



# Effect of promoter deposition order on platinum-, ruthenium-, or rhenium-promoted cobalt Fischer–Tropsch catalysts

Kari M. Cook, Hector D. Perez, Calvin H. Bartholomew, William C. Hecker\*

Chemical Engineering Department, Brigham Young University, 350 CB, Provo, UT 84602, USA

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## ABSTRACT

The effect of noble metal (NM) promoter (Pt, Re, or Ru) deposition order was investigated for commercially-representative Co Fischer–Tropsch catalysts (nominally 25 wt% Co on a La stabilized alumina support). The effects of deposition sequence (co-deposition vs. sequential deposition) were studied in terms of NM retention and distribution, Co crystallite size, Co reducibility, and catalyst activity and selectivity. Ru retention was <48% for both sequences with the most severe losses for co-deposition (85% loss). Sequentially deposited Co/Ru showed poor Ru distribution, unlike co-deposited Co/Ru. Excellent retention and uniform distribution were observed for both Pt and Re promoted catalysts. Cobalt crystallite sizes were smaller for all three co-deposited catalysts (~4.2 nm for all NMs) when compared to any of the sequentially deposited catalysts. Although sequentially deposited catalysts required higher reduction temperatures (TPR), they had greater extents of reduction (EORs) relative to co-deposited catalysts. CO depletion rates and turnover frequencies (TOFs) for co-deposited Co/Pt and Co/Re were 2–3 times higher than their sequentially deposited counterparts. Methane selectivities were lower for the same two co-deposited catalysts. It is noteworthy that the smaller Co crystallites, produced by co-deposition, resulted in more active catalysts than those with larger crystallites resulting from sequential deposition. The co-deposited Co/Pt catalyst was found to be statistically more active than the unpromoted Co catalyst, while the corresponding sequentially deposited catalyst was less active. Overall, co-deposited Co/Pt and Co/Re catalysts showed superior catalytic performance by all standards of judgment when compared to their sequentially deposited counterparts.

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## 1. Introduction

Continual research on supported cobalt Fischer–Tropsch (FT) catalysts has led to the formulation of different preparation techniques to produce catalysts with varied FT synthesis performance. Noble metals (NMs) have been widely used as promoters to improve the structure, dispersion, reducibility, selectivity and activity of these catalysts. Although the order in which the Co and NMs are deposited onto the support has been shown to sometimes make a difference, there is no clear answer as to which order is optimal. The two most prevalent deposition sequences described in literature are designated as follows:

(1) Sequential deposition (seq-dep): the cobalt-containing precursor is deposited in one or more steps which are separate from the step in which the NM is deposited.

(2) Co-deposition (co-dep): the cobalt precursor (containing at least part of the total Co loading) is deposited at the same time or in the same step as the NM.

Specific to this study, seq-dep refers to the deposition of the NM in one separate step after Co is deposited onto the support in three previous steps with a high temperature calcination step in between each step; co-dep refers to the deposition of the NM with Co in the third and final Co deposition step.

Co Fischer–Tropsch (FT) catalysts have been prepared by co-dep [1–8] and seq-dep with [9–11] and without [5,12–16] a calcination step in between the Co and NM depositions. There is a lack of agreement in the literature in regards to which deposition procedure is preferable. Beuther has made catalysts by both co-dep and seq-dep and suggests that co-dep is more convenient, although seq-dep with calcinations in between yields similar catalyst performance [17]. Kobylinski also claims that Ru and other promoters (such as La) may be added either together with the Co for convenience or in an additional deposition step [18]. Iglesia suggests that Co reduction promotion requires calcination of the NM and Co together,

\* Corresponding author. Tel.: +1 801 422 6235; fax: +1 801 422 0151.  
E-mail address: [hecker@byu.edu](mailto:hecker@byu.edu) (W.C. Hecker).

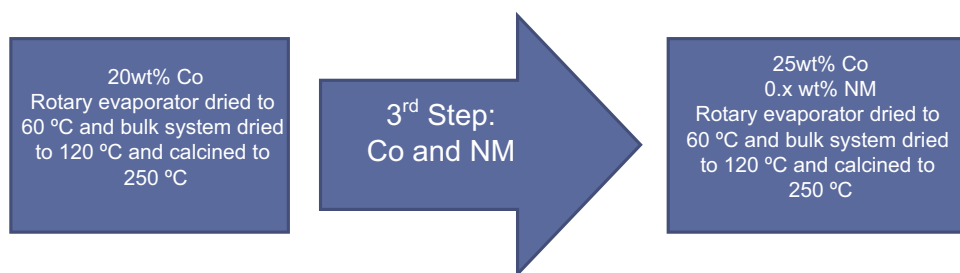


Fig. 1. Depiction of co-dep step.

