

CO Oxidation over Mono and Bi-Metallic Sequentially Impregnated Pd-Pt Catalysts

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The CO oxidation capability of sequentially impregnated Pd-Pt/ γ -Al₂O₃ bimetallic catalysts was tested. The CO oxidation light-off curves were hierarchically spaced between monometallic Pd and monometallic Pt, which showed the highest and lowest activity, respectively, indicating that sequential impregnation did not result in the formation of bimetallic particles, but that the catalysts remained as monometallic entities over the support surface. An investigation of the effect of CO partial pressure on the reaction rates over monometallic catalysts indicated that in the presence of excess CO the surface of Pt was poisoned. On the other hand, in the presence of excess CO the reaction rates over Pd catalysts remained constant due to the availability of the subsurface oxygen pools in PdO layers.

Key Words: CO oxidation, bimetallic catalysts, palladium, platinum.

Introduction

Due to its cost advantage, Pd is frequently used (in monometallic or bimetallic form) in oxidation catalysts for lean burning engines. Furthermore, Pd-Pt bimetallic catalysts are used in hydrogenation reactions due to their sulfur resistance.¹⁻⁵ It has been demonstrated that the presence of Pd improves methane oxidation kinetics and CO oxidation reactions over supported Pt catalysts⁶ Despite the widespread use of Pd-Pt catalysts, the nature of their sites and their role in the overall reaction are little understood.

Bimetallic catalysts exhibit synergy upon alloying. The surface composition of alloys, and especially the composition of the outermost surface layer, is generally different from the bulk due to segregation processes.⁷ The surface composition of bimetallic alloys is generally considered to be determined by the following parameters:^{8,9} (i) temperature, (ii) metal surface free energies, (iii) heat of mixing, (iv) metal atomic size, and (v) the presence of adsorbates. Formation of alloys can change the electronic structure

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of the metals, accompanied by a change in bond strength of adsorbed species. Furthermore, alloying may suppress competitive reactions or prevent deposition of non-reactive species on the surface by changing active ensemble size.¹⁰ If mixing is exothermic, the metals tend to form alloys. Depending on the extent of their exothermic mixing behavior, one can talk about strong or weak alloying. Park and Lee¹¹ estimated the heat of mixing of Pd and Pt is -0.03 eV/atom, supporting a slightly exothermic behavior upon mixing; therefore, it can be said that Pd-Pt systems may form weak alloys at all compositions, or that individual components may preserve their identity.

In accordance with the general rules of thermodynamics, it is expected that Pd should segregate to the surface of a bimetallic cluster because its melting temperature and heat of vaporization values are lower compared to those of Pt.^{6,9,12,13} As a result, it is expected that Pd should be lower coordinated than Pt, which was also demonstrated experimentally;¹⁴ however, catalyst preparation protocols can significantly affect the formation of alloys. In the present work we explored the CO oxidation kinetics over mono- and bimetallic catalysts prepared by the sequential impregnation method. We present results indicating that the sequential impregnation method did not result in the formation of alloy particles.

Methods

Catalyst preparation

The incipient wetness technique was used to prepare alumina impregnated monometallic and bimetallic Pd and Pt catalysts. Onto gamma-alumina (γ -Al₂O₃) supports was loaded 1 wt% of Pd, Pt, or Pd-Pt by impregnating the supports with a sufficient precious metal precursor solution to bring about incipient wetness (\sim 1-2 mL solution/g of support). For bimetallic catalysts the Pd-Pt atomic ratios selected were 1:3, 1:1, and 3:1. The bimetallic catalysts were prepared by sequential impregnation of Pt(NH₃)₄Cl₂.H₂O (Johnson Matthey) and Pd(NO₃)₂ (Johnson Matthey), because mixed aqueous solutions of Pt(NH₃)₄Cl₂.H₂O and Pd(NO₃)₂ salts resulted in precipitation. The catalysts were dried at room temperature for 6 h and at 393 K for 12 h. Finally, the catalysts were calcined at 723 K for 4 h. Part of these catalysts was used as such, and the other part was washed with hot distilled water (\sim 350 K) until it was free of Cl⁻ ions (based on testing with an AgNO₃ solution) and then calcined again at 673 K for 4 h.¹⁵

