

CO OXIDATION ON Pt/Al₂O₃ AND Pd/ Al₂O₃ TRANSIENT RESPONSE AND CONCENTRATION CYCLING STUDIES

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ABSTRACT

By combining transient response experiments with forced concentration cycling, we were able to determine the reactive surface intermediates responsible for the large rate enhancements observed during periodic operation. According to the IR evidence on Pt the reactive surface species is a CO molecule adsorbed on a platinum atom sharing a chemisorbed oxygen with a neighbor. On Pd two different history dependent mechanisms were found to exist. One of these mechanisms is active only during concentration cycling and accounts for the major portion of the rate enhancement.

KEYWORDS

CO oxidation, transient response, concentration cycling, ir spectroscopy, platinum, palladium, rate enhancement.

INTRODUCTION

Oxidation of CO Over supported Platinum group metals is known to exhibit a number of complex behavior patterns such as self sustained oscillations (Hugo and Jakubith,1972; Scheintuch and Schmitz,1977) and enormous rate enhancements during forced concentration cycling (Cutlip,1979; Barshad and Gulari,1985a). These behavior patterns have resulted in making CO oxidation on platinum group metals the subject of many investigations. Engel and Ertl (1979) have reviewed all the available high vacuum results. There is general agreement that at steady state the rate of reaction is inhibited by strong CO adsorption and that dissociative chemisorption of oxygen is necessary for the reaction. Engel and Ertl (1978) present strong evidence in favor of a Langmuir-Hinshelwood type mechanism (reaction occurring between adsorbed CO and oxygen) on Pd. In the same work they also show that on a carbon-contaminated Pd (111) surface there are three distinct CO species taking part in the reaction. Efforts to model CO oxidation on Pt with a bimolecular Langmuir Hinshelwood (L-H) type rate expression have resulted in limited success (Herz and Marin,1980). Behm and co-workers (1983, 1984) have observed adsorbate induced surface reconstruction and believe it to be the cause of sustained oscillations. Yeates and co-workers (1985) however rule surface reconstruction out at atmospheric pressure and instead have proposed surface oxidation of platinum as the major reason for self sustained oscillations.

In previous investigations (Barshad and Gulari,1985a; Zhou and Gulari, 1985) we showed that by forced concentration cycling of the feed between CO/N₂ and O₂/ N₂ streams the

time averaged rates of reaction on Pd/Al₂O₃ and Pt/Al₂O₃ could be increased by as much as two orders of magnitude over that of the best steady state rate possible at the same temperature. We also found out that the transient response of the rate of CO₂ production to step changes in CO and oxygen concentrations exhibited complex behavior. This investigation was initiated in order to understand the surface processes responsible for the increased rates of reaction observed during concentration cycling. An equally important goal was to obtain information about the reaction mechanisms and, if possible, determine the nature of the reactive surface species.

EXPERIMENTAL

A. Reagents and catalysts

The gases used were 99.99% pure N₂ (Air Products), 99.6 % pure O₂ (Matheson), 99.998 % pure Ar (Air Products), and 99 % pure CO (Air Products). Iron carbonyl in CO was removed by decomposing it at 700 K. Identical results were found with or without the carbonyl trap. 6.2 wt% Pt/Al₂O₃ and 8 wt% Pd/Al₂O₃ powder catalysts were used for surface transient studies. 1 wt% Pd/Al₂O₃ and Pt/Al₂O₃ monolith catalysts were used for gas phase transient studies. The preparation procedures can be found elsewhere (Barshad and Gulari, 1985a ; Zhou and Gulari 1985).

B. Apparatus

All the periodic operation and transient response studies were carried out with a computer controlled reactor system previously described (Barshad and Gulari, 1985a). The main advantage of this system is that it can perform repetitive square wave concentration cycling with a time period as short as two seconds. The gas phase transients were studied with a see-through reactor (Barshad and Gulari , 1985b) using a monolithically-supported catalyst and an FTIR as the primary detector. Use of the FTIR as the main detector allows inside the reactor detection of the gas phase concentrations with a time resolution of 0.15 seconds.

IR transients of the surface CO species were obtained using a 20 mm diameter pellet mounted inside a modified transmission IR liquid cell (Harrick). The flow pattern in this reactor is single pass with the gas flowing parallel to the pellet on both sides. With the very short residence times used in this study (<0.5 sec) the residence time distribution was intermediate between a gradientless reactor and a plug flow reactor.

