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The Gas Phase and Electrochemical Oxidation of Carbon Monoxide on Platinum, Palladium and Ruthenium Catalysts: A Comparative Study

Processes occurring in gas–solid heterogeneous catalysis and electrocatalysis have certain features in common since they both involve reaction at an interface containing two or more distinct phases. The principal difference between the two fields of study is that, for electrode processes the reaction rate may be altered by varying the potential at the electrode/electrolyte interface.

The similarities between the gas phase and electrochemical catalysis have been reviewed previously (*1*, *2*). However, there has been no comparative study on a specific system carried out in the same laboratory. Therefore, we report a study comparing the kinetics of CO oxidation on Pt, Pd and Ru in the gas phase and in an electrochemical cell. It is our purpose to attempt a reconciliation of the interpretation of gas phase heterogeneous catalysis and electrocatalysis data in a more generalized and unifying concept. This, although difficult, should be possible since both disciplines are concerned with the activity of a catalyst surface and this reaction has been extensively studied (*3–11*).

The electrochemical measurements were carried out in the cell described previously (*11*) using high area metal blacks for the electrode catalysts. Figure 1 shows the current/potential curve for CO oxidation for a gas stream containing 200 ppm CO in air. The potential range in which measurements were made was limited either by large cathodic background currents due to oxygen electroreduction or by large anodic background currents due to oxygen evolution. In particular, CO oxidation crrrents could be measured on Ru electrodes only over a very limited potential range (Fig. 1). The data for Pt was reported previously (*11*) and is shown here for comparison.

At selected potentials for Pt (0.9, 1.1 and 1.3 V) and Pd (0.8 and 1.2 V) the current due to CO electrooxidation was measured and in each case the current was directly proportional to the gas concentration.

The gas phase reaction was carried out in a fixed bed integral flow reactor (*12*). The supported catalysts were prepared by stirring the silica in a solution of the relevant metal chloride, evaporating to dryness and then reducing in hydrogen.

Figure 2 shows the percentage conversion of CO as a function of temperature for the three catalysts. While the percentage conversion of CO for such a reactor does not vary linearly with catalytic activity for high conversions (*13*), it is a qualitative indication of the reaction rate.

Figure 2 shows that the reaction order, α, with respect to the CO concentration is temperature dependent for Pt and Pd. At $T < 500$ K, $\alpha < 0$ for Pt and Pd, while at $T > 550$ K, $\alpha > 0$ for Pt and Pd, however, for Ru, α was zero at all temperatures within the experimental precision.

The data in Fig. 1 for Pt and Pd are qualitatively similar to that in Fig. 2 for Pt, Pd and Ru, i.e., the reaction rate initially increases with increasing potential (temperature) and subsequently decreases with increasing potential (temperature). Therefore, potential and temperature are

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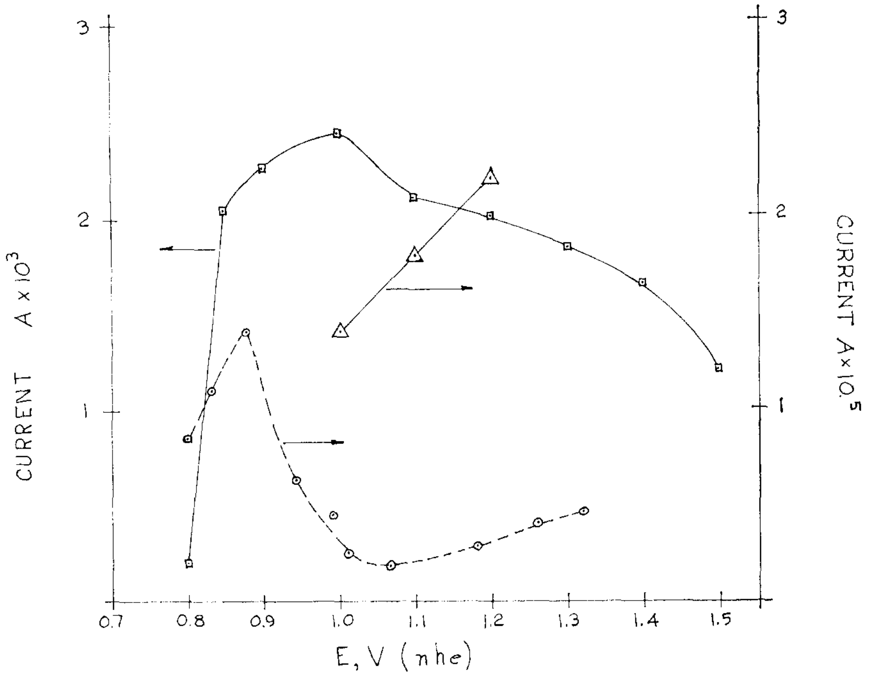

FIG. 1. CO oxidation currents as a function of electrode potential. 200 ppm CO, balance air. Metal black catalyzed diffusion electrodes of Pt (□), Pd (○) and Ru (△).

affecting the catalytic reactions in the same way by changing the chemical nature (and hence activity) of the catalyst surface.