Catalysts characterization

In this study active metal dispersions were determined by a large quantity of hydrogen at 298 K, as measured by volumetric chemisorption methods.¹⁶ Adsorption experiments were performed in a manifold, as described elsewhere.¹⁷ Prior to reduction, about 2 g of catalyst was heated to 423 K and kept at that temperature for 30 min under vacuum (10^{-4} Torr). The samples were reduced under static hydrogen at 623 K for 2 h, during which time the surface was exposed to hydrogen 3 times (20-25 min each time); following each exposure the gas in the manifold was replenished. After evacuation and cooling, total and weak hydrogen isotherms were measured. Dispersions were calculated assuming a hydrogen stoichiometry of H/Pd = 1 or H/Pt = 1.

Activity measurements

Measurement of CO oxidation activity over the prepared catalysts was conducted in a horizontal fixed-bed reactor made of a quartz tube (13 mm ID) under atmospheric pressure. We placed 100 mg of catalyst diluted

with 900 mg of γ -Al₂O₃ in the reactor. The catalyst bed was supported by quartz wool at both ends. A thermocouple was placed externally with one end touching the catalyst zone in order to measure the bed temperature. The quartz reactor was placed inside a temperature-controlled tubular oven. The temperature of the oven was increased from room temperature to the reaction temperature (approximately 350 K); then the catalysts were conditioned with a stoichiometric gas mixture of 5% CO, 2.5% O₂, and N₂ for 30 min. Inlet gas composition was controlled by an MKS 1179A mass flow controller and analysis of the product gases was carried out using an on-line gas chromatograph (HP 4890) equipped with a thermal conductivity detector (TCD) and a Porapak Q column with N₂ as the carrier gas. Total gas flow rate through the reactor was maintained constant at 200 mL/min. The effect of bimetallic interaction on the CO oxidation reaction was first studied by dynamic light-off experiments. The catalyst bed was heated at a rate of 1 K/min, and CO consumption and CO₂ formation rates were monitored with the gas chromatograph until 100% CO conversion was obtained. The reaction orders, with respect to CO and O₂, were measured at the temperatures for which CO conversion was below 5% so that the differential reactor assumption was valid.

Results and Discussion

Dispersion of the sequentially impregnated Pd-Pt catalysts was characterized by the strong hydrogen chemisorption technique and their activity in the CO oxidation reaction was evaluated. Dispersion measurements are reported in Table 1, for both unwashed and washed catalysts. It is clearly seen from the data presented in Table 1 that Pt catalysts had higher dispersion than Pd catalysts and that the dispersion of the catalysts gradually decreased as the amount of Pd increased. It was also observed that the dispersion of the catalysts decreased upon washing, most probably due to the second calcination performed after the washing step. Finally, it is worth mentioning that the number of metal atoms accessible for hydrogen chemisorption did not differ much along the catalyst series.

Table 1. Dispersion values of the sequentially impregnated palladium and platinum monometallic and bimetallic catalysts based on H₂ chemisorption.

Catalyst	Pd:Pt	Dispersion (%)		Surf atom (mol)/g of Catalyst	
		Unwashed	Washed	Unwashed	Washed
1% Pt/ γ -Al ₂ O ₃	0:1	70.4	60.8	36.1	31.2
1% Pd-Pt/ γ -Al ₂ O ₃	1:3	62	42.5	35.9	24.5
1% Pd-Pt/ γ -Al ₂ O ₃	1:1	N/A	38.3	N/A	25.4
1% Pd-Pt/ γ -Al ₂ O ₃	3:1	40.7	44.6	31.7	34.9
1% Pd/ γ -Al ₂ O ₃	1:0	34.3	32.9	32.2	30.9

The light-off curves of the sequentially impregnated bimetallic catalysts (Figure 1) during CO oxidation under a stoichiometric gas mixture were hierarchically spaced between the light-off curves of monometallic Pd and monometallic Pt. This fact was interpreted as evidence that Pd and Pt in sequentially impregnated bimetallic catalysts could be observed as separate entities on the support surface. In contrast, over the co-impregnated catalyst series, the bimetallic catalysts behaved identically to the monometallic Pd catalysts.⁶

