Pervasiveness of Surface Metal Oxide Phases in Mixed Oxide Catalysts

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Mixed oxide catalytic materials possess two or more metal oxide components as found in bulk mixed metal oxides (stoichiometric oxides as well as solid solutions), polyoxo metalates (POMs), molecular sieves, zeolites, clays, hydrotalcites and supported metal oxides. Although it is now well established that two-dimensional surface metal oxide phases are present for supported metal oxides on traditional supports (e.g., Al₂O₃, TiO₂, ZrO₂, SiO₂, etc.), it is not currently appreciated that such surface metal oxide species or phases are also present for other types of mixed oxides. For example, recent surface analyses have demonstrated that stoichiometric bulk mixed metal oxides also possess surface metal oxide phases that control their catalytic activity. For example, the catalytic active sites for methanol oxidation to formaldehyde over the bulk Fe₂(MoO₄)₃ mixed oxide catalyst are surface MoOₓ species and not the bulk Fe₂(MoO₄)₃ phase as previously thought in the catalysis literature. The nanometer sized clusters in POMs also possess surface species when a second metal oxide component is introduced (e.g., H₃+xPW₁₂-xMₓO₄₀). Deposition of metal oxides into molecular sieves, zeolites, clays and hydrotalcites also results in the metal oxide additive usually being present as surface metal oxide species that are the catalytic active sites for many redox and acid reactions. The formation of these surface metal oxide phases is driven by their low surface free energy and low Tammann temperature for many metal oxides of interest in catalysis (e.g., VOₓ, MoOₓ, CrOₓ, ReOₓ, WOₓ, etc.).

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