on the supported Pd/Al_2O_3 system, Iglesias-Juez *et al.* [7] reported that Pd(I) may be involved in the active surface with a higher activity for CO/NO+O_2 recycling.

Our previous model studies demonstrated that there exists a highly active state for CO oxidation on Rh, Pd, and Pt when O_2/CO ratio is higher than stoichiometric value [8,9]. By using a wide spectra range (4000–450 cm^{-1}) *in-situ* reflection absorption infrared spectroscopy (IRAS) combined with isotopic $^{18}O_2$ [10], we demonstrated that the most active state corresponds to a metallic Pd surface that is rich of chemisorbed oxygen. In this study, we carefully compared the relative activities for CO oxidation on the pre-reduced and pre-oxidized supported Pd catalysts, 0.2 wt% and 1 wt% Pd/SiO_2, Pd/Al_2O_3 and Pd/TiO_2, using temperature-programmed reaction (TPRe). Detailed studies of the relative reactivities of different partially oxidized Pd(100) surface with CO by IRAS were performed for comparison.

2 Experimental

2.1 Catalyst preparation and characterization

Commercial high-surface area SiO_2, Al_2O_3 and TiO_2 were used as supports. Pd was deposited onto the supports by an impregnation method using $Pd(acac)_2$ toluene solution as a precursor. The supports were added into the certain amount of the precursor solution by stirring at room temperature for an hour, and then aged for 12 h. The mixtures were dried by warming up, and conditioned at 373 K for 2 h. The obtained precursors were calcined at 573 K for 2 h. Particle sizes and Pd dispersion were determined by powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Nitrogen physisorption at 77 K (BET measurement), transmission electron microscope (TEM) and *in-situ* Fourier transmission infrared spectroscopy (FTIR). The detail preparation and characterization results were reported previously [11].

2.2 Temperature-programmed reaction

The CO oxidation reaction was carried out in a continuous-flow fixed-bed quartz micro-reactor. The amount of catalyst used was 500 and 100 mg for the 0.2 wt% and 1.0 wt% catalysts, respectively. The pre-oxidized catalyst was pretreated with O_2 at 573 K for 30 min, while the pre-reduced one was pretreated similarly with O_2 following by reduction with H_2 at 573 K for 30 min. Before switching to the reactant gas, the catalyst was purged by He for 15 min. Reaction gas of CO:O_2:He (volume ratio, 1:1:98), pre-purified by a liquid N_2 trap to remove water vapor and other contaminants, was flowed at an ambient pressure through the reference cell of the TCD detector in a gas chromatograph (GC) and then to the catalyst bed at a rate of 50 mL/min. The outlet gas from the catalyst bed was trapped by another liquid nitrogen trap to remove the formation CO_2, and then flows through the measuring cell of the TCD detector. The CO conversion was calculated from the change in concentration between the inlet and outlet gases measured by the TCD detector, and crosschecked with an on-line GC equipped with a methanation convertor and a flame ionization detector (FID) [12]. The catalytic activity was indicated by the formation rate of CO_2 per loaded Pd atom per second (turnover frequency). The temperature increasing rate in TPRe is 10 K/min.

2.3 Model catalyst study

Model studies were carried out in a batch reactor connected to an ultrahigh vacuum (UHV) system and equipped with basic surface science techniques. The reactor was also furnished with an *in-situ* Bruker vacuum-type infrared reflection absorption spectrometer (Germany) and a MKS precise pressure sensor. The sample was heated resistively with the temperature measured by a C-type thermocouple. This system can accommodate a pressure range of UHV to 1 atm and sample temperature range of 80–1200 K. A Pd(100) sample purchased from Princeton Scientific Corporation was used. The sample was cleaned by repeated Ar^+ sputtering following a subsequent annealing at 1100 K in UHV. The cleanness was confirmed by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). The clean sample was then transferred into the reaction cell under UHV for *in situ* IRAS measurements [10]. The high purity CO and O_2 (Hong Kong Specialty Gases Co., Ltd., China) were further cleaned by a liquid nitrogen trap before being introduced into the reaction cell. Note that the vapor pressures at the liquid nitrogen temperature are about 395 Torr for CO and 152 Torr for O_2, which are much higher than the pressures used in the present experiments.

