The effect of electrochemical oxygen pumping on the rate of CO oxidation on Au electrode-catalyst

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The effect of electrochemical pumping of oxygen on the rate of carbon monoxide oxidation on Au electrode-catalyst in a solid oxygen conducting electrolyte cell has been demonstrated. The induced change in the reaction rate at the cathodic polarization of an Au electrode was an order of magnitude higher than the rate of O^{2-} pumping from the reaction zone through the electrolyte. The anodic polarization of the Au electrode (O^{2-} pumping to the reaction zone through the electrolyte) caused purely Faradaic changes in the reaction rate.

Keywords: Carbon monoxide oxidation; gold electrode-catalyst; solid oxide elcctrolytc; oxygen pumping

1. Introduction

In recent years much attention [1,2] has been paid to the study of the oxidative transformation of gases on the electrodes-catalysts in high-temperature electrochemical cells with solid oxygen-conducting electrolyte of type:

gaseous reactants, metal catalyst $|ZrO_2(8–10\ mol\%\ Y_2O_3)|$ metal, O_2

In particular it was found that during the oxidation of CO on Pt [2,3] and Pd [2] the catalytic activity of metal catalysts can be altered dramatically and in reversible manner by the passing of an electric current through the cell (a flow of O^{2-} oxygen anions through the electrolyte). The induced change in the catalytic rate was one-two orders of magnitude higher than the rate of O^{2-} pumping through the electrolyte.

This effect is of interest for heterogeneous catalysis and is known as the non-Faradaic electrochemical modification of catalytic activity (NEMCA) [2].

The present paper is devoted to the investigation of the influence of electrochemical oxygen pumping on the CO oxidation on gold electrode-catalyst in the cell with the solid oxygen-conducting electrolyte:

$CO + O_2$, Au $|ZrO_2(10\ mol\%\ Y_2O_3)|$ Ag, PrO_{2-x}, air.

It is worth noting that in accordance with data available in the literature gold is a catalyst for the CO oxidation [4–6] and is an active electrode for the electrochemical oxidation and reduction of oxygen in the cell with a solid oxygen-conducting electrolyte [7,8].

2. Experimental

The electrochemical cell was a tube closed at one end made from yttria stabilized zirconia solid electrolyte (YSZ). The electrolyte tube was 9 mm in diameter, 200 mm in length and had 1 mm wall thickness.

The gold (working) electrode was deposited on the outer surface of the zirconia tube. To isolate this electrode from ambient air the zirconia tube was enclosed in a quartz tube. The reaction mixture flowed in the annulus space between the quartz and zirconia tubes. A silver electrode contained praseodymium oxide was deposited on the inner surface of the zirconia tube and served as a counter and reference electrodes simultaneously. The geometrical area of the electrodes was ~ 10 cm^2.

All data reported here were obtained after pretreatment of electrodes carried out at 750°C in air during 20 h by passing an anodic or/and cathodic current. The CO oxidation reaction was studied at atmospheric pressure and temperatures 460–560°C. A flow of CO, oxygen and insert gas was fed to a gold electrode-catalyst at 2 cm^3/s. The counter electrode was blown with air. The concentrations of CO and O_2 in the initial gas mixture were varied in the ranges 0.5–5 vol% and 5–21 vol%, respectively.

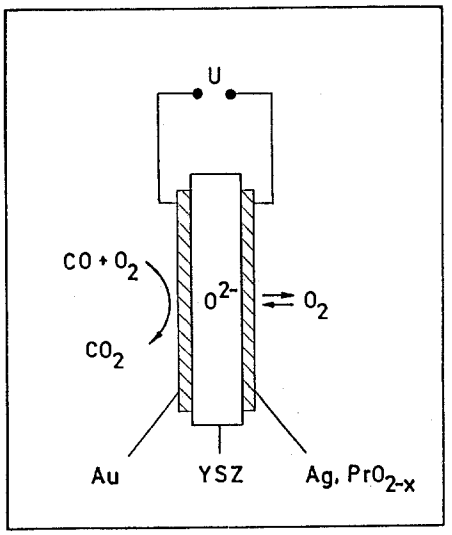

Fig. 1. Schematic diagram for CO oxidation in an electrochemical cell.

