

# Effect of Catalyst Preparation Solvent on the Activity/Selectivity and Physical Properties of a Co/Ru/La-Al<sub>2</sub>O<sub>3</sub> Fischer-Tropsch Catalyst

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## Introduction

Some non-aqueous preparation methods have been found to produce active, selective lab-scale cobalt catalysts for Fischer-Tropsch synthesis (FTS) [1]. However, producing industrial scale quantities of catalyst with highly volatile and flammable solvents may be problematic. Accordingly, aqueous methods that result in catalysts of comparable activity may be preferred. In this work differences in structural and catalytic properties among cobalt catalysts made with aqueous and non-aqueous methods were investigated.

## Materials and Methods

Catalysts with dispersions of 10-20% at loadings of 25 wt% cobalt and 0.3 wt% ruthenium on lanthanum-treated alumina were prepared by evaporative deposition using water, ethanol/acetone, ethanol, and isopropanol solvents. Characterization techniques, including hydrogen chemisorption, H<sub>2</sub>-TPR, TEM, SEM and activity/selectivity studies in a fixed-bed reactor were used to study these catalysts. Prior to activity tests, previously reduced, passivated samples (0.25 g) were re-reduced *in situ* in H<sub>2</sub> at maximum reduction temperature (T<sub>redn</sub>) for 4 h. The non-condensed gas products were analyzed online by gas chromatography. Reported catalytic performances are stabilized values after 2 days of operation.

## Results and Discussion

N<sub>2</sub> adsorption measurements show similar pore volume and pore diameter for both catalysts prepared by aqueous (*aq*) using water: 0.33 cm<sup>3</sup>/g and 11.8 Å and non-aqueous (*naq*) using acetone/ethanol: 0.39 cm<sup>3</sup>/g and 10.6 Å deposition. On the other hand, the lower BET surface area of the *aq*-deposited (120 m<sup>2</sup>/g) catalyst relative to its *naq*-deposited (135 m<sup>2</sup>/g) counterpart is most probably due to the high surface tension of water that might have caused the collapse of pores [2]. Extent of reduction, H<sub>2</sub> chemisorption, and dispersion data for Co/Ru/La-Al<sub>2</sub>O<sub>3</sub> catalysts are summarized in Table 1. Further H<sub>2</sub> uptake and EOR measurements are underway for samples of the *naq*-deposited catalyst reduced at 350 and 360°C, since the EOR of 61% is lower than desired.

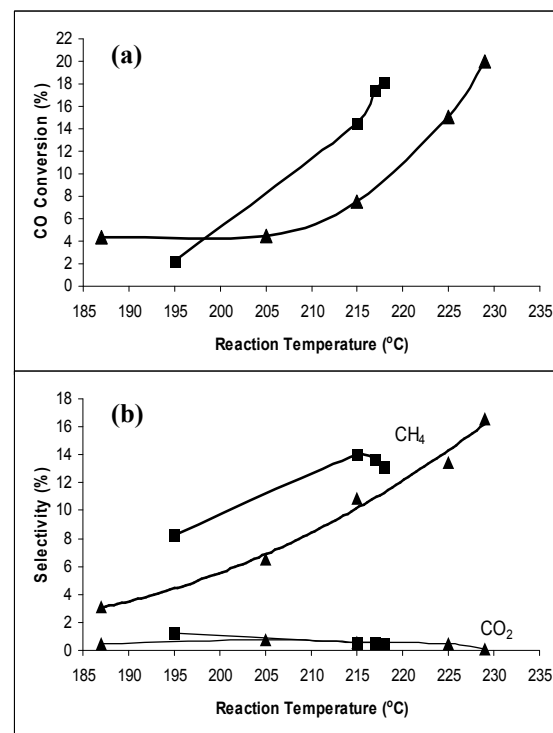
**Table 1. Extents of reduction, H<sub>2</sub> uptakes, and Co dispersions for FT catalysts**

Catalyst <sup>a</sup>	T <sub>redn</sub> (°C) <sup>a</sup>	EOR (%) <sup>b</sup>	H <sub>2</sub> uptake (μmol/g <sub>cat</sub> ) <sup>c</sup>	Dispersion (%) <sup>c</sup>
aq	352	96	295	14
naq	290	61	279	22

<sup>a</sup> Catalyst calcined at 250°C in air for 8 h and reduced at 1°C/min to T<sub>redn</sub> and held 16 h.

<sup>b</sup> Extent of reduction (EOR) at 400°C measured by TGA and corrected for Ru and La.

<sup>c</sup> H<sub>2</sub> chemisorption at 100°C; following purge at -84°C; desorbed H<sub>2</sub> measured while heating to 450°C with TCD; data are average of 3 measurements %D = 1.18X/EOR/w [3].



**Figure 1.** Activity and selectivity performance for Co/Ru/La-Al<sub>2</sub>O<sub>3</sub> catalysts prepared by: (■) non-aqueous and (▲) aqueous deposition. Reaction conditions: 300 psi, H<sub>2</sub>/CO = 2:1 (volume ratio), GHSV 18,000 h<sup>-1</sup> at STP.

Activity and selectivity data for Co/Ru/La-Al<sub>2</sub>O<sub>3</sub> catalysts at different temperatures, but the same space velocity, are shown in Figures 1a and 1b. By comparing the catalysts at 215°C, the CO conversion for the *naq*-deposited catalyst (14%) is twice that for the *aq*-deposited one (7%). While the selectivity for CO<sub>2</sub> is similar for both catalysts essentially zero, the *naq*-deposited catalyst is slightly more selective for CH<sub>4</sub> than its counterpart. Despite the lower EOR for the *naq*-deposited catalyst, both catalysts contain similar number of surface Co<sup>0</sup> species available for reaction. Thus, a comparison of turnover frequencies would give similar differences to that observed for conversion (TOF<sub>aq</sub> = 0.0098 s<sup>-1</sup> and TOF<sub>naq</sub> = 0.0190 s<sup>-1</sup> at 215°C). Effects of additional changes in solvent mixture and pre-treatment conditions on catalyst dispersion and activity will also be reported.

## Significance

This study in progress is expected to provide insight into the influence of solvent nature on Co catalysts and develop an industrial procedure to prepare more economically viable catalysts for the FTS.

## References

1. Khodakov, A.Y., W. Chu, and P. Fongarland, *Chem. Rev.* 107, 5 (2007).
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3. Bartholomew, C.H. and R.J. Farrauto, "Fundamentals of Industrial Catalytic Processes". 2<sup>nd</sup> ed. p. 65. Wiley-Interscience, New Jersey, 2006.