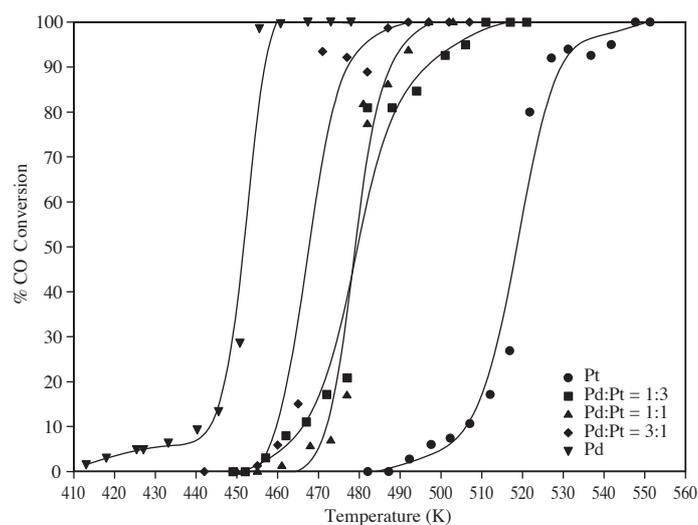


Figure 1. Light-off curves of the unwashed catalysts. Feed gas composition: 5% CO, 2.5 % O₂, balance N₂. $\dot{V}_{\text{total}} = 200$ mL/min.

Washing did not improve the light-off performance of the sequentially impregnated catalyst group, excluding the monometallic Pt catalysts, as seen in Figure 2. After washing, the reaction onset temperature decreased by 50 K and the T_{50} value decreased by 25 K on the 1% Pt/ γ -Al₂O₃ catalyst. On the monometallic Pd and bimetallic catalysts, no improvement was observed in the light-off behavior of the sequentially impregnated catalysts upon washing.

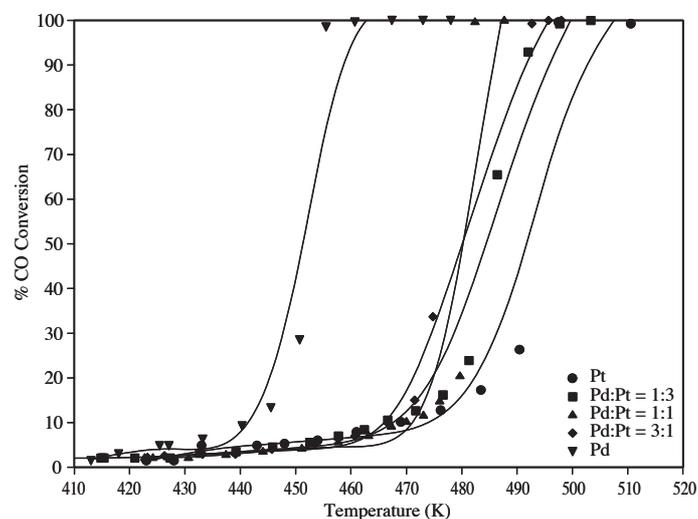


Figure 2. Light-off curves of washed catalysts. Feed gas composition: stoichiometric, 5 % CO, 2.5% O₂, balance N₂. $\dot{V}_{\text{total}} = 200$ mL/min.

The apparent activation energies and reaction orders, with respect to CO and O₂, are presented in Table 2. CO and O₂ orders were estimated at constant temperature over a narrow range of CO and O₂ partial pressures, assuming a power law-type rate expression. CO orders were measured by changing the amount of CO in the gas phase (in the 2%-6% range) while maintaining O₂ at the 2.5% level. On the other

hand, O₂ orders were measured by keeping the CO level at 4% and changing O₂ values in the 1%-5% range. CO orders estimated in the isokinetic region on all catalysts were close to -1, except for the monometallic Pd catalysts. On the monometallic Pd catalyst (prepared from a Pd(NO₃)₂ precursor) the CO order was -0.47. In a previous study the presence of bridge-bonded CO over similar catalysts was noted. Monteiro et al.¹⁸ clearly demonstrated that the position of CO IR absorption frequencies depended on the nature of Pd precursors. In addition to the 2 infrared absorption peaks of CO (linear and bridged), they observed a third small peak related to bridge-bonded CO on a catalyst prepared from a Pd(NO₃)₂ precursor. If the bridge-bonded CO is the most abundant reactive intermediate, the coverage of the vacant sites¹⁹ and O₂ can be estimated as follows:

Table 2. Reaction orders and activation energies of CO oxidation reaction over sequentially impregnated catalyst group. The activation energies were measured under a stoichiometric feed gas composition: 5% CO, 2.5% O₂, balance N₂. $\dot{V}_{\text{total}}=200$ mL/min.

