In situ XPS and PM IRRAS study of methanol and ethanol oxidation over Pt(111)

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The oxidation of methanol on a Pt(111) single crystal was studied using X-ray photoelectron spectroscopy (XPS) and polarization-modulation infrared reflection absorption spectroscopy (PM IRRAS). Both methods make it possible to study the catalyst directly under reaction conditions. XPS allows determination of the chemical state of a catalyst and the presence of reaction intermediates on its surface, including adsorbed carbon atoms [1]. A distinctive feature of PM-IRRAS is the ability to simultaneously record vibrational spectra of species adsorbed on the catalyst surface and molecules in the gas phase over the catalyst [2,3]. The combined use of these methods allows to obtain detailed information on the mechanism of the catalytic reaction under study.

The experiments were performed in a temperature range between 300 and 600 K. It was shown that the oxidation of methanol starts at approximately 350 K, and methanol is oxidized mainly to CO_2 and methyl formate. CO was not found among gas-phase products in the whole temperature range. A small amount of formaldehyde was detected in the gas phase only at 350–450 K. On the platinum surface, methyl formate, CO, formates, carbonates, and carbon atoms were detected under reaction conditions. Their concentrations depended on the reaction temperature and the methanol/oxygen molar ratio. Formates were detected only at 300 K, indicating their low thermal stability. Both CO and formate are the key intermediates in the total oxidation of methanol, which can proceed via two different pathways: a CO-based route and a non-CO-included route. Carbonates are formed from formates and demonstrate extremely high thermal stability. This leads us to propose that not only CO but also carbonates can poison the platinum surface and prevent the oxidation of methanol.

Similar picture was observed in the study of the oxidation of ethanol. The main reaction products were CO, CO_2, acetaldehyde, and acetic acid. The yield of CO depends on the concentration of oxygen in the gas phase. The overall mechanisms of the oxidation of methanol and ethanol on platinum are discussed.

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