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The Influence of Electrochemical Pumping of Oxygen through a Solid Oxide Electrolyte on the Catalytic Properties of Platinum in Methane Oxidation

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The effect of electrochemical pumping of oxygen on the rate of complete oxidation of methane on Pt electrode–catalyst in a solid oxygen-conducting electrolyte cell has been demonstrated.

The present work is devoted to the investigation of the influence of electrochemical pumping of oxygen on the complete oxidation of methane on a platinum electrode–catalyst in a cell (1) with a solid oxygen-conducting electrolyte.

$$CH_4 + O_2, Pt|ZrO_2\ (10\ mol\%\ Y_2O_3)|Pt, O_2 \qquad (1)$$

The electrochemical cell was a tube closed at one end made from a solid oxygen-conducting electrolyte, with platinum electrodes supported on the inner and outer surfaces of the tube. The geometrical area of the electrodes was 12 cm^2.

The methane oxidation reaction was studied at atmospheric pressure over the temperature range 400–600 °C. A flow of methane, oxygen and inert gas was fed to the platinum electrode inside the tube at 1–5 $cm^3\ s^{-1}$. In this case the outer electrode was fed with air. The concentrations of methane and oxygen in the initial gas mixture were varied in the ranges 0.5–16 vol.% and 20–90 vol.%, respectively.

The principle of the experiments is shown in Fig. 1. With an open electrical circuit in the cell, an ordinary heterogeneous catalytic reaction, complete oxidation of methane, takes place on the Pt electrode–catalyst.

When an electric current is applied to the cell, the electrode–

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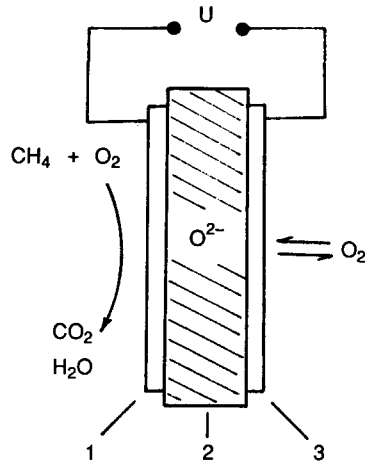

Fig. 1 Schematic diagram for complete oxidation of methane in an electrochemical cell with a solid oxygen-conducting electrolyte. 1, Pt electrode–catalyst; 2, solid oxygen-conducting electrolyte containing ZrO_2 (mol 10% Y_2O_3); 3, Pt counter electrode.

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 *i.e.* on the surface of the catalyst while the latter leads to electrochemical removal of oxygen from the reaction zone through the solid electrolyte. The aim of the present study was to investigate this effect on the rate of the complete oxidation of methane.

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 techniques used for the electrochemical and kinetic measurements have been presented in detail elsewhere.[1] Here, we need only 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 oxygen and methane in the reaction volume can be considered to be constant and equal to those at the inlet.

Investigation of the reaction kinetics in the above-mentioned range of reagent concentrations in the case of an open electrical circuit of the cell ($I = 0$) has shown that the oxidation rate of CH_4 is independent of O_2 concentration and is first order in methane.

An electric current through the cell exerts a significant influence on the reaction rate. Indeed, can be seen from Fig. 2,

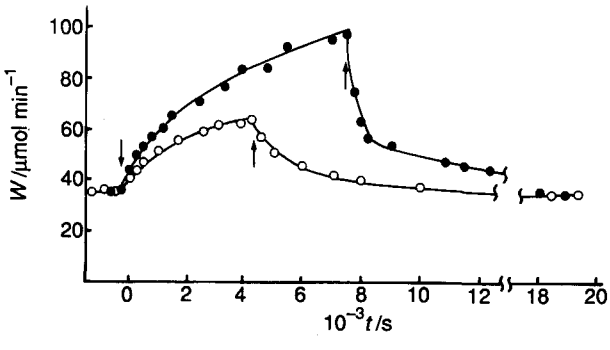

Fig. 2 Influence of oxygen supply to the reaction zone through the electrolyte on the rate of methane oxidation (W) on Pt electrode–catalyst. ↓↑, time intervals of current switching on and off. Experimental conditions: $T = 590$ °C; initial concentrations $CH_4 = 16$ vol.%; $O_2 = 84$ vol.%; flow rate of reaction mixture 1.2 cm^3 s^{-1}. (○) $I = 10$, (●) $I = 50$ mA, corresponding to flow of O^{2-} anions through the electrolyte of 10 and 50 mA.

