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NOTE

Electrochemical Promotion of the NO + Ethylene Reaction over Platinum

Electrochemical promotion (EP) of the catalytic activity of metal films was first reported by Vayenas *et al.* (1) who went on to show that the phenomenon could be induced for a range of reactions (2–4) and with a variety of solid electrolytes, including oxygen (2, 3), sodium (2, 4), fluorine (5), and hydrogen (6) ion conductors. It is proposed (1, 2) that spillover ions pumped from the electrolyte modify the metal surface work function with concomitant changes in adsorption enthalpies and reaction activation energies: the available data appear to be in good quantitative accord with this model. Recently, the effect has also been observed by Haller and co-workers for methanol oxidation over platinum (7). These EP systems are characterized by a very large value for the ratio (Λ) between the rate of charge transport through the electrolyte and the change in turnover rate. That is, they are highly non-Faradaic, and one is certainly not dealing with conventional electrocatalysis. Reported gains in reaction rate ($r/r_0 = \rho$) with respect to the unpromoted rate lie in the range 2–70 (2).

Here we report an independent confirmation of the electrochemical promotion effect in a study of the oxidation of ethylene by NO over Pt films supported on β'' alumina, (an Na^+ conductor). Catalytic reduction of NO by hydrocarbons is of considerable interest with respect to control of automotive emissions: for example, with respect to the development of fuel efficient lean-burn gasoline engines working at high air:fuel ratios. Our catalytic data for Pt/β'' alumina are supplemented by spectroscopic and kinetic results obtained with a well characterised Na-dosed Pt(111) model catalyst. A (111)-oriented single crystal was chosen because the polycrystalline surface of the supported Pt catalyst consists mainly of (111) planes.

Electrochemical studies at atmospheric pressure were performed in a CSTR reactor (volume 60 cm^3), product analysis being carried out by means of a Balzers QMG 064 quadrupole mass spectrometer. A porous but continuous thin film Pt working electrode (active metal area $\sim 1 \times 10^{-6}$ mol Pt; total loading $\sim$1.0 mg Pt) and Au reference and counter-electrodes were deposited on a disc of Pt/β'' alumina (2.8 mm thick × 16 mm diameter) following the method described in Ref. 8. The surface area of the catalyst film may be conveniently estimated from the initial rate of change of the voltage between the catalyst and the reference electrode (V_{wr}) on passage of a pulse of constant current. Changes in V_{wr} are equal to the change in the work function of the catalyst film. (1, 2); they are caused by the spillover of sodium ions from the electrolyte to the platinum surface. Therefore, if the sample is held at a sufficiently high positive bias to ensure a sodium free surface prior to application of the current pulse, the initial change in V_{wr} is given by (2):

$$\frac{ed(V_{wr})}{dt} = eP_0\frac{dC_{Na}}{dt} = \frac{eP_0 I}{\varepsilon_0 e A_c} = \frac{P_0 I}{\varepsilon_0 A_c}$$

where I = current; C_{Na} = atoms of sodium/m^2; P_0 = initial dipole moment of sodium on platinum = 1.75×10^{-29} cm; and A_c = surface area of the catalyst in m^2 (1, 2). It has been shown that this method gives reasonable agreement with more conventional surface area measurements (2); in the present case we obtain a value of 90 cm^2 for the area of the metal film. Catalytic rate measurements under potentiostatic or galvanostatic conditions were carried out using an Amel type 553 galvanostat–potentiostat. Most observations were carried out in potentiostatic mode by following the effect of the potential difference between the catalyst and the reference electrode (V_{wr}) on the reaction rate. 1.0% NO in He, He (Distillers MG) and ethylene (B.O.C.) were fed to the reactor without further purification.

Complementary experiments were carried out using a Pt(111) single crystal model catalyst which could be translated between a UHV chamber (XPS, TPD, Na dosing, Ar^+ etching) and a pressure cell (30 cm^3) which was operated as a differential batch reactor. Reactant and product concentrations were monitored mass spectrometrically (VG Q7) and the elapsed time between pumping out the reactor and transferring the sample to a UHV environment was typically 10 min. TPD spectra were recorded in multiplexed mode with a heating rate of 20 K/s. XP spectra were acquired with a VSW HA-100 instrument using Mg $K\alpha$ radiation with electron binding energies referenced to the Pt $4f_{7/2}$ peak at 71.07 eV. Na dosing was by means of a collimated evaporation source (SAES

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Getters), Na coverage calibration being achieved by TPD and XPS. Note that in any given experiment an equivalent amount of Na was deposited on *both* surfaces of the Pt(111) wafer.