Temperatures of both reactors were controlled to ± 1 °K with feedback controllers. Gas phase temperatures were measured with fast response thermocouples and the catalyst surface temperature was monitored with an Omega IR emission thermometer having a precision of ± 0.5 K. Some of the gas phase transients were also analyzed with an on line mass spectrometer (Balzers QMG 212) with a time resolution of approximately 0.5 seconds.

RESULTS

Forced concentration cycling and single transient response experiments were used as complimentary techniques. We will first discuss the findings from concentration cycling experiments.

A. Time averaged concentration cycling results

Figure 1 shows the transition from steady state to cyclic operation for Pt/Al₂O₃ (Pd/Al₂O₃ results are similar). It is clear that as soon as cyclic operation is started the reaction rate increases dramatically. Steady periodic operation is also reached within a few periods. This rapid transition is indicative of a transition due to surface coverage rather than a catalyst surface reconstruction.

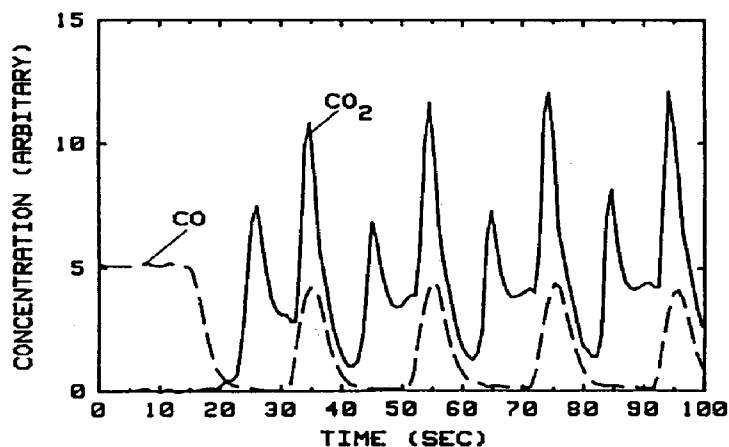


Fig. 1 CO and CO₂ responses to transition from steady state to periodic operation as detected inside the monolithic reactor.

By integrating the CO₂ produced over many cycles one can obtain the time averaged rate of reaction as a function of the cycling parameters. For both catalysts the optimum point of cyclic operation has a much higher time averaged rate than the highest steady state rate possible at the same temperature (Barshad and Gulari, 1985a; Zhou and Gulari, 1985). For periods shorter than the optimum the dependence of the average rate on cycle period is very strong. Above the optimum point the time averaged reaction rate has a much weaker dependence on the cycle period. This is due to compensating effects of increased surface coverage with increased exposure time and averaging over longer cycle periods. Since the adsorption capacity of the surface is limited, averaging over longer time periods eventually leads to lower time averaged rates.

There is a subtle but important difference between the two catalysts in the dependence of the time averaged rates on CO duty fraction. For Pt past the optimum duty fraction and cycle period the iso-rate contours show significant dependence on both variables. For Pd, on the other hand, there is no dependence on CO duty fraction until the duty fraction is very high. This is due to the fact that on Pt the CO adsorbed on platinum oxide surface is very unreactive (Barshad, Zhou and Gulari, 1985; Herz, 1984).

B. Results of transient response experiments

Figure 2 shows the CO and CO₂ gas phase transient responses to a step up and down of

10% CO in N_2 with a continuous flow 10% O_2 over the monolithically supported platinum catalyst. The transient responses are obtained by inside the reactor FTIR detection. Again we see that the rate of reaction during the transient is several orders of magnitude higher than the steady state portion. With the palladium catalyst both the CO on and CO off transients are double peaked. The complex structure of the CO off portion of the transient is probably due to CO adsorbed on different planes.