3 Results and discussion

The activities for CO oxidation over various supported Pd catalysts measured by TPRe are shown in Figure 1. The CO oxidation was carried out at a wide temperature range of 300–500 K with a same weight hourly space velocity of 300 L/(g_{Pd} h). The Pd/TiO_2 catalysts show better low-temperature catalytic activities, and even more obvious as the Pd loading decreased. For the different supports, as shown in Figure 1, catalytic activities displayed an increasing order of Pd/SiO_2<Pd/γ-Al_2O_3<Pd/TiO_2, which had been shown to be related with the support and the dispersion of Pd [11]. Of all the six investigated catalysts, the activities on the pre-reduced ones are significantly higher than those on the corresponding pre-oxidized ones. Note that an oxygen excessive reactant, CO:O_2:He=1:1:98, was used. This demonstrates that the oxidized Pd surface is less active for CO oxidation than the reduced one at the present investigated

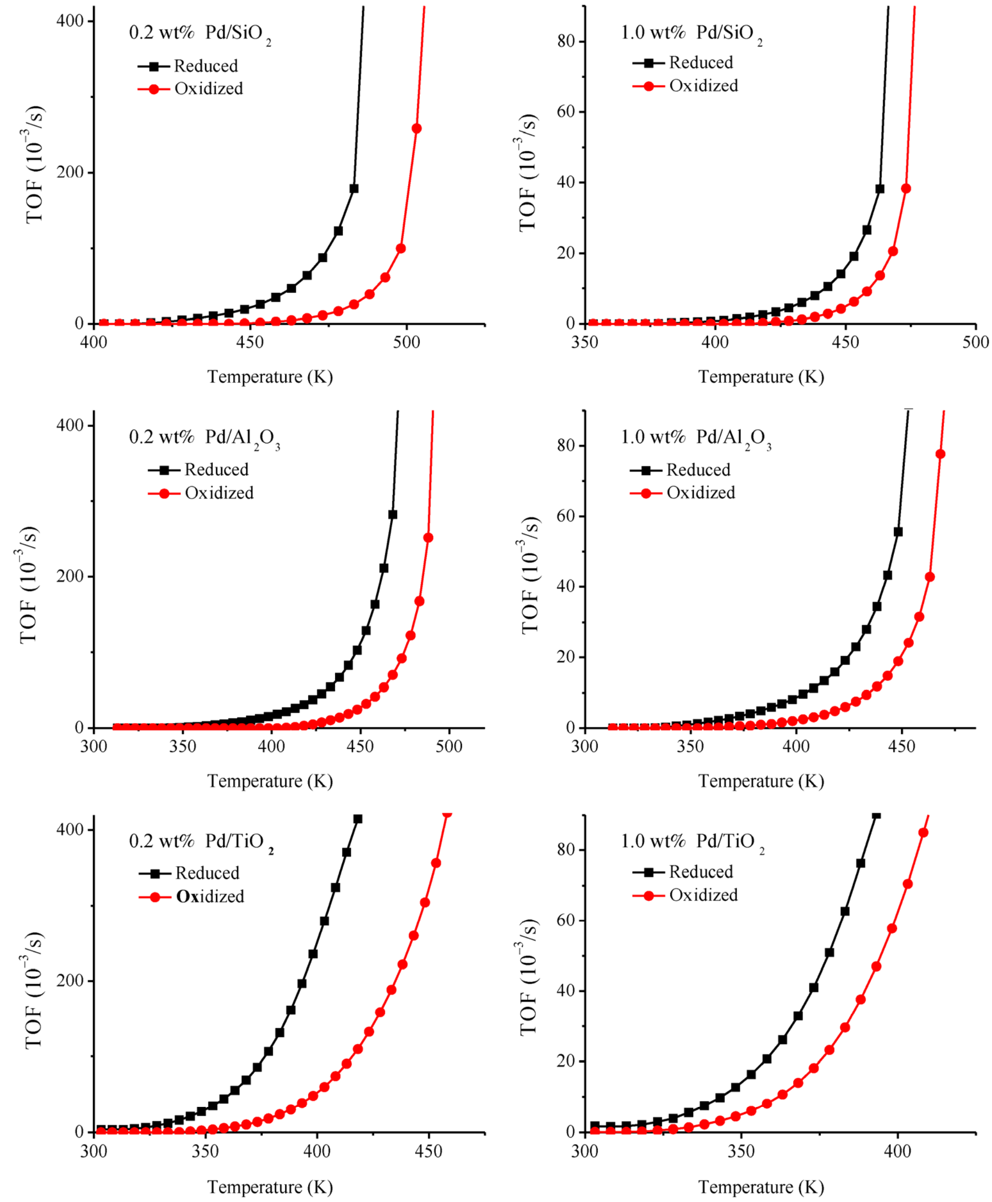
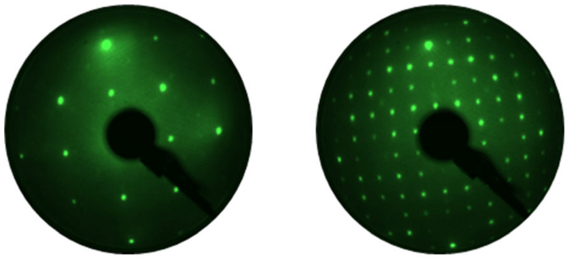