Pd:Pt	E_a (kJ/mol)	CO Order Measurement Temperatures (K)	CO orders	O ₂ Order Measurement Temperatures (K)	O ₂ Orders
0:1	57.0	448	-0.81	455	1.84
1:3	56.7	458	-0.74	458	1.46
1:1	59.6	450	-0.86	450	1.31
3:1	50.2	453	-0.89	443	1.16
1:0	74.0	423	-0.47	423	1.23

$$\theta_v = 1/(K_{CO}P_{CO})^{1/2} \quad (1)$$

$$\theta_O = (K_{O_2}P_{O_2})^{1/2}\theta_v = (K_{O_2}P_{O_2})^{1/2}/(K_{CO}P_{CO})^{1/2} \quad (2)$$

Given that CO coverage is ~ 1 , the resulting reaction rates in a Langmuir Hinshelwood model becomes

$$Rate = k\theta_{CO}\theta_O = k\theta_O = k(K_{O_2}P_{O_2})^{1/2}/(K_{CO}P_{CO})^{1/2} \quad (3)$$

The approximate negative half orders measured over Pd catalysts for CO suggest that bridge-bonded CO species are involved in the reaction, based on the analysis presented above. The CO orders on all other catalysts were about -0.8, indicating Pt-dominant behavior in CO oxidation kinetics. As the Pd weight fraction increased a decrease in O₂ order from 1.84 to 1.16 was observed. The reaction order, with respect to O₂ on the monometallic Pt catalyst, was much higher than that of the other catalysts.

The effect of CO partial pressure on catalyst performance was investigated for monometallic Pd and Pt catalysts, starting from O-rich conditions. During these measurements the CO partial pressure increased while the partial pressure of O₂ and N₂ was kept constant. The steady-state reaction rate was plotted against CO partial pressure for Pt (Figure 3) and Pd (Figure 4) catalysts. The reaction rate increased as the CO fraction increased, until a critical CO/O₂ ratio was reached, at which time the system switched to a CO-rich surface prevailing steady-state on both the monometallic Pd and Pt surfaces. The response to Pt and Pd catalysts under increased CO partial pressure was different beyond the stoichiometric point (dashed lines in Figures 3 and 4). Over the Pt surface, excess CO led to poisoning and the rate decreased as the CO partial pressure increased, while over Pd the rates did not change as CO partial pressure increased.

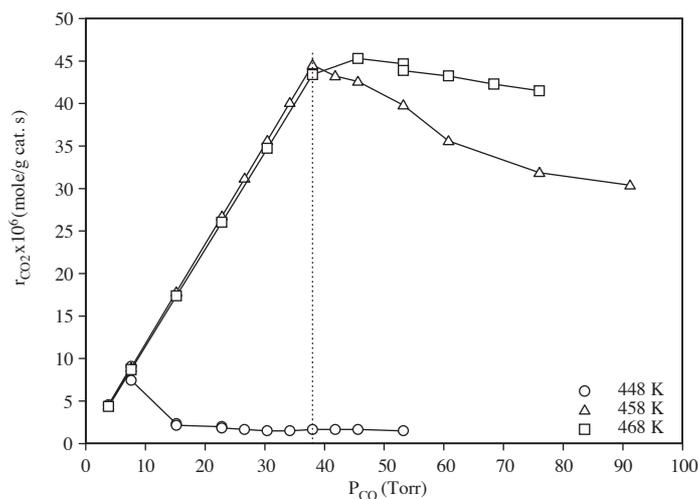


Figure 3. Change in the rate of the reaction over 1% Pt/ γ -Al₂O₃ with increasing partial pressure of CO. Feed gas composition: 2.5% O₂, balance N₂. $\dot{V}_{total} = 200$ mL/min. Dashed lines show stoichiometric point.

