

## Group 11 promotion of Co/Al<sub>2</sub>O<sub>3</sub> catalysts for Fischer-Tropsch synthesis

Gary Jacobs<sup>1</sup>, Wenping Ma, Mauro Ribeiro, Yaying Ji and Burtron H. Davis\*

<sup>1</sup>Center for Applied Energy Research, 2540 Research Park Drive, Lexington, KY 40511

\*davis@caer.uky.edu

### Introduction

The active sites of supported cobalt catalysts are surface cobalt metal atoms [1], but extent of cobalt reduction is an issue [2]. A variety of in Group 11 (i.e., Cu, Ag, and Au) promoted 15%Co/alumina catalysts were prepared by an aqueous impregnation method. Catalysts were characterized by TPR, in-situ EXAFS/XANES spectroscopies, and H<sub>2</sub>-chemisorption. The Group 11 promoters significantly facilitated reduction of cobalt oxide species interacting with the support [3]. The promoters were most effective only after an initial reduction step, and should be transferred directly to the reactor and not passivated prior to use. EXAFS/XANES results indicate that the promoting effect is significantly diminished if the catalysts are first passivated and re-reduced due to changes in the structural properties of the promoter in relation to the active Co component. Catalysts were tested in a CSTR slurry reactor, and the influence of the Group 11 promoter was concluded to be due to increases in surface cobalt metal active site densities arising from an increase in extent of reduction of cobalt oxides. Catalysts were first tested at the same space velocity on a per gram of catalyst basis, in order to determine the increase, if any, in CO conversion rates. Then, space velocity was adjusted to achieve the same level of conversion, to compare selectivities (e.g., CH<sub>4</sub>).

### Materials and Methods

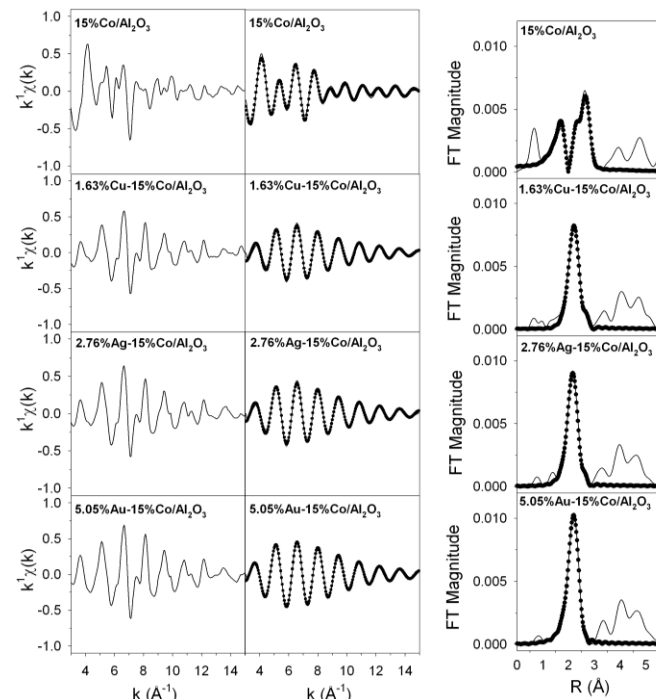
Catalysts were prepared by standard impregnation methods and characterized by H<sub>2</sub> chemisorption/pulse reoxidation, XRD, and EXAFS/XANES. CSTR reactor conditions: 220 °C, 210 psig, 4.2 NL/g-cat/h, H<sub>2</sub>/CO = 2.0, TOS = 24-98 h.

### Results and Discussion

Testing of a 1.5% Au-15% Co/Al<sub>2</sub>O<sub>3</sub> catalyst in the CSTR resulted in conversion rate of ~49% compared to ~29% with the unpromoted catalyst, due to an increase in surface site densities, as shown in Table 1. The CH<sub>4</sub> selectivity was less for the 1.5% Au-15% Co/Al<sub>2</sub>O<sub>3</sub> by 1.0%, (8.2% versus 9.2%) compared with the unpromoted catalyst.

**Table 1. Results of hydrogen chemisorption/pulse reoxidation and XRD.**

Catalyst Description	μmol H <sub>2</sub> desorbed per g cat	Uncorrected % Dispersion	Total μmol O <sub>2</sub> consumed per g cat	Total μmol O <sub>2</sub> consumed by Co <sup>0</sup> per g cat	% Reduction	% Reduction of cobalt**	Corrected % Dispersion	Crystallite Diameter estimate from XRD
15%Co/Al <sub>2</sub> O <sub>3</sub>	52	4.1	694	694	40.9	40.9	10.0	7.2
w/ 0.49% Cu	140	10.7	1217	1178	70.3	69.4	15.2	-
w/ 1.63% Cu	172	12.3	1712	1584	93.9	93.3	13.1	7.7
w/ 0.83% Ag	158	12.1	1470	1470	87.0	86.6	13.9	-
w/ 2.76% Ag	145	10.1	1663	1663	98.2	98.0	10.3	6.9
w/ 1.51% Au	194	14.4	1597	1597	94.3	94.1	15.3	-
w/ 5.05% Au	192	13.3	1383	1383	83.2	81.5	16.0	7.3



**Figure 1.** EXAFS results after in-situ reduction in H<sub>2</sub> of (top) unpromoted and Group 11 promoted 15%Co/Al<sub>2</sub>O<sub>3</sub> catalysts after 30 min in H<sub>2</sub>, including 1.63%Cu, 2.76%Ag, and 5.05%Au, and cooling to liquid nitrogen temperatures in H<sub>2</sub>. While the unpromoted catalyst remains unreduced, the Group 11 promoter clearly facilitates reduction, as observed by the peak for Co-Co metal coordination at ~2.2 Angstroms (phase uncorrected).

### Significance

Work represents a way of increasing site densities by significantly improving Co extent of reduction using Group 11 promotion. The method may lead to catalyst cost reductions.

### References

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3. Jacobs, G., Das, T.K., Zhang, Y., Li, J.,Racoillet, G., and Davis, B.H., Appl. Catal. A 233 (2003) 263.