Figure 1 CO_2 formation rates as functions of the reaction temperature for CO oxidation on various supported Pd catalysts: black and red denote pre-reduced and pre-oxidized, respectively. The reaction was carried out under atmospheric pressure at a CO:O_2:He ratio of 1:1:98 and flow rate of 50 mL/min. The amounts of catalysts used were 500 and 100 mg for the 0.2 wt% and 1 wt% catalysts (60–80 mesh), respectively. The temperature ramping rate is 10 K/min.

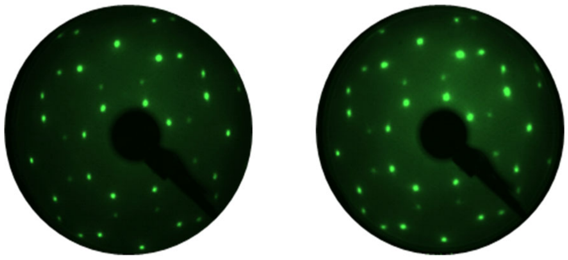
temperature range, confirming our previous observation that oxidized surface is not the most active surface [9,10].

To understand the surface changes during CO oxidation, we performed surface chemistry study on a Pd(100) surface. First, LEED patterns were recorded for different pre-treated surfaces, including chemisorbed oxygen covered surface, surface oxide and bulk-like surface oxide. The clean (100) surface shows a sharp diffraction pattern of (1×1). After exposing the Pd(100) surface to O_2 at a pressure of 1×10^{-7} Torr (60 L) at a temperature of 450 K for 10 min, a sharp *p*(2×2) pattern was observed (as showed in Figure 2(a)). The *p*(2×2) structure had been shown to be a chemisorbed oxygen surface with an oxygen coverage of 0.25 ML [13,14]. At higher amount of O_2 dosing and higher temperature, surface oxides with *p*(5×5) or ($\sqrt{5}\times\sqrt{5}$)R27° structures were observed (as showed in Figure 2(b) and (c)). A trilayer structure of O–Pd–O– was proposed for the ($\sqrt{5}\times\sqrt{5}$)R26.7°–O on both Pd(100) [15] and Pd(111) [16]. Orent *et al.* [17] proposed that the *p*(5×5) and ($\sqrt{5}\times\sqrt{5}$)R27° arrangements resemble the PdO(110) and (001) planes with oxygen coverages of 0.7 and 0.8 ML, respectively.