but that deposition order is not significant as long as there is not a calcination in between the depositions. This claim is based on the finding that calcination with both Co and NM present allows for the migration of NM and Co surface oxides, which produces the intimate contact required for catalytic reduction promotion [19]. Furthermore, Iglesia indicates that a re-reduction along with the calcination is required for the best results [12]. On the other hand, not all studies agree with this idea, as Vada found that both Pt and Re promote reduction of Co when the catalyst is prepared by seq-dep with calcinations in between the deposition steps [9]. In fact, a review of Vada and Kobylinski's studies suggest that either intimate contact necessary for reduction promotion is achieved with seq-dep or it is not required.

While literature reports are scarce in describing the effects of deposition order in FT catalysts, a comparative literature review suggests that deposition order does affect catalyst particle size and overall performance. For example, Co agglomeration is considered to occur during thermal treatments [20], which leads to the hypothesis that the seq-deposited catalysts would have larger Co crystallite sizes due to the additional drying and calcination steps. This effect on crystallite size distribution may also affect activity/selectivity and reducibility of the catalysts, as small particles (specifically, less than 6 nm) have been found to be less active, more selective to methane, and more difficult to reduce [21].

Previous studies from our laboratory reported the effects of different NMs (Pt, Re, or Ru) added by seq-dep to promote alumina-supported Co FT catalysts [22]. These studies reported the effects of the three NMs on several catalyst properties, including metal retention, metal distribution and oxidation state/bonding, as well as Co reducibility and crystallite size, with only a brief comparison of activity/selectivity properties. The objective of the current work is to take the previous work a step further by comparing and contrasting the performance of alumina supported Co FT catalysts prepared by both the co-dep and seq-dep methods for all three NMs (Pt, Re, or Ru). The performance indicators that were studied include NM retention and distribution, Co crystallite size, Co reducibility, and catalyst activity/selectivity. It should be noted that while all of the results reported in this work for the co-dep catalysts are new and original to this publication, many of the results reported for the seq-dep catalysts are the same as reported in the previous publication [22] in order to compare the effects of co-dep to seq-dep.

## 2. Experimental

### 2.1. Catalyst preparation

NM-promoted 25% Co/La/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by a three-step (co-dep) or four-step (seq-dep) wet impregnation (see Section 2.1 in the previous work [22] for a detailed description of the carrier material and its preparation). The distinguishing steps of these two processes, co-dep and seq-dep, are depicted in Figs. 1 and 2, respectively. The first two steps in both deposition

techniques were the same—Co nitrate impregnations to 10 wt% and 20 wt% Co, each followed by drying in a rotary evaporator and then drying and calcining in flowing air. The third step of the co-dep process included simultaneous additions of the NM (as a chloride salt) and sufficient Co nitrate to reach a total of 25 wt% Co. The seq-dep process included a third step in which Co nitrate was added to reach a total of 25 wt% Co and a fourth step to deposit the NM (as the chloride salt). The targeted NM loadings in each of these processes were in the range of 0.3–0.6 wt% (a NM/Co molar ratio of 0.007).

### 2.2. Surface area, pore volume, and pore size

BET surface area, pore volume, and average pore size were measured by N<sub>2</sub> physisorption at –196 °C using a Micromeritics TriStar 3000 automated system. The samples (0.15–0.25 g) were degassed overnight in N<sub>2</sub> at atmospheric pressure (~0.862 bar) and 120 °C and measurements were taken immediately after degassing. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure close to unity with the assumption that the pores were filled with the condensate in the liquid state. The pore size distribution curves were calculated from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) formula [23].

### 2.3. Metal retention and distribution

Atomic adsorption-inductively coupled plasma (ICP) measurements were made to determine Co and NM weight loadings for each of the calcined catalysts. Electron microprobe scans on pellets of each catalyst were also obtained to determine the distributions of Co, NMs, and La across the pellets [22].

### 2.4. Co crystallite size

TEM measurements were done on several hundred Co crystallites (400+) of each catalyst with the same method described previously [22]. These images were used to determine average Co crystallite diameters (ACDs) and Co crystallite size distributions (CSDs). Surface mean ACDs were calculated from the following equation:

$$d_{\text{surfaceavg}} = \frac{\sum_i d_i^3}{\sum_i d_i^2} \quad (1)$$

where  $d_i$  is the measured diameter of each particle and  $d_{\text{surfaceavg}}$  is the surface averaged particle diameter [24].

### 2.5. Noble metal oxidation state and bonding

X-ray adsorption fine structure (XAFS) experiments were performed at Argonne National Laboratory's (Argonne, IL) Advanced

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