Figure 1 shows CSTR CO_2 rate data as a function of V_{wr} at 675 K for three different gas compositions—in every case the rate rises sharply with decreasing catalyst potential. The top abscissa shows sodium coverages derived from separate galvanostatic experiments by determining the length of time required for a constant current (20 μA) to change V_{wr} from the clean surface value of $\geq$200 mV to the value of interest. This procedure yields the total number of sodium atoms pumped to the catalyst, and quoted sodium fractioinal coverages (θ_{Na}) are expressed as the number density of Na atoms relative to the Pt(111) plane. The rate of disappearance of NO and C_2H_4 tracked the rate of formation of CO_2; measurement of N_2 and NH_3 yields was precluded by mass spectral interferences at 17 and 28 amu.

The exponential dependence of rate on V_{wr} above a certain threshold value is characteristic of EP behaviour where the rate can be described by (1)

$$\ln \frac{r}{r_0} = \alpha_{EP} \frac{F\Delta V_{wr}}{RT}$$

where α_{EP} is a constant specific to the reaction and catalyst. In the present case we find $\alpha_{EP} = 0.25$ in reasonable agreement with earlier work (2). It can be seen that the rate is relatively insensitive to gas composition over the limited range investigated. Figure 2 shows a comparison between rate data obtained in potentiostatic experiments and those obtained under the same conditions whilst passing a pulse of constant current, a galvanostatic transient, through the sample. The agreement is good and shows that Na coverages obtained from the galvanostatic transient are consistent with the potentiostatic data. Most importantly, the results show that the rate is linearly dependent on θ_{Na} at low and intermediate coverages.

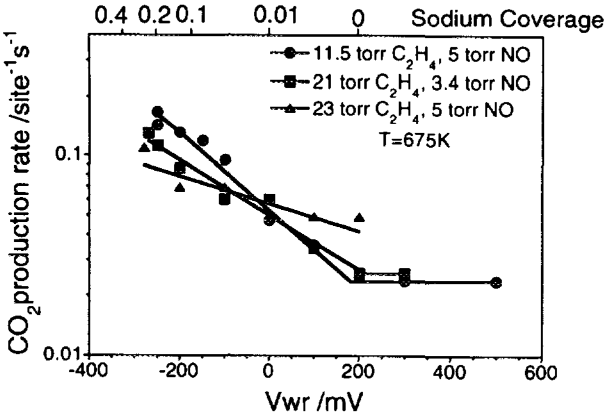

FIG. 1. Dependence of (CSTR) rate on V_{wr} for 3 different gas compositions.

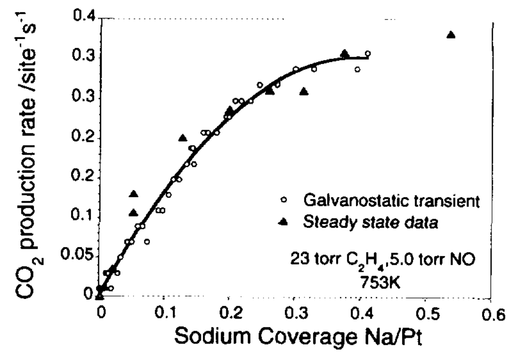

FIG. 2. Electrochemically promoted rate as a function of Na coverage for data obtained under both potentiostatic (steady state) and galvanostatic (transient) conditions.

Note that under these conditions the initial rate on clean platinum is immeasurably small so that the rate gain factor (ρ) is therefore nominally infinite; a finite value of $\rho = 15$ was obtained under different conditions of temperature and gas composition (Fig. 1). This is the first time such behaviour has been observed for this electrolyte. Figure 3 shows the temperature dependence of the kinetic data from the single crystal reactor. The results agree qualitatively with those from the CSTR in that at high temperatures the rate rises monotonically with sodium coverage. (The temperature regime of the CSTR data was not accessible in the single crystal batch reactor because of the requirement of low total conversion.) The apparent activation energies derived from these data range from 64 ± 20 kJ mol^{-1} for the clean surface to 100 ± 10 kJ mol^{-1} or $\theta_{Na} = 0.25$. Thus a relatively small increase in activation energy is overwelmed by a large increase in the pre-exponential (by a factor of 2600 over this coverage regime).