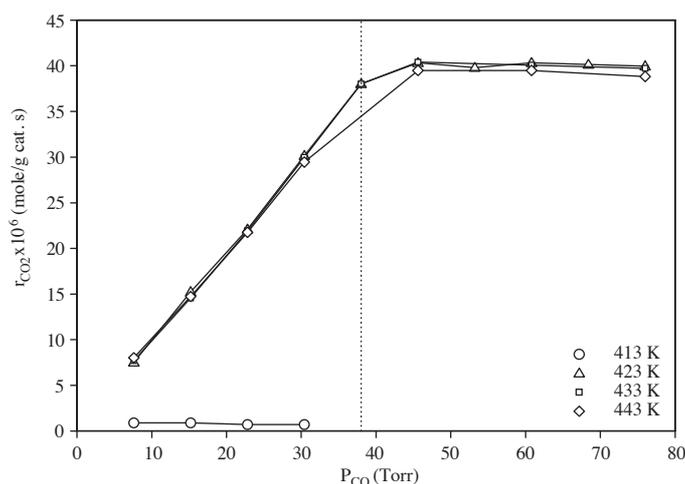


Figure 4. Change in the rate of the reaction over 1% Pd/ γ -Al₂O₃ with increasing partial pressure of CO. Feed gas composition: 2.5% O₂, balance N₂. $\dot{V}_{total} = 200$ mL/min. Dashed lines show stoichiometric point.

The point at which the steep drop in the reaction rate for Pt was observed was related to CO poisoning. Below the critical pressure the surface O₂ population was sufficient to sustain the steady state conversions, but chemisorbed CO became predominant above the critical pressure, and oxygen adatoms decreased to negligible amounts, i.e. from $\theta_O > \theta_{CO}$ to $\theta_O \ll \theta_{CO}$ with increasing CO pressure. Apparently, the excess CO over the surface inhibited O₂ adsorption after the stoichiometric point.

In contrast, the reaction rate did not change with changes in CO partial pressure after the stoichiometric point over Pd catalysts (Figure 4). This was independent of the temperatures investigated in this work (423, 433, and 443 K). The behavior observed on the Pd catalyst after the rate maximum could be explained by Pd-O interaction. Apparently, the kinetics over the Pd catalyst after the stoichiometric point was dominated by O₂. Meusel et al.²⁰ reported that starting at temperatures below 300 K Pd particles rapidly incorporated large amounts of O₂, finally reaching stoichiometries of PdO > 0.5. Their STM data showed

that neither the overall particle shape nor the dispersion was affected by O₂ and CO treatment. Pd particles in Pd/Al₂O₃ were initially composed of smaller, randomly oriented crystals of both PdO and Pd, but in oxidizing atmospheres the clusters became more oxidized and formed larger crystals.²¹ The interactions of Pd with O₂ were investigated by Penner et al.²² They reported that at low O₂ pressures surface oxygen adatoms moved to subsurface sites starting at 400 K, and almost all oxygen atoms moved to subsurface sites by 750 K, desorbing only at higher temperatures. On the other hand, at high pressures the conversion of Pd in small nanoparticles (≥ 0.6 -nm thick) to a PdO-like species, due to the transformation of bulk Pd to bulk PdO, was observed. They did not record any decomposition of this oxide into Pd nanoparticles with O₂ gas until 200 K, higher than the bulk PdO.

The surface and subsurface oxygen pools present over Pd catalysts must be sufficient to sustain a steady state CO conversion under excess CO coverage while the surface and subsurface oxygen reservoirs are replenished at their own rate. PdO particles covered by reduced metallic layers²³ should be responsible for sustaining sufficient CO coverage and fast rates of atomic oxygen accessible to the surface CO. Beyond the rate maximum (stoichiometric point), oxygen atoms located in the near-surface region will segregate to the surface and react with chemisorbed CO.²⁴

Conclusions

The CO oxidation reaction was studied over sequentially impregnated Pd-Pt monometallic catalysts. The CO oxidation light-off data indicated that sequentially impregnated Pt and Pd metals remained as monometallic entities over the support surface. The effect of CO partial pressure on the reaction rates over monometallic surfaces indicated that the Pd catalysts were more resistant to CO poisoning, probably due to the subsurface oxygen pools.

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