

Surface science investigations of the selective oxidation of methanol on mixed oxide catalysts

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Industrial catalysts for the oxidation of methanol to formaldehyde consist of iron molybdate [$\text{Fe}_2(\text{MoO}_4)_3$]. Using a variety of techniques, including aberration corrected STEM and EELS, based at SuperSTEM, Daresbury, and XAS at Diamond, we have shown that the surface of these catalysts is segregated in MoO_3 . In order to understand the relationship between surface structure and reactivity for these systems we have carried out surface science studies of this system using model, single crystal oxides.

Model catalysts of molybdenum oxide nanoparticles and films on $\text{Fe}_3\text{O}_4(111)$ and $\text{Fe}_2\text{O}_3(0001)$ were fabricated by the hot-filament metal oxide deposition technique (HFMOD), that is, molybdenum oxides were produced by using a molybdenum filament heated in an oxygen atmosphere. The filament heating current, the oxygen pressure, and the depositing time are the main deposition parameters and their effects on the deposition was studied, using mainly STM, XPS and ISS. The Mo forms in the highest oxidation state, 6^+ , and is remarkably stable to thermal treatment, remaining on the surface even up to 700°C . Above that temperature cation mixing begins to occur, forming an iron molybdate structure. TPD shows that the reactive properties of the layer change significantly upon increasing the Mo coverage, changing from complete combustion to CO_2 (via a formate intermediate) on the iron oxide, to partial oxidation to CO, to the selective reaction, that is, formaldehyde production, at high coverage (via a methoxy intermediate). These data are then compared with those for the real high surface area catalyst.