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Structure Sensitivity in Methanol Oxidation over Model Rhenium Oxide Catalysts

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The catalytic oxidation of methanol into products that serve as primary reagents for organic synthesis, such as formaldehyde, is a leading process in the chemical industry. Metal oxide catalysts are conventionally used in methanol oxidation, but understanding the active phases in these catalysts is challenging since they usually have a wide range of geometric structures and oxide compositions. Using soft x-rays produced at the National Synchrotron Light Source, scientists at Rutgers University and the University of North Carolina have shown a direct correlation between the presence of rhenium oxides in low oxidation states and catalyst deactivation. Disordered oxygen phases are revealed to enhance catalytic activity and the formation of these phases is affected by catalyst structure.

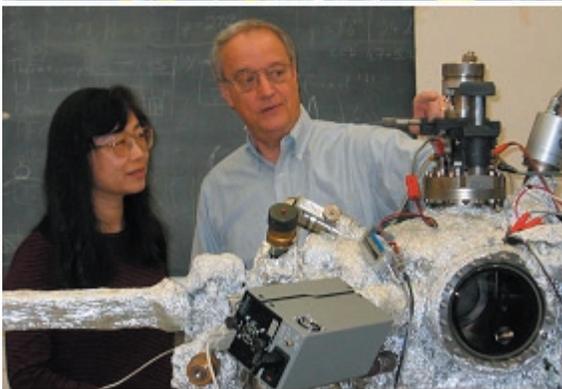
How active a catalyst is depends strongly on its morphology and surface structure. Most industrial catalysts contain an active component, typically nanometer-scale particles of transition metals and oxides, which are dispersed on a high-area support made of a relatively inert oxide. In these composite materials, catalyst particles of varying sizes expose a number of different structural planes, each with its own contribution to the overall catalytic activity. Because the complex structures of a real catalyst often hinder the development of rational connections to its performance, studies on model catalysts with well-defined structures allow scientists to establish more precise structure–activity relationships in catalysis.

We prepared model rhenium (Re) oxide catalysts with different morphologies, atomic-scale structures, and oxidation states, since Re oxides are demonstrated to be selective catalysts for

methanol oxidation reactions. Using soft x-ray photoelectron spectroscopy (SXPS) at NSLS beamline U4A, we characterized the chemical states of Re atoms and cations on the surfaces of the model cata-

lysts. The energy range of soft x-rays at beamline U4A matches the binding energies of Re states well, which allows us to probe the surface region of the model catalysts—where chemical reactions take place—with ultrahigh sensitivity and resolution. We also tested the chemical reactivity of these model catalysts towards methanol by applying temperature programmed reaction spectroscopy.

We chose the atomically rough Re (12 $\bar{3}$ 1) surface, shown in **Figure 1**, because it easily converts to different structures when treated with oxygen. When covered with oxygen at room temperature, this surface retains its planar form. When heated in small quantities of oxygen, however, Re (12 $\bar{3}$ 1) undergoes massive structural rearrangements to build nanosized 'hill-and-valley' facets that cover the entire surface. These tiny facets have (11 $\bar{2}$ 1) and (01 $\bar{1}$ 0) surface structures,



Rutgers team (clockwise from top left): Hao Wang, Ally Chan, Theodore Madey, and Wenhua Chen.

each of which is much smoother on the atomic scale than the planar ($1\bar{2}\bar{3}1$) surface. SXPS data show that both planar and faceted Re remain covered with an oxygen layer, such that Re atoms at the surface are bonded to 1, 2, and 3 oxygen neighbors. But the planar surface has a broader distribution of these Re–O bonds, indicating more disorder in this oxygen overlayer compared to the faceted surface. On both surfaces, a small amount of oxygen also reacts with the metal to form an oxide, ReO.

To increase oxide formation, Re ($1\bar{2}\bar{3}1$) is exposed to a high overpressure of oxygen at an elevated temperature. This produces a thin

oxide film on the facets composed of Re cations in low oxidation states, mainly ReO and Re_2O_3 (**Figure 1**). So, we can prepare oxygen-covered rhenium surfaces with different planar and faceted structures, as well as rhenium oxide films, in order to investigate how surface structure and oxide composition affect the activity of methanol oxidation catalysis.

Methanol reacts on the planar and faceted surfaces to yield the oxidation products, formaldehyde and carbon monoxide, as shown in **Figure 2**. A competing reaction to methanol oxidation is non-selective decomposition of methanol to its constituent atoms. Notably, the

faceted surface is much less active towards methanol conversion, and a portion of methanol leaves the surface unreacted. In contrast, the thin oxide film exhibits virtually no activity for methanol reaction.

Our studies indicate that rhenium oxides in low oxidation states are completely inert towards methanol, and that surface structure plays a key role in enhancing the activity of oxide catalysts towards oxidation reactions. These findings were made possible by the application of soft x-ray photoelectron spectroscopy in characterizing the catalytically active states on the model catalysts.

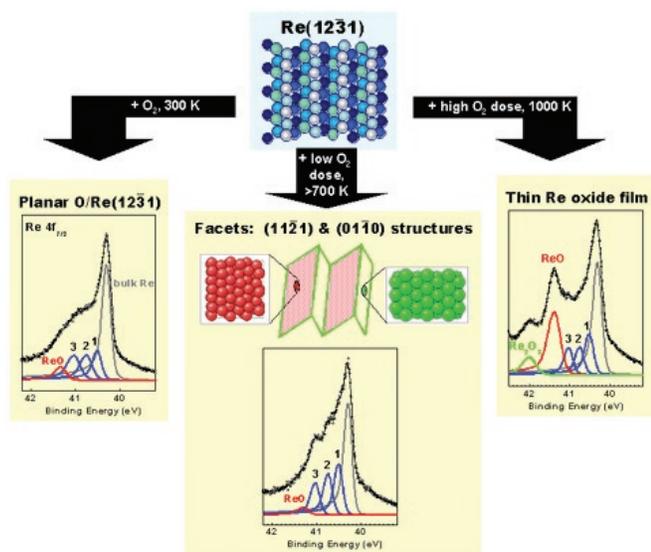


Figure 1. (Top) Surface structure of atomically rough Re ($1\bar{2}\bar{3}1$). (Bottom) High resolution soft x-ray photoelectron spectra (SXPS) of the planar and faceted oxygen-covered Re surfaces, and of the thin Re oxide film, formed by different oxygen treatments to the Re ($1\bar{2}\bar{3}1$) surface.

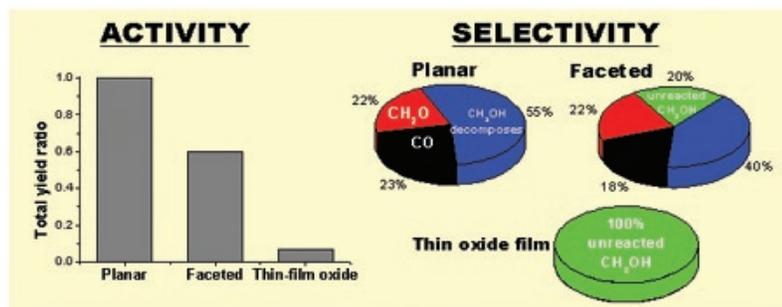


Figure 2. Methanol conversion activity and product selectivity from the model Re oxide catalysts.