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Electrocatalysis of the Anodic Oxidation of Methanol by Metals

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The electrocatalysis of the anodic oxidation of methanol has been examined on several metals both in acidic and alkaline solutions. A principal aim was to investigate the factors that determine the oxidation rates of methanol on oxide-covered electrodes. It is found that in alkaline solutions in which a protective oxide can be easily formed on a number of metals, the rate of oxidation is related to the appropriate measure of the metal–oxide (M–O) bond energy in a volcanic manner. The significance of this observation is discussed in relation to volcano relationships observed for other cases of heterogeneous catalysis and electrocatalysis.

INTRODUCTION

There are several studies in the literature on the electrocatalysis of the hydrogen evolution reaction (*1–6*) and the oxygen reduction reaction (*7*). Electrocatalysis of redox reactions (*8*), ethylene oxidation (*9*) and oxygen evolution (*10*) has also been examined. The manner in which a film-covered metallic electrode influences the rate of a reaction has received some attention (*11*). The influence of electrode material on a variety of electroorganic reactions (*12*) has not been examined very extensively. Some notable studies have, however, appeared on the subject, e.g., electrocatalysis of methanol oxidation by noble metals and alloys (*13*), electrocatalysis of the hydrazine oxidation by noble metals (*14*), and, a variety of electroorganic reactions on oxide-covered Ni, Ag, Cu and Co electrodes (*15*). These investigations (*1–15*) must be regarded only as a representative fraction of the large amount of the previous similar work.

The object of the present work is to examine the influence of electrode material on the oxidation of methanol both in acidic and alkaline solutions. The electrodes chosen cover a wide range of noble and nonnoble metals: Au, Pb, Fe, Pt, Ir, Rh, Pd, Ag, Co, Ni, Sn, Re, Mo and W. The aim was to investigate the electrocatalysis of the oxidation of methanol on these metals in the potential range 0–1.8 V (vs RHE). In this potential spectrum, the oxidation of methanol can proceed on oxide-free surface in the potential range ca. 0.3–0.7 V (at least on noble metals) and can also occur at oxide-covered electrodes at potentials greater than ca. 1.3 V. Of special interest in the present study was the electrocatalytic behavior of oxide-covered electrodes for the oxidation of methanol.

EXPERIMENTAL METHODS

The experiments were conducted in a three-compartment Pyrex cell as in the previous work (*16,17*). Helium was bubbled in the working and the counter compartments. Hydrogen was used in the reference compartment since hydrogen reference electrodes were employed. The details on gas purification, preparation of conductivity water, cell and electrode cleaning, etc., are as in the previous work (*16*). All potentials to be given here in the various diagrams and the text refer to the hydrogen electrode in the same solution. The instruments have been described previously (*16*) and the technique employed in the present work consisted of potentiostatic, steady-state current–potential relationships. For every metal (except those which corroded very actively and for which quantitative data could not be obtained – see under Results and Discussion) the electrode was polarized for 30 min at 1.8 V and the current–potential relationship was obtained by lowering the electrode potential at the rate of 50 mV/2 min. This procedure was adopted since a principal aim of the present work was to examine the electrocatalysis of the methanol oxidation on oxide-covered electrodes. All experiments were conducted at room temperature.

The working electrodes were made of smooth wires, of purity better than 99.9% in every case. These metals were obtained either from Engelhard or the A. D. Mackay Co. The wires were sealed into Pyrex tubing by means of a heat-shrinkable Teflon, for all cases except Pt which was sealed directly into the glass. The electrodes were thoroughly cleaned, degreased in boiling trichloroethylene and dried before use. The electrolyte solutions were made up from Ultrex H_2SO_4 (Baker), Spectroscopic grade methanol (American Chemicals), A.C.S. grade KOH (Fisher certified) and triply distilled (the last two distillations being over alkaline $KMnO_4$) water.

RESULTS AND DISCUSSION

Methanol Oxidation on Oxide-Covered Electrodes

On each of the 14 metals, current–potential relations were obtained in the following four solutions: (i) 1 *N* H_2SO_4; (ii) 1 *N* H_2SO_4 + 5 *M* CH_3OH; (iii) 1 *N* KOH; (iv) 1 *N* KOH + 5 *M* CH_3OH. It was observed that of all the metals studied in 1 *N* H_2SO_4, only Rh, Ir, Au, Pd and Pt achieved "passivation." For the present work, "passivation" was arbitrarily defined as background corrosion current less than 2×10^{-6} A cm^{-2} at 1.4 V; the choice of 1.4 V is dictated by the fact that this potential is sufficiently anodic (0.17 V more anodic to the reversible oxygen potential) to give an oxidized surface but is not anodic enough to give appreciable rates of oxygen evolution reaction. In 1 *N* KOH solutions, a substantially larger number (Co, Ag, Rh, Ir, Ni, Au, Fe, Pd, Pt) of metals showed "passivation" as defined above. The rates of methanol oxidation at 1.4 V at various "passivated" metals in 1 *N* KOH and 1 *N* H_2SO_4 have been summarized in Table 1.