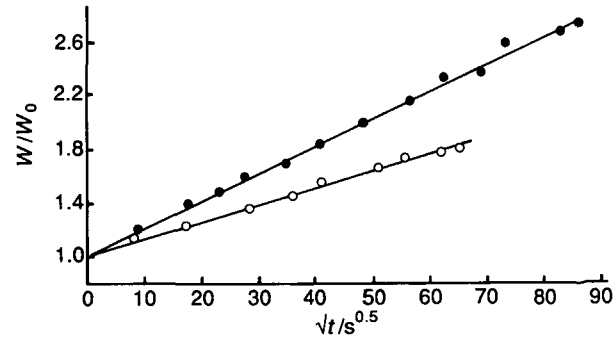

Fig. 3 Dependence of the relative rate of CH_4 oxidation (W/W_0 on the square root of time (t) during oxygen supply to the reaction zone through the electrolyte. W_0 is the reaction rate at $I = 0$; W is the reaction rate at $I \neq 0$ after supply of oxygen during time t. Values W and W_0 as in Fig. 2. (○) $I = 10$, (●) $I = 50$ mA.

the supply of the oxygen to the reaction zone through the electrolyte (anodic polarization of the electrode–catalyst) leads to an increase of the reaction rate. At 10 mA current the rate increases by 1.7 times during 60 min, and at 50 mA current the growth is more than twice the initial stationary reaction rate in the case of an open circuit. It should be noted that a steady increase in rate is observed in the case of anodic polarization of the electrode, and the new stationary state has not been reached, even after 150 min.

It can be seen from Fig. 3 that the relative growth of the reaction rate is directly proportional to the square root of the time of action of the electric current. This indicates a diffusional character for the process, leading to the increase in reaction rate.

The passage of current through the cell in the reverse direction (*i.e.* removal of oxygen from the reaction zone) produces a decrease in the rate of reaction. When the cell current is switched off, the rate of reaction returns to its initial value both in the case of supply (Fig. 2), and removal of oxygen through the electrolyte. Switching the current back on leads to effects analogous to those mentioned above. The influence of electrochemical supply and removal of oxygen on the reaction rate is thus reversible.

There are several possible reasons for the variation of the reaction rate during the passage of electric current through the cell, as follows. (*i*) The change of oxygen concentration in the reaction zone due to its supply or removal through the electrolyte. (*ii*) The direct electrochemical oxidation of methane. (*iii*) Modification of the surface of the electrode with consequent variation of its catalytic activity under the influence of active states of oxygen formed as a result of the electrochemical reactions. Analysis of the data obtained shows that (*i*) and (*ii*) cannot produce significant variation in the rate.

As mentioned above, the relative change of oxygen concentration due to the passage of the current was not greater than 1–2%, and, moreover, the rate of methane oxidation did not depend on the concentration of oxygen in the gas phase.

In the case of direct electrochemical oxidation of methane the change of the reaction rate should be equivalent to the rate of oxygen transfer through the electrolyte: see eqn. (2), where

$$\Delta W_{CH_4} = 0.5\, W_{O_2} = 77.7\, I \qquad (2)$$

ΔW_{CH_4} is the variation of reaction rate (μmol min^{-1}), W_{O_2} is the rate of oxygen transfer through the electrolyte (μmol min^{-1}) and I is the current in the cell (A).

In our experiments the observed variations in reaction rate were greater than those calculated from eqn. (2). Thus, in the case of anodic and cathodic polarization of the electrode the rate increased 50 and 4 times, respectively. An analogous modification of catalytic activity was observed recently[2] for the oxidation of CO, C_2H_4 and MeOH, also on a platinum electrode in a cell with a solid oxide electrolyte.

