IN-SITU FTIR STUDIES ON THE ELECTRO-CATALYSIS OF SMALL ORGANIC MOLECULES ON THE RU(0001) ELECTRODE AS A FUNCTION OF TEMPERATURE AND PH

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Variable-temperature *in-situ* time-resolved FTIR spectroscopy has been used as the primary tool to investigate the effects of temperature and pH on the adsorption and electro-oxidation of CO, formaldehyde, formic acid and methanol at the Ru(0001) electrode, and the results interpreted in terms of the surface chemistry of the Ru(0001) electrode.

Both linear (CO_L) and threefold-hollow (CO_H) binding CO adsorbates (bands at 1970-2040 cm^{-1} and 1770-1820 cm^{-1}, respectively) were observed on the Ru(0001) electrode in both 0.1 M $HClO_4$ and 0.1 M NaOH solutions from the CO adsorption. In the acid solution, CO_L was detected as the main adsorbed species on Ru(0001) surface over all the potential region studied. In contrast, in the alkaline solution, more CO_H than CO_L was detected at lower potentials, whilst increasing the potential resulted in the transformation of CO_H to CO_L. At higher potentials, the oxidation of the adsorbed CO took place via reaction with the active (1 x 1)-O oxide/hydroxide.

It was found that formaldehyde and formic acid did undergo dissociative adsorption to form linear (CO_L) and 3-fold-hollow (CO_H) binding CO adsorbates. In contrast to the adsorption of CO, it was found that increasing the temperature to 60 °C markedly increased the amount of CO adsorbates formed on the Ru(0001) surface from the adsorption of formaldehyde and formic acid.

It was found that no dissociative adsorption or electro-oxidation of methanol took place at the Ru(0001) at potentials below 900 mV *vs* Ag/AgCl in perchloric acid solution at both 20 and 60 °C. However, in the alkaline solution, methanol did undergo dissociative adsorption, to form linearly adsorbed CO, (CO_L), with little or no CO adsorbed at threefold-hollow sites, (CO_H), at both 20 °C and 60 °C. Increasing the temperature from 20 °C to 60 °C clearly facilitated the methanol dissociative adsorption to CO_L and also enhanced the electro-oxidation of the CO_L. At the higher potentials, significant oxidation of methanol to CO_2 and methyl formate in acid solution and to bicarbonate and formate in alkaline solution, was observed, which was attributed to the formation of an active RuO_2 phase on the Ru(0001) surface, in agreement with our previous studies.