The principle of the experiments is shown in fig. 1. With an open electrical circuit in the cell, an ordinary heterogeneous catalytic reaction of CO oxidation takes place on the Au electrode-catalyst. When an electric current is applied to the cell, the electrode-catalyst, depending on the polarity of the applied current, can behave either as an anode, or as a cathode. The former leads to electrochemical supply of oxygen into the reaction zone through YSZ while the latter leads to electrochemical removal of oxygen from the reaction zone through YSZ. The aim of the present study was to investigate this effect on the CO oxidation rate.

The electric current (I) flowing through the cell was controlled by a potentiostat. The composition of the gas mixture before and after passing through the cell was analysed by chromatography.

The flow of oxygen through the electrolyte (V_{O_2}) was calculated from

$$V_{O_2} = I/4F$$

where F is Faraday's constant. The reaction rate was determined as

$$r = 25CV$$

where r is the CO_2 formation rate (μmol/min), C is the CO_2 concentration (vol%) and V is the space velocity of the gas mixture (cm^3/s).

The techniques used for the electrochemical and kinetic measurements have been described in detail elsewhere [9]. Here we need only to draw attention to the fact that conversion of the reagents was insignificant in all experiments. The rate of oxygen pumping through the electrolyte was essentially lower (by more than two orders of magnitude) than the oxygen flow through the reaction volume. In these circumstances the concentrations of O_2 and CO in the reaction volume can be considered to be constant and equal to those at the inlet.

It should be noted that in a blank test without deposition of gold electrode-catalyst on the YSZ tube the rate of CO oxidation was $< 5\%$ of the rates obtained with Au.

3. Results and discussion

CO OXIDATION UNDER OPEN-CIRCUIT CONDITIONS

When CO-O_2 mixtures are fed through the reactor the open-circuit potential takes values between -180 and -290 mV. This indicates that oxygen activity (a) on the electrode-catalyst determined from ref. [1,3] as

$$a = (0.21)^{1/2} \exp(2FE/RT)$$

is lower than the gas phase oxygen activity $a_0 = P_{O_2}^{1/2}$, where P_{O_2} is the oxygen pressure. Thus, under reaction conditions oxygen adsorbed on the Au surface is

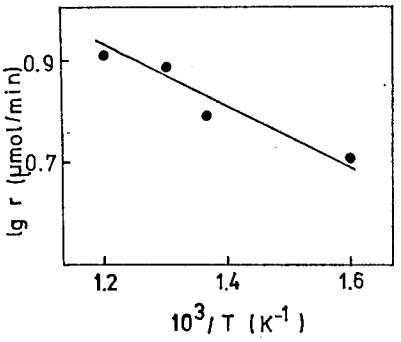

Fig. 2. Temperature dependence of the rate of CO_2 formation (r) under open-circuit conditions. $C_{O_2} = 21$ vol%, $C_{CO} = 1.8$ vol%.

not in equilibrium with the gaseous oxygen. The same results were obtained during CO oxidation on the Pt electrode-catalyst [3].

Figs. 2 and 3 show the effect of temperature and concentration of reagents on the rate of CO oxidation. It can be seen (fig. 2) that the reaction rate increases insignificantly with increasing temperature. At a temperature range from 460 to 560°C an apparent activation energy of the reaction is 4 kcal/mole.

As shown in fig. 3, the production of CO_2 is first order in carbon monoxide and zero order in oxygen. The same concentration dependences on the rate were determined over the temperature range from 460 to 560°C.

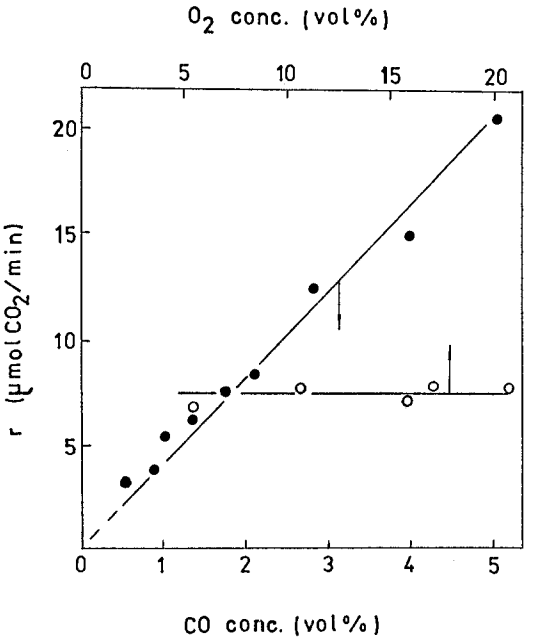

Fig. 3. Effect of gaseous compositions on the rate of CO_2 formation (r) under open-circuit conditions at $T = 495$°C. (●)–$C_{O_2} = 21$ vol%, (○)–$C_{CO} = 1.8$ vol%.