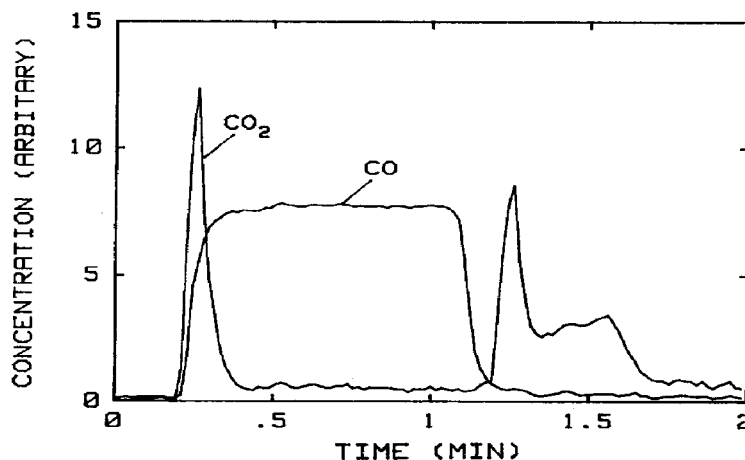


Fig. 2 Transient CO and CO_2 responses of the monolithically supported Pt catalyst to a step up and down of CO in the feed with continuous oxygen feed.

When there is a continuous CO feed no overshoots are observed. If the surface is CO pretreated and gas phase CO is purged from the reactor transients similar to those shown in Fig. 2 are observed. There is however, one significant difference: when the catalyst surface is CO pretreated a temperature dependent induction time is observed. The induction time is comparable to the the cycle time giving the best rate enhancement during concentration cycling. With palladium the transients observed are always double peaked.

Figure 3 shows the transient response of the surface CO species to a gas phase CO step obtained after oxygen pretreatment of the Pd catalyst pellet. We start seeing CO_2 in the gas phase as soon as CO enters the reactor. Spectra of the surface CO region contains a surprise: there is a sharp band at 2156 cm^{-1} . This band can be either due to a physisorbed CO or CO adsorbed in the middle of an oxygen island, forming a 2×2 surface structure with an equal local CO and O coverage (Conrad, Ertl and Kuppers, 1978). At the temperature of the transient, $150\text{ }^\circ\text{C}$, the surface species giving rise to this band can not be physisorbed CO but has to be chemisorbed CO. The integrated intensity of this band correlated extremely well with the gas phase CO_2 concentration (Zhou and Gulari, 1986). Stuve, Madix and Brundle (1984) using a Pd (100) surface observed a similar band appearing at 2125 cm^{-1} under UHV conditions. We are not sure whether the frequency difference is due to the difference in the catalysts or is an instrumental problem. Careful investigation of the integrated absorbance areas of the bands assigned to bridge and linearly bonded CO species revealed that if the surface is oxygen covered the bridge bonded species chemisorb at a faster rate. If the surface is CO covered and oxygen is

introduced into the reactor the reverse occurs, however under those conditions no band at 2156cm^{-1} is visible.

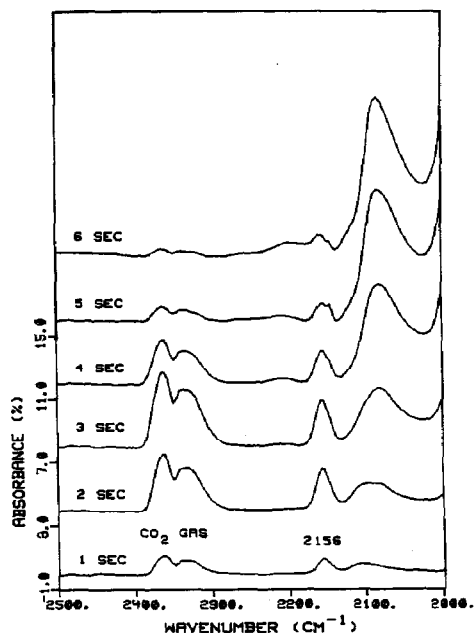


Fig. 3 Transient response of the gas phase CO_2 and surface CO species in the high wavenumber region to a CO step up. Gas phase CO spectra has been subtracted for clarity. $T = 154^\circ\text{C}$, the surface of the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst was oxygen pretreated and purged before the introduction of 10 % CO in N_2 .