Theoretically, the rates of CH_3OH oxidation should be compared on various metals at the reversible potential but for methanol oxidation this is not possible either for the oxide-covered or for the "bare" electrodes. This is because the cur-

TABLE 1
OXIDATION OF METHANOL ON OXIDE-COVERED METALS AT 1.4 V

Metal	KOH[a] (A cm^{-2})	H_2SO_4[b] (A cm^{-2})
Co	1.9×10^{-3}	—
Ag	1.3×10^{-4}	—
Rh	1.5×10^{-5}	7.5×10^{-6}
Ir	7×10^{-6}	2.5×10^{-5}
Ni	5.5×10^{-3}	—
Au	1.0×10^{-6}	1.05×10^{-5}
Fe	$(9 - 2.5) = 6.5 \times 10^{-6}$	—
Pd	1.7×10^{-5}	7.0×10^{-4}
Pt	3.1×10^{-4}	2.2×10^{-5}

[a] In KOH solutions, no passivation was observed on W, Pb, Mo, Re, Sn; for the case of iron, corrosion current was significant (2.5×10^{-6} A cm^{-2}), though not intolerable, and was subtracted from the total rate in CH_3OH + KOH solutions in order to obtain the net rate of oxidation of CH_3OH.

[b] Of all the metals studied in H_2SO_4, only Rh, Ir, Au, Pd and Pt achieved "passivation" (i.e., the background corrosion current less than ca. 2×10^{-6} A cm^{-2} at 1.4 V).

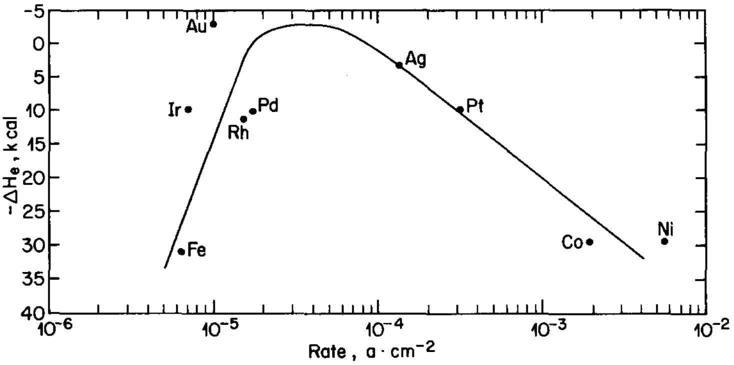

FIG. 1. The rate of methanol oxidation, on the oxide-covered shown metals (at 1.4 V) in 1 N KOH + 5 M CH_3OH, plotted vs the heat of formation per equivalent of the respective oxides. A volcano relationship may be noted. The rate data for this figure are given in Table 1 and its significance is discussed in the text.

rent-potential relationships (presented below) show complicated transition and inhibition regions and are not merely Tafel lines. It should be added here that any possible comparison of electrode reaction rates at the potentials of zero charge are theoretically not valid (*18,19*).

In Fig. 1, the rate vs bond energy [where bond energy is equal to heat of formation per equivalent (*20–22*)] curve for various oxides shows a volcano plot. Volcano plots in catalysis were introduced by Sabatier (*23*), developed by Balandin (*24*) and first applied to the case of electrode reactions by Parsons (*25*) and Gerischer (*26*). Since then (*25,26*) these plots have been observed in several electrode reactions as reviewed recently (*19*).

The fundamental idea of these volcano plots (*24–27*), to be called Sabatier–Balandin plots below, is that if formation or rupture of an M–O bond is involved in a reaction, the catalytic activity is related to the M–O bond energy in a volcanic manner such that a maximum in activity with *increasing* bond energy is involved. In this sense, the volcano in Fig. 1 is different from the Sabatier–Balandin plot because a maximum in activity with increasing bond energy is not observed. Instead one obtains a moderate rate corresponding to the lowest bond energy and very high or very low rates associated with the high values of bond energy. Conceptual similarities between this volcano relation and the Sabatier–Balandin plots may be noted, however. On one arm of the volcano, the activity increases with *decreasing* $-\Delta H_e$ values whereas on the other arm, the activity increases with *increasing* $-\Delta H_e$ values. Volcano plots similar to those in Fig. 1 have recently been also observed for the gas-phase catalytic decomposition of N_2O on oxide catalysts (*21*). It should be added that the role of M–O bond energy in several gas-phase heterogeneous oxidations has been discussed previously (27–33).

An important feature of Fig. 1 and Table 1 may also be mentioned here. Assuming that electrode *stability* can be achieved, the catalytic behavior in electrode reactions should correspond to the catalytic behavior in gas-phase catalysis. It appears that at anodic potential in KOH solutions, Co and Ni form protective oxides which impart them electrode stability; under these conditions the oxide-covered Co and Ni electrodes are in a position to display high electrocatalytic activity (even higher than Pd, Rh and Pt) in a way very similar to the high catalytic activity of oxides of Co and Ni in the gas phase (*22*).

