Catalysis science of methanol oxidation over iron vanadate catalysts

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Bulk mixed metal oxide compounds are employed as industrial oxidation catalysts for many reactions, but there is still debate in the heterogeneous catalysis literature about the nature of their catalytic active sites as well as their location in the catalyst that is responsible for the chemical transformations.

Lehigh University's department of chemical engineering (ChE) and department of material science (MatSci) teamed up to put this debate to rest.

Authors Kamalakanta Routray (ChE), Wu Zhou (MatSci), Christopher J. Kiely (MatSci), and Israel E. Wachs (ChE, Principal Investigator) used a multitude of characterization techniques to solve this long-standing debate with Infrared (IR) and Raman spectroscopy, High Resolution Transmission Electron Microscopy (HRTEM), Temperature Programmed Surface Reaction (TPSR) spectroscopy and steady-state kinetic analysis. Their results have been chosen for publication in the first issue of the new *American Chemical Society: Catalysis* peer-reviewed journal released for January 2011.

This article examines one model system, the bulk mixed metal oxide $FeVO_4$, for the oxidation reaction of methanol (CH_3OH) to formaldehyde (HCHO). For comparison, the systems of crystalline V_2O_5 and α-Fe_2O_3 phases and supported 4% V_2O_5/α-Fe_2O3, possessing a two-dimensional surface VO_x layer, were also studied in order to elucidate the contributions of pure phases and the surface vanadium phase to that

of the bulk $FeVO_4$ catalyst.

Raman spectroscopic analysis confirmed that the bulk $FeVO_4$ catalyst is indeed of pure FeVO4 phase (not possessing extraneous V_2O_5 or α-Fe_2O_3 phases) and that the supported 4% V_2O_5/α-Fe_2O_3 catalyst only contains the vanadium oxide as an amorphous surface VO_x monolayer on the bulk α-Fe2O3 support. The surface composition of all the samples was further probed with CH_3OH adsorption and monitored with IR spectroscopy. The CH_3OH-IR results revealed that the surfaces of V_2O_5, bulk $FeVO_4$, and 4% V_2O_5/α-Fe_2O_3 all look the same, indicating that their surfaces consist of a surface VO_x layer.

The presence of an enriched VO_x layer of ~1 nm thickness on the surface of the bulk $FeVO_4$ catalyst was directly confirmed with High Resolution Transmission Electron Microscopy (HRTEM). The presence of such an amorphous layer is usually quite difficult to detect by more conventional methods (XRD, X-ray Absorption Spectroscopy (XAS), solid state 51NMR spectroscopy, Electron Spin Resonance (ESR), Raman spectroscopy, etc.) that tend to be dominated by the signal from the bulk phase.

Spectrokinetic analyses definitively revealed that the catalytic active sites for methanol oxidation to formaldehyde and water by the bulk FeVO4 catalyst are the surface VO_x species. The role of the bulk $FeVO_4$ phase is simply to store the lattice oxygen that is used to reoxidize the surface VO_x sites and the gas phase molecular O_2 does not directly oxidize the reduced surface VO_x sites (Mars-van Krevelen reaction mechanism).

“This new insight is causing a paradigm shift in how catalytic reactions proceed by bulk mixed metal oxide catalysts that will require an examination of the previously accepted models for chemical transformations by bulk mixed metal oxide catalysts,” says Dr. Wachs.

More information: The article is published in *ACS: Catalysis* 2011, 1, 54-66. dx.doi.org/10.1021/cs1000569