For Pt electrodes, the increase in CO oxidation current with increasing potential between 0.8–1.1 V parallels the increase in reversibly bound OH species on the Pt surface (*11, 14*), such that $\theta_{OH} = 1$ at 1.1 V where a maximum in CO oxidation rate occurs. The subsequent decrease in CO oxidation current at increasing potentials is associated with the diminished availability of surface PtOH groups due to their conversion to Pt–O (*13*) i.e., conversion of the catalytically active species to a catalytically inactive one. The CO oxidation current at potentials less than 0.8 V was not determined due to the large oxygen reduction current. However, from measurements made in de-aerated electrolyte (*9–11*), it is known that CO is not oxidized at potentials more cathodic than 0.8 V and this is consistent with the low oxide coverage on the electrode surface in this potential region (*14*).

Athough Pd and Ru electrode surfaces are also readily oxidized in the potential range of interest (*15*), their lower electrocatalytic activity for this reaction (Fig. 1) suggests that the surface coverages of the catalytically active oxide species is several orders of magnitude lower than for Pt electrodes.

For the gas phase heterogeneous carbon monoxide oxidation on Pt, the negative reaction order at temperatures less than 500 K shows that CO poisons the surface. Therefore, the increase in reaction rate with temperature is consistent with an increase in adsorbed oxygen on the catalyst surface (since $\theta_{O_2} = 1 - \theta_{CO}$). Further evidence demonstrating the increase in adsorbed oxygen with increasing temperature is given from the values of the sticking probabilities of these molecules on Pt (*6*). The subsequent decrease in reaction rate with

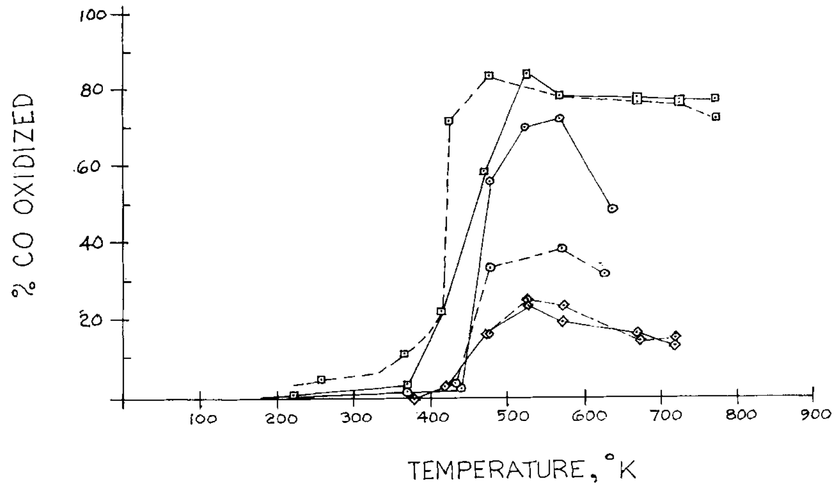

FIG. 2. CO(%) oxidized as function of temperature, (——) 200 ppm CO, balance air; (- - -) 100 ppm CO, balance air. Silica supported Pt (□), Pd (○) and Ru(◇).

increasing temperature parallels the decrease in sticking probabilities of the reactants and hence reduced adatom concentration of O_2 on Pt at higher temperatures (*8*), i.e., a decrease in the concentration of the catalytically active oxygen species. Similar arguments can be proposed to explain the gas phase oxidation on Pd and Ru catalysts.

It is noteworthy that, although Pd and Ru were less active than Pt, the maximum CO oxidation rate was also observed in the temperature range 500–550 K. Such fortuitous behavior is not expected on the basis of complex mechanistic and coadsorption considerations. However, it is known that the heat of adsorption at low coverage of CO on Ru, Pt, and Pd is 29, 30, and 34 kcal/mole, respectively (*16*). Since the residence time for CO is given by $T = T_0 \exp(E_d/RT)$ and CO desorption on these metals is essentially nonactivated (*17*), similar residence times for CO on all three catalysts would be expected accounting for the similar temperature at which the maximum rate is observed.

Therefore, for both the electrochemical and gas phase system, the specific condition of the surface (i.e., whether CO or active O species coverage predominates) provides us with the explanation of the shape of the reaction rate–potential (temperature) curves. It should be noted that this is not a general conclusion but holds only for this particular case where adsorbed oxygen plays such an important role.

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