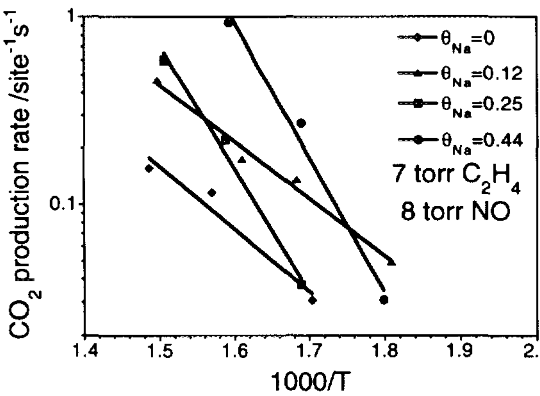

FIG. 3. Pt(111)/Na model catalyst. Dependence of Arrhenius plots on Na loading.

Co-adsorbed alkali metals are known to promote dissociation of NO (9), a process which may be rationalised in terms of the traditional Blyholder model (10). A more rigorous treatment due to Lang *et al.* (11) shows that alkali adatoms can induce the dissociation of neighbouring diatomic molecules *via* a short range screened electrostatic interaction which induces surface → molecule charge transfer. In the present case, we have confirmed that interaction with adsorbed Na does indeed cause NO dissociation on Pt(111): thus N_2 and NO TPD spectra (not shown) taken as a function of Na coverage following NO chemisorption show a rapidly increasing degree of NO dissociation with increasing Na coverage.

We therefore propose that the promotion observed when sodium is supplied either electrochemically or by dosing from the gas phase is due to a large increase in the concentration of oxygen adatoms available for reaction: this would also provide a natural explanation for the large rise in the pre-exponential. Since the apparent the activation energy rises with sodium coverage, the rate determining step is unlikely to be NO dissociation. Comparison with activation energies reported for the various elementary steps (12) indicates that the surface reaction CO + O is the most likely rate limiting step in the present case. This conclusion seems plausible, given that sodium should increase the bonding of both O and CO to the surface, thereby increasing the activation energy for reaction between them.

Postreaction XPS and XAES analysis indicate the formation of a two-dimensional carbonate-like surface compound under reaction conditions. This phase is characterised by an O 1*s* signal at 530.7eV binding energy (Fig. 4A) which may be reproduced in control experiments by adsorption of CO_2 onto a Na-predosed Pt(111). Its identification as a carbonate is supported by TPD data which show simultaneous ion peaks for Na^+ and CO_2^+ in the interval 750–900 K. The large shift of the sodium $KL_{2,3}L_{2,3}$ X-ray excited Auger electron feature from 992.5 to 990.0 eV (Fig. 4B) (also observed in control experiments with CO_2/Na/Pt(111)) provides further evidence of surface compound formation (13, 14). The lack of any measurable shift in the Na 1*s* emission is confirmation that this compound is not an oxide (14). Its essentially two-dimensional nature is suggested by the invariance of the Na 1*s* integrated intensity between pre- and postreaction spectra; the implication is that significant agglomeration to form 3-D crystallites does not occur.

Our principal conclusions may be summarised as follows. EP of a Pt film on β'' alumina reversibly increases the rate of ethylene oxidation by NO; the relative effect is large and may have technological significance. Parallel kinetic and spectroscopic studies with Pt(111)/Na indicate that a principal effect of Na pumping to the catalyst is enhancement of NO disocciation. The surface species present under reaction conditions is a compound of Na, probably carbonate, which wets the surface rather effectively. We suggest that this surface compound is the electrochemically controlled promoter.

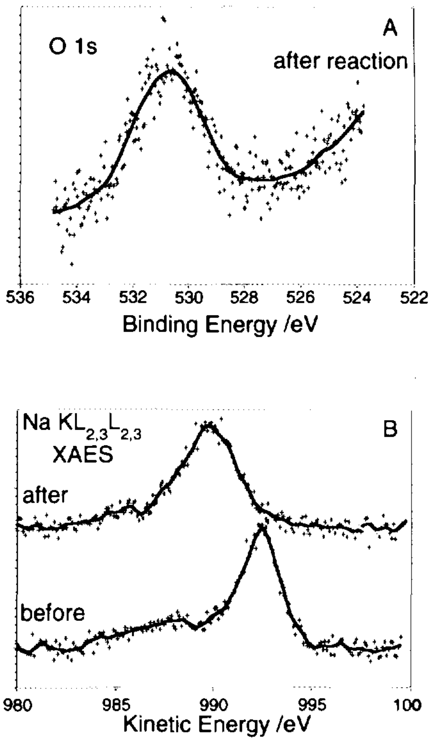

FIG. 4. Pt(111)/Na model catalyst. (A) postreaction O 1*s* XP spectrum. (B) Na KLL Auger spectra taken before and after reaction.

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