

Abstract No. Jaco0003

Impact of Water on the Deactivation of Noble Metal Promoted Co/Al₂O₃ Catalysts for Fischer-Tropsch Synthesis

G. Jacobs, P.M. Patterson, T.K. Das, J. Li, and B.H. Davis (U. Kentucky CAER)

Beamline(s): X18B

Introduction: Fischer Tropsch synthesis is an important reaction whereby coal or natural gas-derived syngas is converted to a distribution of paraffinic and olefinic hydrocarbons, which can be upgraded to produce an ultra-clean, virtually sulfur-free diesel. The effect of water for supported cobalt FTS catalysts still eludes researchers, and while some supports, like SiO₂ [1], have yielded a positive effect with water addition, supports with stronger interactions with cobalt, like TiO₂ [2] and Al₂O₃ [3], have resulted in negative impacts on the rate. In one experiment, the impact of water on the deactivation of a 0.5%Pt promoted 15%Co/Al₂O₃ catalyst was studied by reaction testing and XAFS. The small amount of platinum was added to promote the catalyst reduction [4]. Synthesis operating conditions were maintained constant while argon balancing gas was systematically replaced by added water, in order to maintain constant reactant partial pressures and space velocity. XAFS and activity tests suggest two regions for the water effect: at low H₂O/CO ratios, H₂O impacts CO conversion by reversible kinetics; at high H₂O/CO ratios, oxidation of cobalt by reaction with Al₂O₃ results in irreducible Co species and permanent irreversible activity loss.

Methods and Materials: Used catalysts were withdrawn from the CSTR and cooled in the solid wax product in order to encapsulate the catalyst particles, and analyzed in at the boiling temperature of N₂ in a XAFS cell [5].

Results: Below 25% added water, the slight negative effect on activity was reversible (see below), and no changes were observed in the EXAFS or XANES spectra, suggesting the effect is kinetic. However, EXAFS (lower left) and XANES (lower right) results strongly suggest that, above 25% water addition, the sudden irreversible loss in activity is due to reaction of the Co clusters with the support, forming irreducible cobalt aluminate-like species.

Conclusions: XAFS and activity tests indicate there are two regions for the H₂O effect: at low H₂O/CO ratios, H₂O influences CO conversion by reversible kinetic effects, but at high H₂O/CO ratios irreversible cobalt oxidation occurs.

Acknowledgments: US DOE (contract # DE-AC22-94PC94055) and the Commonwealth of KY. Also NSLS at BNL, supported by US DOE, Divs. of Mats. Sci. and Chem. Sci. Special thanks to Dr. Syed Khalid (X18b).

References: [1] J. Li, G. Jacobs, Y. Zhang, T. Das, B.H. Davis, Appl. Catal., in press, [2] J. Li, G. Jacobs, T. Das, B.H. Davis, Appl. Catal. 233 (2002) 233, [3] J. Li, G. Jacobs, X. Zhan, Y. Zhang, T. Das, B.H. Davis, Appl. Catal. 228 (2002) 203, [4] G. Jacobs, T. Das, Y. Zhang, J. Li, G. Racoillet, B.H. Davis, Appl. Catal. 233 (2002) 263, and [5] G. Jacobs, P.M. Patterson, Y. Zhang, T. Das, J. Li, and B.H. Davis, Appl. Catal. 233 (2002) 215.