It should be added here that the M–O bond rupture involved in the oxidation

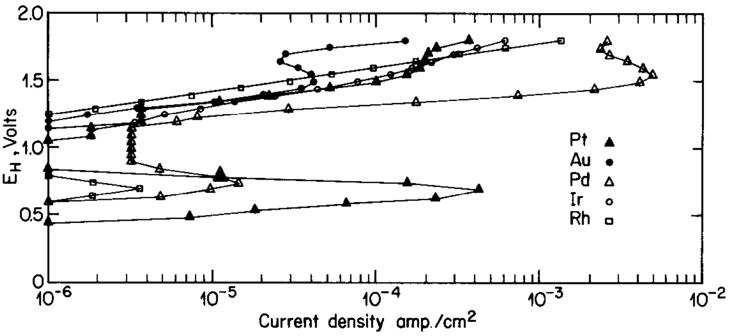

FIG. 2. Steady-state current–potential relationships observed, in the descending direction of potentials, on the shown metals in 1 N $H_2SO_4 + 5$ M CH_3OH.

reaction such as

$$3M\text{-}O + CH_3OH \rightarrow 3M + CO_2 + 2H_2O \quad (1)$$

may not necessarily lead to the reduction of M–O to M; in fact, the reduction of the surface oxide by methanol, such as in reaction (1), may lead to a lower oxide instead of the complete reduction all the way to the metal. Similarly, the inverse reaction in which the anodic oxide is formed [instead of being reduced as in Eq. (1)] may involve either the oxidation of the metal M or the oxidation of a lower oxide to yield a higher oxide.

As regards the data in the acidic solutions (Table 1), no correlation between catalytic activity and $-\Delta H_e$ values of the oxides could be found. This is partly owing to the fact that the accessible data are for a few metals only thus limiting the possibility of detecting any rough general trends.

Current–Potential Relationships for Methanol Oxidation on Various Metals

Although current–potential relationships for the oxidation of methanol have been reported for some noble metals and alloys (*13,34,35*), an examination of this reaction on several *oxidized* metals, both in acidic and alkaline solutions, has not appeared in the literature. It is of interest, therefore, to present here these relationships for cases for which the data are accessible (Table 1). In Fig. 2, the current–potential relationships obtained on Pt, Pd, Rh, Ir and Au in 1 N $H_2SO_4 + 5$ M CH_3OH solutions are depicted. The data in alkaline solutions pertain to nine metals (Table 1) and hence

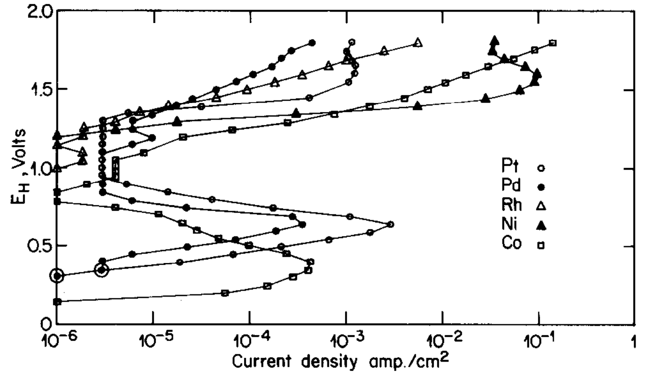

FIG. 3. Steady-state current–potential relationships observed, in the descending direction of potentials, on the shown metals in 1 N KOH + 5 M CH_3OH.

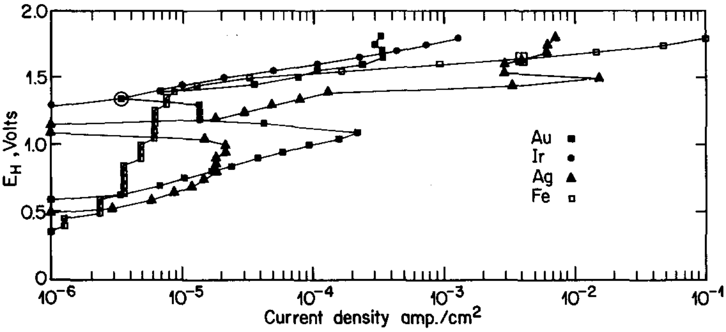

FIG. 4. Steady-state current–potential relationships, taken in the descending direction of potentials, on the shown metals in 1 *N* KOH + 5 *M* CH_3OH.

cannot be presented in the same figure without creating an enormous overlap and confusion; these data, therefore, have been arbitrarily divided into two figures, Figs. 3 and 4, in order to facilitate their presentation. The current–potential curves obtained in the background electrolytes, namely, 1 *N* H_2SO_4 and 1 *N* KOH are not given here since the relevant information regarding the stability of the electrodes to be derived from them has been summarized in the footnotes to Table 1. Two points in Figs. 2–4 merit a particular mention. In our work no significant oxidation of methanol is observed on Ir at low anodic potentials, which is at variance with some previous observations (*36*). Breiter found (*37*) comparatively little oxidation of methanol on platinum on sweeping from positive to negative potentials at a sweep rate of 30 mV/sec. In our case, significant oxidation at 1.4 V on Pt is observed, however, probably because our experiments were carried out under steady-state conditions with a potential variation of 50 mV/2 min.

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