The Pd(100)–($\sqrt{5}\times\sqrt{5}$)R26.7°–O surface with a sharp LEED pattern prepared by oxidizing the clean Pd(100) surface in 10^{-4} Torr O_2 at 600 K shows a clear IR band at



(a) 60 L O_2 at 450 K (b) 600 L O_2 at 500 K



(c) 600 L O_2 at 550 K (d) 10^{-4} Torr O_2 at 600 K for 10 min

Figure 2 The LEED patterns of (a) $p(2\times2)$, (b) $p(5\times5)$, (c, d) $(\sqrt{5}\times\sqrt{5})$R27° of O/Pd(100) surfaces prepared by controlling the different oxygen exposing amount and temperatures. The beam energy for the LEED patterns is E_p=60 eV.

548 cm^{-1}, which can be attributed to the asymmetrical vibration of Pd$^{\delta+}$–O (Figure 3). In contrast, the surface bulk-like oxide (PdO) was confirmed both by the O/Pd AES ratio and the two IR bands at 669 and 615 cm^{-1} using IRAS [10] when exposing the surface to O_2 with a pressure higher than 0.01 Torr at 600 K. Note that such surface bulk-like oxide does not show a sharp LEED pattern due to lack of long-range ordering, and that it mimics the pre-oxidized surface of powder oxide supported Pd catalysts.

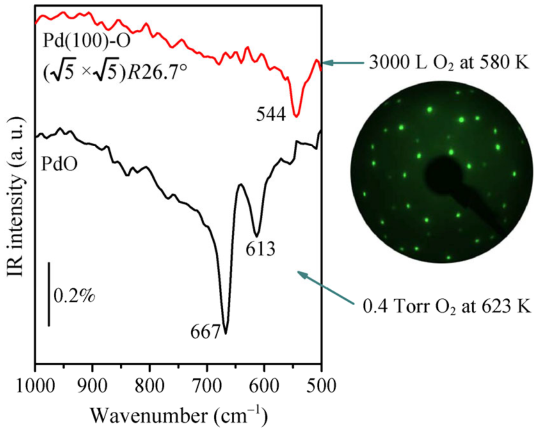


Figure 3 IRAS spectra for a Pd(100)–$(\sqrt{5}\times\sqrt{5})$R26.7°–O and a bulk-like PdO/Pd(100). The Pd(100)–$(\sqrt{5}\times\sqrt{5})$R26.7°–O surface was prepared by exposing the Pd(100) surface to 10^{-4} Torr O_2 at 580 K, which shows a sharp $(\sqrt{5}\times\sqrt{5})$R26.7° LEED pattern. The bulk-like PdO was prepared at 623 K in 0.4 Torr O_2 for 10 min.

Next, the reactivities for the above partially oxidized surfaces with CO were investigated by *in-situ* IRAS. The $p(2\times2)$ chemisorbed O covered palladium surface was cooled down to 90 K to get a background, and then exposed to 0.01 Torr O_2, no peak was observed between 1700–2500 cm^{-1} (Figure 4(a)). The IR bands at 1986 and 2100 cm^{-1} appear after the surface was exposed to 0.01 Torr CO. The sample was annealed to the indicated temperatures in the mixture of CO/O_2 and then cooled to 120 K for IR measurements. According to Goodman *et al.*, 1986 cm^{-1} was assigned to the adsorption of CO in the two-fold bridging sites on Pd(100), and 2100 cm^{-1} presented the CO atop adsorption on the Pd atom that is directly bonded to an O atom(s) (Figure 5). However, the intensity of 1986 cm^{-1} peak