Our kinetic results for the CO-O_2 reaction on gold agree with those in refs. [4,5] showing a near zero activation energy but disagree somewhat in the concentration dependences of the reaction rate. The authors of ref. [5] reported that the reaction orders in CO and O_2 were zero at 200–300°C. But authors of ref. [4] observed a decrease of reaction orders in CO and O_2 from 1 to 0 with an increase of the concentration of reagents at the temperature below 100°C.

From our point of view, the discrepancy in the reaction orders may be due to the different temperature range used in the present study and in refs. [4,5].

The observed kinetic data permit us to make some conclusions about the mechanism of CO oxidation on gold. It seems reasonable to suppose that the $CO + O_2$ reaction follows the Eley-Rideal mechanism with the participation of a strongly bound oxygen state O_s, whose surface coverage is close to unity:

$$O_2 \rightarrow 2O_s$$

$$O_s + CO \rightarrow CO_2.$$

In this case the reaction orders in CO and O_2 should be equal to 1 and 0, respectively, which is in agreement with experimental data. A strongly bound oxygen state on Au, stable up to 800°C in vacuum, was detected by various surface science techniques after exposure of gold in O_2 at low pressure (10^{-6} Torr) and temperature above 200–300°C [10–15]. The formation of this oxygen state is caused by the presence of typical impurities such as Ca or Si on the gold surface [13–15].

The surface of the Au electrode used in the present study was not purified by UHV cleaning procedures and was probably contaminated. The formation of a strongly bound oxygen state could occur on the Au electrode surface.

An alternative Langmuir-Hinshelwood mechanism can also be proposed. For example, it is possible that a weakly bound molecular state of CO as well takes part in the process.

THE EFFECT OF CURRENT ON CO OXIDATION RATE

The effect of a current passing through the cell on the CO_2 formation rate and on a catalyst-electrode potential at two temperatures are shown in fig. 4a, b. It should be noted that the current is positive when O^{2-} is pumped to the catalyst (anodic polarization of electrode) and negative when O^{2-} is pumped from the catalyst (cathodic polarization of electrode). All results reported here were obtained in the potentiostatic mode of the cell operation, i.e., a constant potential was applied between the catalyst and the counter electrodes, and after the achievement of steady-state current and reaction rate values.

It can be seen (fig. 4) that anodic and cathodic polarizations of the gold electrode enhance the reaction rates (r) with respect to their open-circuit values (r_o). The observed changes in the r vs I were detected under all experimental

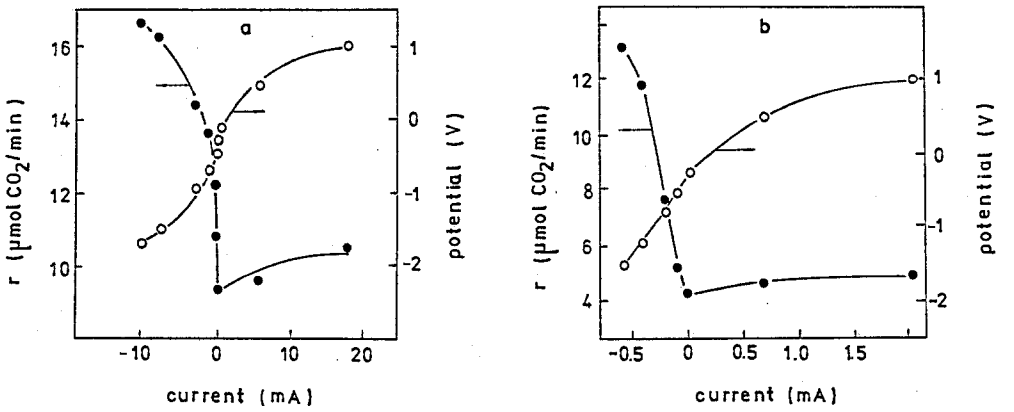

Fig. 4. Effect of the applied current on the rate of CO_2 formation and on the IR-free gold electrode-catalyst potential. (a)–$T = 560$°C, $C_{CO} = 1.8$ vol%, $C_{O_2} = 21$ vol%; (b)–$T = 460$°C, $C_{CO} = 1.4$ vol%, $C_{O_2} = 21$ vol%.

conditions and were quite reversible. When the cell current was switched off, the rates return to their initial values. Now we discuss these data in detail.