It is quite probable that the change in catalytic activity of the

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platinum electrode for methane oxidation during the passage of current through the cell is stimulated by modification of the platinum surface by active states of oxygen, arising from the electrochemical reactions. Further studies are needed to clarify this point.

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References

1 V. D. Belyaev, V. A. Sobyanin, V. A. Arzhannikov and A. D. Neuimin, *Dokl. Akad. Nauk SSSR*, 1989, **305**, 1389.
2 C. G. Vayenas, S. Bebelis, S. Neophytides and I. V. Yentekakis, *Appl. Phys. A*, 1989, **49**, 95.

Stereochemistry of Cobalt(III) Complexes Containing (N,O)-Five and Six-membered Aminoalcohol Chelate Rings

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^{59}Co NMR (94.45 MHz) has been used to study Co^{III} complexes formed by reaction of cobalt(II) chloride with 2- and 3-aminoalcohols; mononuclear molecular tris-O,N-chelate complexes of $Co^{III}L_3$ ($L = NH_2CH_2CH_2O^-$ and $NH_2CH_2CH_2CH_2O^-$) are produced in both geometric *mer*- and *fac*-forms, the *mer*-isomers being thermodynamically unstable and spontaneously rearranging to the *fac*-form in solution; the analogous complex $L = NH_2CHEtCH_2O^-$ exists only in the *fac*-form; 2-aminoalcohols also yield trinuclear complexes $[Co^{II}(Co^{III}L_3)_2]^{2+}$, in which pseudo-contact interaction of the Co^{II} and Co^{III} atoms occurs; the crystal structure of $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}\cdot Cl_3(NH_3CH_2CH_2OH)\cdot 2H_2O$ has been determined.

When 2-aminoethanol reacts with Co^{II} salts in the presence of alkali a molecular tris-O,N-chelate complex of cobalt(III) $[Co(NH_2CH_2CH_2O)_3]$[1–4] is formed which exists in two isomeric forms [δ_{mer} 1913; δ_{fac} 2066, relative to $Co(NH_3)_6Cl_3$].

The *mer*-isomer is unstable in aqueous solution (pH 7) and spontaneously isomerizes to the *fac*-form with time. In this case the *mer*→*fac* isomerization reaction is first order ($K_S = 5.2 \times 10^{-4}$ s^{-1}; $\Delta H^{\ddagger} = 59.44$ kJ mol^{-1}; $\Delta S^{\ddagger} = -0.11$ kJ mol^{-1} K^{-1} at 25 °C). The relatively low values of the activation parameters may indicate an intramolecular character of the *mer*→*fac* isomerization process (twist-mechanism). One can assume that on dissolving the *mer*-isomer in water the dipole–dipole interaction of the complex with solvent molecules causes *mer*→*fac* isomerization, because the presence of negative charge on one side (side OOO) and positive charge on the opposite side (side NNN) increases the dipole of the *fac*-isomer. When the less polar solvent methanol is used then *mer*→*fac* isomerization proceeds four times slower than in aqueous solution. It should be noted that during *mer*→*fac* isomerization, when the concentration of both isomers became approximately equal within a short period, signals (δ 3250 and 3560) characteristic of $Co^{III}(N)_2(O)_4$ type complexes were registered in the ^{59}Co NMR spectra. Thus, the mechanism of *mer*→*fac* isomerization can also include cleavage of the metal—ligand bond through the nitrogen atom (or complete cleavage of both cobalt—ligand bonds) with the participation of the solvent molecules. The cobalt—nitrogen bond in the *mer*-isomer can break in two different places (on N—Co—N and N—Co—O coordinates); this fact explains the presence of two bands from the intermediate complex $Co(N)_2(O)_4$ in the spectrum.

