

Observation and Elucidation of the Bimetallic Structure of MoO₃-promoted Rh Catalysts for Syngas Conversion to Alcohols using *in-situ* XAS

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The development of high-pressure *in-situ* capabilities for catalyst characterization at the Stanford Synchrotron Radiation Lightsource has been used to gain insight into the structure-activity relationship of silica-supported MoO₃-promoted Rh catalysts for syngas conversion to higher alcohols. Rh shows promise to convert syngas (H₂ and CO), derived from coal, natural gas, biomass or other sources, into higher oxygenates but catalytic performance is hindered due to competing side reactions on varied surfaces and bonding sites of the Rh. The addition of a promotor, an alkali or transition metal oxide, has been shown to alter the activity and/or selectivity to higher oxygenates with little understanding as to what is the structure of the promoted catalyst or why the promotor changes catalytic performance.

Atomic layer deposition was used to selectively deposit controlled amounts of MoO₃ onto the silica-supported Rh nanoparticles to understand the role of the promotor in altering catalyst performance. X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the Rh and Mo K-edges were collected on the catalyst under i) as prepared conditions, ii) during reduction in H₂ at 250°C, and iii) under reaction conditions (250°C, 20 bar, flow of 2:1 H₂:CO). The as prepared catalyst was characterized as a MoO₃ over layer on a Rh₂O₃ particle. TPR XANES showed that the Mo in the presence of Rh was able to reduce at lower temperatures than conventional MoO₃-only catalysts (250°C vs. 400°C). The reduced catalyst was characterized as Mo substituted into the surface of the *fcc* lattice of the Rh nanoparticle. This model and conclusion was only able to be made after the Fourier-transform of the EXAFS of Rh foil [*fcc*], Mo foil [*bcc*], and Mo and Rh edges of the catalyst were compared. Under reaction conditions the Mo XAFS changed to a slightly oxidized Mo species, still in the *fcc* lattice, **Figure 1**, while the Rh stayed constant indicating that the Mo was on the Rh particle surface. DFT modeling complemented the XAS results showing that a Mo-OH species can be substituted into the Rh surface, and its presence should stabilize oxygen containing intermediates shifting selectivity from hydrocarbons to methanol and longer carbon chain oxygenates.

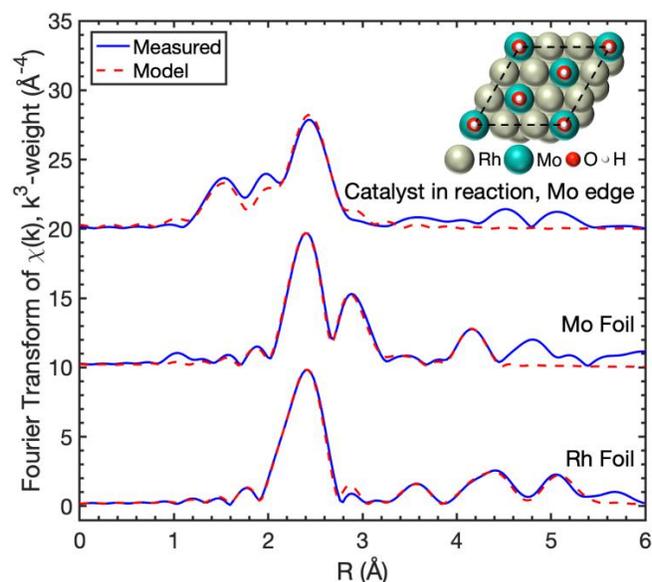


Figure 1. EXAFS data collected at the Rh and Mo K-edges and best fit models characterizing the Rh foil [*fcc*], Mo foil [*bcc*] and the RhMo/SiO₂ catalyst (at the Mo K-edge) under reaction conditions (250°C, 20 bar, flow of 2:1 H₂:CO).