Anodic polarization of working electrode, i.e., oxygen pumping to the catalyst, leads to a slight increase in the reaction rate. Analysis of the data obtained (fig. 4) has shown that this rate increase is purely Faradaic. For example, for the data presented in fig. 4a the enhancement factor Λ [2] defined as

$$\Lambda = \Delta r/(I/2F) \tag{1}$$

where $\Delta r = r - r_0$ is the change in the reaction rate (g-at.O/min) and $I/2F$ is the rate of O^{2-} transport through the electrolyte, has values less than 0.3. It means that only 30% of the oxygen pumped to the catalyst takes part in the CO oxidation reaction, whereas 70% of the oxygen releases electrochemically at the gold electrode: $2O^{2-} = O_2 + 4e^-$. Thus, O^{2-} pumping to Au electrode has not the NEMCA effect on the rate of CO oxidation.

In recent studies [2,3] it has been found that O^{2-} pumping to Pt and Pd electrodes dramatically enhances the CO oxidation rate. The published results show that $\Lambda \sim 10^2$–10^3 and $r/r_0 \sim 1.5$–3, i.e., the observed behaviour was non-Faradaic.

The NEMCA effect for those catalytic systems was explained by taking into account the increase in the catalyst work function during O^{2-} pumping to the Pt and Pd annd the consequent decrease in the strength of the chemosorptive bond of oxygen [2,3].

One might expect that O^{2-} pumping to Au as well as Pt and Pd would be accompanied by dramatic changes in the rate of CO oxidation. However, according to the data obtained, the catalytic properties of Au in contrast to Pt and Pd electrodes [2,3] did not alter essentially.

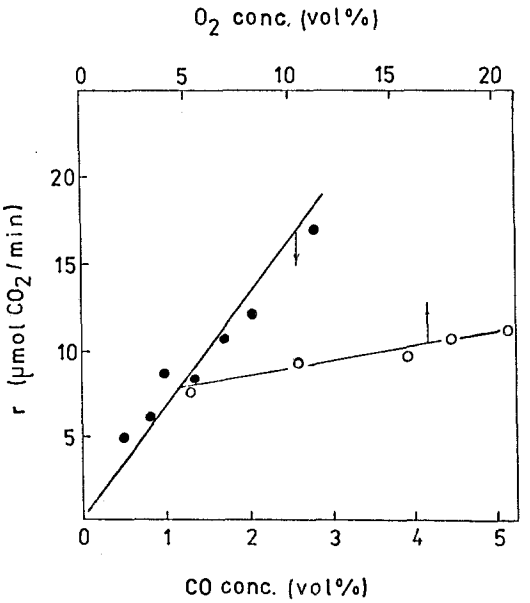

Fig. 5. Effect of gaseous compositions on the rate of CO_2 formation at $T = 495$°C and constant cathodic potential of the Au electrode-catalyst -1.0 V. (●)–$C_{O_2} = 21$ vol%; (○)–$C_{CO} = 1.7$ vol%.

Cathodic polarization of the Au electrode-catalyst, i.e., oxygen pumping from the catalyst, as shown in fig. 4a, b leads to the enhancement of the reaction rates with respect to their open-circuit values. The relative change in the rate r/r_0 is 1.7–3. The corresponding enhancement factor Λ, defined from eq. (1) where $I/2F$ is the oxygen pumping from the catalyst, is more than 1. Λ values decrease from 25 to 3 with an increase of the applied cathodic current at 560°C and are 50–60 at 460°C. Thus, O^{2-} pumping from the Au electrode was found to cause non-Faradaic changes in the CO oxidation rate.

Fig. 5 shows the effect of gaseous compositions on the reaction rate when the constant cathodic potential is applied to the Au electrode. It was found that the production of CO_2 is first order in CO and ~ 0.25 order in O_2. Thus, the cathodic polarization of the Au electrode does not influence the reaction order in CO and changes in oxygen with respect to the open-circuit value (fig. 3).