C. Time averaged IR spectra during periodic operation

In order to better understand the reasons for the large rate enhancements observed, IR spectra of the surface species were measured both on a time averaged basis and during a single cycle transient. Figure 4 shows the results for Pt as a function of cycle time. The spectra above a cycle time of 25 seconds are quite different than the steady state spectrum and those with shorter cycle times. The intensity of the 2120 cm^{-1} peak, assigned to CO adsorbed on platinum oxide (Sheppard and Nguyen, 1980), increases significantly as the cycle time goes through 25 seconds. In addition a new peak at $2087\text{-}2095\text{ cm}^{-1}$ becomes clearly visible in the IR spectra. This band is believed to be due to CO adsorbed on a platinum atom with a δ^+ ($\delta \sim 1$) charge (Sheppard and Nguyen, 1980) possibly due to sharing a chemisorbed oxygen atom. We should note that for this temperature the optimum cycling period was found to be 22 seconds with the monolithically supported catalyst. Since the flow patterns and geometries of the two reactors are totally different, these results clearly show that the rate increases are due to changes in the surface processes and not due to transport phenomena.

D. Transient IR spectra of the surface species in one cycle

According to Fig. 4 the intensities of the CO linearly adsorbed on platinum oxide and platinum sharing a chemisorbed oxygen atom correlate positively with the increases in

rate observed during forced concentration cycling. In order to determine which one of the two was the active intermediate Ir spectra of the surface species during one cycle was measured with one second time resolution. The net result of these measurements was that even though the amount of CO adsorbed on platinum oxide changes significantly from one cycle period to the next the changes occurring during one cycle period are very small and not correlated with the instantaneous reaction rate in contrast the integrated absorbance of the 2090 cm^{-1} band correlated very nicely with the instantaneous rate (Barshad, Zhou and Gulari, 1985).

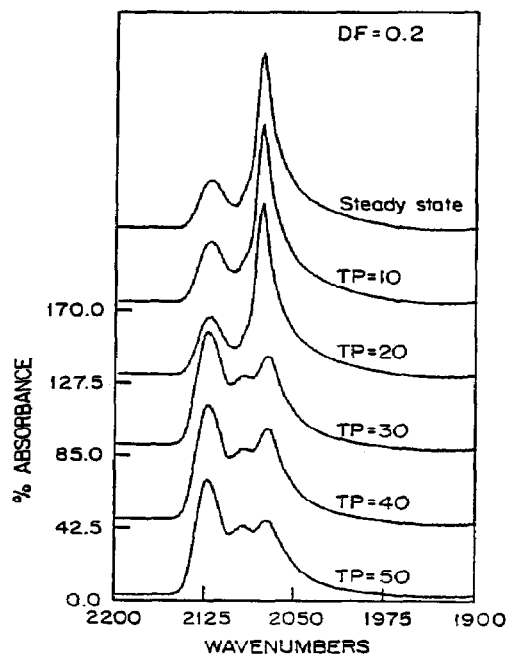


Fig. 4 Time averaged ir spectra of the surface CO species on platinum during concentration cycling. TP is the cycling period in seconds. For 20 % of the cycle time 10% CO in N_2 was fed to the reactor during the remainder of the cycle the feed was 10 % O_2 in N_2 . Temperature 140°C , atmospheric pressure.

With palladium the spectra obtained during one cycle is a sum of the CO on and CO off transients and does not show the presence of any new bands. However, if we divide the spectrum into three (linear, bridge on Pd(100) plane, and bridge on the (111) plane) and follow the changes in the integrated intensities as a function of time during one period, we find that linearly adsorbed CO starts reacting first with a single rate constant. CO adsorbed on Pd(100) shows intermediate reactivity. CO adsorbed on the (111) plane has a very slow rate of reaction initially, and after about a 10 to 15% decrease in the integrated absorbance, the reaction lights off and the rate increases by close to two orders of magnitude.

DISCUSSION

The evidence presented in this paper shows that the rate enhancements observed during forced concentration cycling are due to fundamental changes in the surface processes rather than transport related phenomena. Significant temperature excursions in oxidation reactions have been observed by Kaul and Wolf (1984) under conditions

similar to the single pellet transients used in this study. We were careful to minimize the possibility of thermal excursions. Apart from the normal fast response thermistors and thermocouples an IR emission thermometer with a spatial resolution of 0.1 inches and thermal resolution of 0.5 K was used to monitor the catalyst surface temperatures. We were not able to detect any thermal excursions above 0.5 K that could be correlated with the cycling period. While the conversions used were quite low and the flow rates were high, with the monolithic reactor there is a possibility of having a small temperature gradient along the axial direction (even though we could not detect it). If the rate observed was purely due to transport related phenomena we should have observed similar phenomena with both catalysts yet the observations are dramatically different. Also changing the carrier gas from N₂ to He and thus increasing the thermal conductivity of the carrier did not change the results.

