Multimodal *in situ* Characterization of ZnO-modified Co Catalysts for Alcohol Synthesis

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Producing chemicals and liquid fuels from renewable carbon monoxide and hydrogen (syngas) is a key route for a sustainable economy. Currently there is no industrially-appropriate catalysis for the formation of alcohols beyond methanol from syngas which are key targets for fuel and chemical production. In this work, we utilize atomic layer deposition to synthesize ZnO-modified Co catalysts that exhibit substantial selectivity towards alcohols. We probe the structure of these catalysis using an array of laboratory- and synchrotron-based *in situ* techniques (infrared spectroscopy, x-ray diffraction, and x-ray absorption spectroscopy) to understand their structural evolution in syngas. We discover for the first time that Zn promotion of Co results in Co_2C formation. We propose a mechanism, supported using density functional theory calculations, that explains Co_2C formation in Zn-modified Co and a variety of other promoted Co catalysts. We conclude that Zn acts as a dual role promoter resulting by first enhancing Co_2C formation and then modifying the Co_2C to obtain high performance for alcohol synthesis.