The presence of hydroxy ions in the solution causes the reverse transfer *fac*→*mer*. The kinetics of the *fac*⇌*mer* isomerization catalysed by OH^- ions is described by eqns. (1) and (2),

$$K_{f\to m} = A[OH]^2 \quad (1)$$

$$K_{m\to f} = K_S + K_{[OH]}[OH]^2 \quad (2)$$

where A is a constant, $K_{[OH]}$ the reaction rate constant, being catalysed only by OH^- ions and K_S the spontaneous *mer*→*fac* isomerization rate constant. Acidification by a solution (pH 5) containing the molecular complexes *fac*- and *mer*-$[Co(NH_2CH_2CH_2O)_3]$ first leads to the formation of cationic complexes $[Co(NH_2CH_2CH_2OH)_3]^{3+}$ (δ_{mer} 1205, δ_{fac} 1320), then breakage of the chelate rings through the oxygen atom takes place with time and complexes containing monodentate aminoalcohol *mer*- and *fac*-$[Co(NH_2CH_2CH_2O)_3(H_2O)]^{3+}$ (δ 2590, 2710) are formed. The tris-molecular complex $[Co(NH_2CH_2CH_2O)_3]$, containing O,N-bidentate six-membered 3-aminopropan-1-ol ligands, occurs in *mer*- and *fac*-forms. The *mer*-isomer is thermodynamically unstable and with time spontaneously isomerizes to the *fac*-form, the speed of isomerization being considerably higher in this case than for the analogous tris(2-aminoethanol) complex.

The tris complex $[Co(NH_2CHEtCH_2O)_3]$, containing five-membered O,N-chelate rings, of racemic [(*S*)- and (*R*)-forms] 2-aminobutan-1-ol, should also exist in *mer*- and *fac*-forms. In addition, each of these geometric isomers can form four different diastereoisomers $Co(S)_3$; $Co(S)_2(R)$; $Co(S)(R)_2$ and $Co(R)_3$ having enantiomeric Λ,Δ-configurations. The total number of expected diastereoisomers is 12, as previously recorded by ^{59}Co NMR for solutions with the related tris-chelating complex $[Co(pn)_3]^{3+}$ with racemic propane-1,2-diamine (pn).[5,6] However, only four bands (δ 2160, 2120, 2225, 2290) from the diastereoisomers of *fac*-configuration were recorded in the ^{59}Co NMR spectrum of freshly prepared $[Co(NH_2CHEtCH_2O)_3]$. The presence of only the *fac*-isomer for $[Co(NH_2CHEtCH_2O)_3]$ was also confirmed by ^{13}C NMR spectral analysis. It is interesting to note that the formation of $K_3[Co(cysu)_3]$ containing a five-membered N,S-bidentate ligand, cysu = $[NH_2CH(CO_2)CH_2S(O)_2]^{2-}$, occurs stereoselectively and the only compound obtained is the *fac*-isomer.[7,8] In the course of reaction (3) the *fac*-configuration of the complex

$$[Co(NH_2CHEtCH_2O)_3] \xrightarrow[H_2O]{H^+} [Co(NH_2CHEtCH_2OH)_3]^{3+} \quad (3)$$

remains unchanged, *i.e.* the diastereoisomers (δ 1511, 1515, 1509, 1495) formed in the acidic medium from the cation complex are *fac*-isomers. An attractive peculiarity of the complex *fac*-$[Co(NH_2CH_2CH_2O)_3]$ is its ability to act as a ligand while interacting with Co^{II} salts and to form polynuclear complexes of different compositions by means of the three oxygen atoms.[9,10] We obtained complexes $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}Cl_2$ **1**, $\{Co^{II}[Co^{III}(NH_2CH_2CH_2O)_3]_2\}Cl_3\cdot NH_3CH_2CH_2OH\cdot 2H_2O$ **2** and $\{Co^{II}[Co^{III}(NH_2CHEtCH_2O)_3]_2\}Cl_2$) **3** from methanol solutions. In **1–3** aminoalcohols act as O,N-bidentate ligands and form two octahedral tris-chelating complexes with the two Co^{III} atoms, hving *fac*-configurations ($Co^{III}N_3O_3$), which are bridge-bonded by Co^{II} into a trinuclear fragment through six O atoms ($Co^{II}O_6$).