CONCLUSIONS

1. The rate enhancements observed during Pt and Pd catalyzed CO oxidation are due to changes in surface phenomena occurring on the catalyst surface.
2. There is a significant difference between the behavior of Pt and Pd catalysts due to the formation of a platinum oxide phase.
3. Under cyclic operation conditions new surface species are observed on both Pt and Pd. The concentration of these species correlate positively with the instantaneous rate of reaction.

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REFERENCES

- Barshad, Y. and Erdogan Gulari (1985a). A dynamic study of CO oxidation on platinum. AICHE J., 31, 649 -658.
- Barshad, Y. and Erdogan Gulari (1985b). A novel reactor system for transient response and periodic operation studies. J. Catal., 94, 468-476.
- Barshad, Y., X. Zhou and Erdogan Gulari (1985). A transmission ir study of CO oxidation on supported platinum under transient conditions. J. Catal., 94, 128-141.
- Behm, R. J., P. A. Thiel, P. R. Norton and G. Ertl (1983). The interaction of CO and Pt(100). I. Mechanism of adsorption and Pt phase transition. J. Chem. Phys., 78, 7437-7447.
- Behm, R. J., P. A. Thiel, P. R. Norton and P. E. Bindner (1984). The oxidation of CO on Pt(100) : Mechanism and structure. Surf. Sci., 147, 143-161.
- Conrad, H., G. Ertl and J. Kupperts (1978). Interactions between oxygen and carbon monoxide on a Pd(111) surface. Surf. Sci., 76, 323.
- Cutlip, M. B. (1979). Concentration forcing of catalytic surface rate processes. AICHE J., 25, 502-508.
- Engel, T. and G. Ertl (1978). A molecular beam investigation of the catalytic oxidation of CO on Pd(111). J. Chem. Phys., 69, 1267-1281.
- Engel, T. and G. Ertl (1979). Elementary steps in the catalytic oxidation of carbon monoxide on platinum metals. Advances in Catalysis, Vol. 28. Academic Press, New York. pp. 1-78.

- Herz, R. K. (1984). Paper No. 89d, AIChE annual meeting, San Francisco.
- Herz, R. K. and S. P. Marin (1980). Surface chemistry models of carbon monoxide oxidation on supported platinum catalysts. J. Catal., **65**, 281-296.
- Hugo, P. and M. Jakubith (1972). Dynamisches Verhalten und Kinetik der Kohlenmonoxid-Oxidation am Platin-Katalysator. Chemie-Ing.-Tech., **44**, 383-387.
- Kaul, D. J. and E. E. Wolf (1984). FTIR studies of surface reaction dynamics. J. Catal., **89**, 348-361.
- Sheintuch, M. and R. A. Schmitz (1977). Oscillations in catalytic reactions. Catal. Rev. Sci. Eng., **15**, 107-172.
- Sheppard, N. and T. T. Nguyen (1976). The vibrational spectra of carbon monoxide chemisorbed on the surface of metal catalysts: a suggested scheme of interpretation. Advances in Infrared and Raman Spectroscopy, Vol. 5, John Wiley & Sons, New York. Chap. 2, pp. 67-148.
- Stuve, E. M., R. J. Madix and C. R. Brundle (1984). CO oxidation on Pd(100): A study of CO-adsorption of oxygen and carbon monoxide. Surf. Sci., **146**, 155-178.
- Yeates, R. C., J. E. Turner, A. J. Gellman and G. A. Somorjai (1985). The oscillatory behavior of the CO oxidation reaction at atmospheric pressure over platinum single crystals: surface analysis and pressure dependent mechanisms. Surf. Sci., **149**, 175-190.
- Zhou, X. and Erdogan Gulari (1985). CO oxidation over Pd/Al₂O₃: rate enhancement by concentration cycling. Chem. Eng. Sci., in press.
- Zhou, X. and Erdogan Gulari (1986). CO adsorption and oxidation on Pd/Al₂O₃ under transient conditions, Langmuir, submitted.