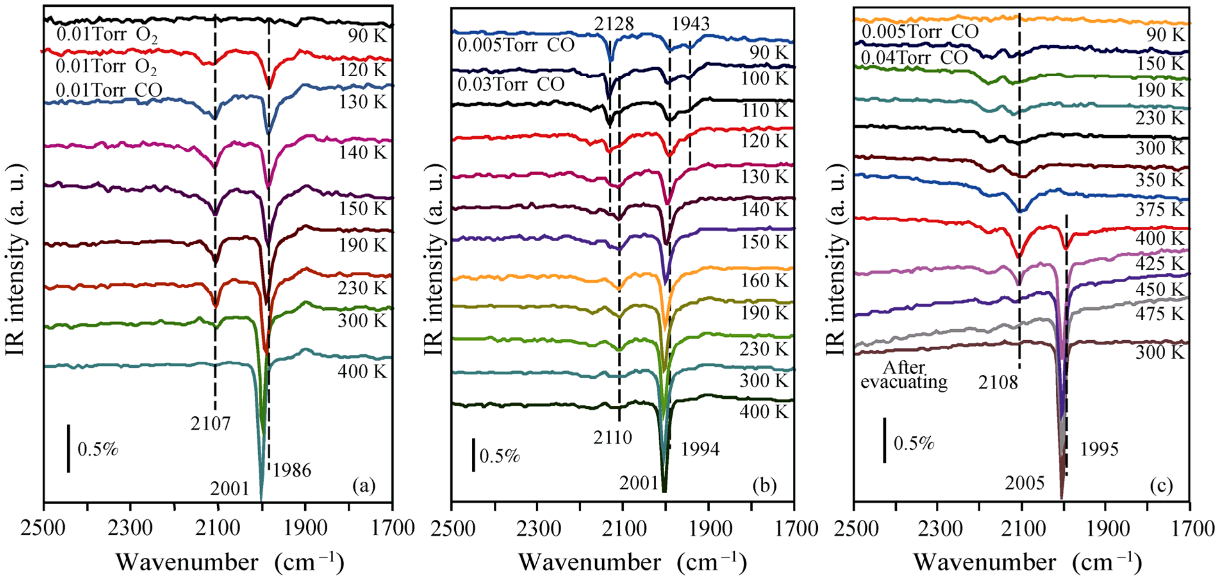


Figure 4 IRAS spectra for CO adsorption as a function of surface temperature on three O/Pd(100) model surfaces. (a) $p(2\times2)$ chemisorbed O covered Pd surface; (b) $(\sqrt{5}\times\sqrt{5})$R27° surface oxide; (c) bulk-like surface oxide.

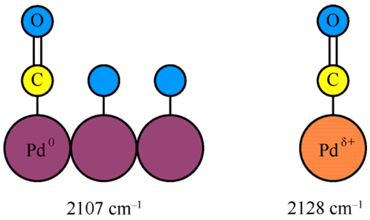


Figure 5 Schematics for IR bands of 2107 and 2128 cm^{-1}.

was increased as the surface temperature increased, while the 2100 cm^{-1} peak vanished when the temperature was higher than 300 K. After annealed to 400 K, CO exhibited a main IR absorption band at 2001 cm^{-1}, corresponding to CO saturation adsorption on the metallic Pd(100) surface [18].