In the case of the platinum catalysed carbon monoxide oxidation NEMCA behaviour was also observed at the cathodic current application [3]. However, the NEMCA effect appeared only in reducing environments (the reaction mixture rich in carbon monoxide), when the applied potential of the platinum electrode is more negative than -1.3 V. In particular under these conditions $r/r_0 < 5$ and $\Lambda \sim 10^3$–10^4. To explain these results the authors of ref. [3] supposed that large cathodic potentials in reducing environments cause CO disproportionation followed by fast combustion of carbon by gaseous O_2. This mechanism of CO_2 formation, which is not available under open-circuit condi-

tions becomes thermodynamically possible since the potential of the electrode-catalyst is more negative than -1.3 V.

It should be emphasized that we observed CO oxidation rate enhancement and the NEMCA effect at cathodic polarization of Au electrode-catalyst for a reaction mixture rich in oxygen, when the applied potential of the gold electrode was more positive than -1.3 V (fig. 4a, b).

According to ref. [3] the cathodic polarization of the Pt electrode in oxidizing environments (reaction mixture rich in oxygen) show the opposite effect on the rates of CO oxidation, that is, lead to the decrease in rates with respect to their open-circuit values.

These crucial differences in the behaviour of Pt and Au electrodes at the current application in the course of CO oxidation can be hardly understood on the basis of the model suggested in [2,3,16] to explain the NEMCA phenomena.

We think that the enhancement of the Au electrode catalytic activity at the cathodic polarization is most probably related to the increase of the coverage of reactive oxygen species such as $O^-_{2\,ads}$ and O^-_{ads}. Under open-circuit conditions the coverage of this oxygen species is very low. The $CO + O_2$ reaction as discussed above occurs with the participation of the strongly bound oxygen state.

In accordance with [8] oxygen species O^-_{2ads} and O^-_{ads} are intermediate states at the cathodic reduction of gaseous oxygen on the Au electrode in the cell with the solid oxygen-conducting electrolyte. The mechanism of the cathodic reduction of O_2 suggested in that study can be written as follows:

1. $O_{2(g)} + V_{(ZrO_2\text{-}g)} \rightleftarrows O_{2(ZrO_2\text{-}g)}$

2. $O_{2(ZrO_2\text{-}g)} + V_{(ZrO_2\text{-}Au)} \rightleftarrows O_{2(ZrO_2\text{-}Au)} + V_{(ZrO_2\text{-}g)}$

3. $O_{2(ZrO_2\text{-}Au)} + e^-_{(Au)} \rightleftarrows O^-_{2(ZrO_2\text{-}Au)}$

4. $O^-_{2(ZrO_2\text{-}Au)} + V_{(ZrO_2\text{-}Au)} + e^-_{(Au)} \rightleftarrows 2O^-_{(ZrO_2\text{-}Au)}$

5. $O^-_{(ZrO_2\text{-}Au)} + V_{0(ZrO_2)^{00}} \rightleftarrows O_{0(ZrO_2)^0} + V_{(ZrO_2\text{-}Au)}$

6. $O_{0(ZrO_2)^0} + e^-_{(Au)} \rightleftarrows O_{0(ZrO_2)^x}$

where $V_{(ZrO_2\text{-}g)}$ is an adsorption site on the electrolyte/gas interface, $O_{2(ZrO_2\text{-}g)}$ is an adsorbed oxygen molecule on the electrolyte/gas interface, $V_{(ZrO_2\text{-}Au)}$ is an electrochemical reaction site on the electrolyte surface in the two-phase ZrO_2-Au region, $O_{2(ZrO_2\text{-}Au)}$ is an adsorbed oxygen molecule on the electrolyte surface in the two-phase region, $V_{0(ZrO_2)^{00}}$ represents an oxygen vacancy in the bulk electrolyte and $O_{0(ZrO_2)^x}$ is an oxygen ion in the bulk electrolyte.

Considering step 5 to be rate determining in accordance with ref. [8] it can be shown that the concentration of O^-_{2ads} ($O^-_{2(ZrO_2\text{-}Au)}$) and O^-_{ads} ($O^-_{(ZrO_2\text{-}Au)}$) may be increased by increasing the cathodic overpotential. From our point of view this

leads to CO oxidation rate enhancement and to the change of the reaction order in O_2 at the cathodic polarization of the gold electrode.

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