On the $(\sqrt{5}\times\sqrt{5})\mathrm{R}27^\circ$−O surface, IR bands of 2128, 1994 and 1943 cm^{-1} appear at 120 K (Figure 4 (b)), which can be attributed to CO adsorbed on a partially oxidized Pd surface [14,19,20]. The bands of 2128 and 1943 cm^{-1} eventually disappear, while a new band of 2110 cm^{-1} appears together with the 1994 cm^{-1} band as the temperature increases up to 110 K. These features are similar with those on the chemisorbed oxygen covered surface, which means that the $(\sqrt{5}\times\sqrt{5})\mathrm{R}27^\circ$−O surface is reduced to a chemisorbed oxygen covered surface even in a CO and O_2 mixture at temperatures between 100–130 K. In contrast, there are no obvious CO adsorbed peaks on the bulk-like surface oxide (Figure 4(c)), which is consistent with previous observation [14,20,21]. Only at temperature higher than 350 K there appears an IR band of 2108 cm^{-1} and follows by a 1994 cm^{-1} peak as the temperature increases up to 375 K. These features are similar with those on the metallic surface, suggesting that bulk-like PdO was directly reduced to a metallic Pd surface at 350 K. This confirms that PdO is not very active and unstable at the active reaction temperatures under the reaction conditions.

The above *in-situ* IRAS measurements show that all the three O/Pd surfaces, chemisorbed oxygen covered surface, surface oxide and bulk-like surface oxide, can be reduced to the metallic surface in CO:O_2=1:1 mixture at a temperature below the reaction temperature (about 500 K on bulk-like Pd). Among which the chemisorbed oxygen covered surface and surface oxide exhibit much higher reactivities toward CO even in the presence of O_2. This suggests that oxides may not exist under the reaction conditions with sufficient amount of CO. The significantly low catalytic activities for CO oxidation on the pre-oxidized catalysts than those on the pre-reduced ones observed in the TPRe evidences that oxide surfaces are less active for CO catalytic oxidation. Regarding that the pre-oxidized surface may have been partially reduced during TPRe, the observed catalytic contribution on the pre-oxidized surfaces might mainly be attributed from such partially reduced sites at low temperature. This is supported from that the on-set temperatures on the pre-oxidized catalysts are much higher than those on the pre-reduced ones (Figure 1). In fact, the second run of the TPRe on the pre-oxidized catalysts is comparable with that of the pre-reduced ones, confirming that the surface is fully reduced under the reaction conditions at sufficient high temperature, as shown in Figure 6. All together, the palladium oxide surface is highly impossible as a catalytically active surface corresponding to a higher reaction rate observed in oxygen rich condition.

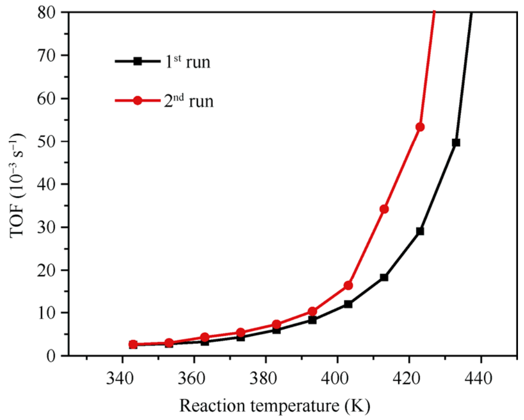


Figure 6 CO_2 formation rates as functions of the reaction temperature for CO oxidation on the pre-oxidized 1 wt% Pd/Al_2O_3 catalyst. The reaction was carried out under atmospheric pressure at a CO:O_2:He ratio of 1:1:98 and flow rate of 50 mL/min. The amount of the catalyst used is 100 mg. The reaction mixtures were analyzed for a reaction time of 10 min at each reaction temperature. The 2nd run was performed after the first run with the temperature increasing to 450 K to achieve the fully conversion of CO and then cooled down to 70 K.

4 Conclusions

The activities for the oxidation of CO on the pre-reduced supported Pd catalysts are significantly higher than the pre-oxidized ones. This demonstrates that palladium oxide is less active for CO oxidation than the metallic Pd surface. The surface chemisorbed oxygen and surface oxide can be reduced by CO at low temperature. While the bulk-like PdO on Pd(100) is not very active toward CO reduction and can still be reduced with increasing temperature. The results demonstrated that palladium oxide surfaces are highly impossible as catalytically active surfaces responsible to the high reaction rates.

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