

Effect of Ru Deposition Order on Co Fischer-Tropsch Catalysis

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Introduction

The technical and economic feasibility of the Fischer-Tropsch (FT) process is largely dependent on the catalyst type. The high cost of noble metal promoters requires they be used efficiently. Previous studies have shown that preparation method and pretreatment conditions affect dispersion, extent of reduction, location, and density of Co and promoter species in FT catalysts.[1] In this work, we investigate how the deposition order of Co and Ru affects physiochemical and activity/selectivity properties of FT catalysts.

Materials and Methods

25 wt% Co and 0.3 wt% Ru were evaporatively deposited on lanthanum stabilized [2] alumina pellets. The deposition of Co included three steps. Ru was deposited either in the 3rd Co deposition (co-deposition) or in a 4th deposition step (consecutive deposition). After each deposition, dried catalyst particles were pelletized, crushed, sieved to -28 +65 mesh, and then calcined. After the final calcination step, 2-5 g of catalyst was reduced and passivated according to procedures determined from TGA-TPR experiments for use in further characterizations and tests. Dried, calcined and passivated catalysts were characterized by nitrogen adsorption (BET), H₂ chemisorption, transmission electron microscopy (TEM) and extent of reduction by oxidation (EOR), and tested for activity and selectivity in a fixed bed microreactor under typical FT operating conditions.

Results and Discussion

Table 1 shows the physical properties of the catalysts prepared by co- and consecutive deposition. Evidently, the deposition order of promoter has little effect on the BET surface area, pore volume, and average pore diameter of the Co/Ru/La-Al₂O₃ catalysts.

Table 1. Surface area, pore volume and porosity measurements from physisorption of nitrogen at -196°C for the Co/Ru/La-Al₂O₃ catalysts.

Preparation Method	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Pore diameter (Å)
Co-deposition	130	0.38	12.2
Consecutive deposition	135	0.39	10.6

H₂-TPR profiles of the Co/Ru/La-Al₂O₃ catalysts (Fig. 1) have two distinct features, a peak close to 200°C assigned to reduction from Co₃O₄ to CoO and a broader peak situated close to 320-350°C for the reduction from CoO to Co⁰. It appears that promoter addition by consecutive deposition facilitates H₂ spillover [3] and shifts the second broad peak to lower temperatures when compared with the co-deposition method.

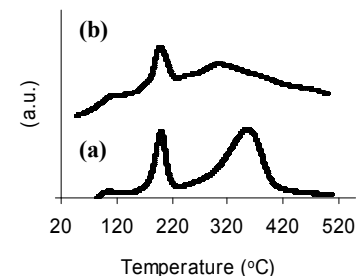


Figure 1. TPR profiles for Co/Ru/La-Al₂O₃ catalysts a) co- and b) consecutive deposition

EOR determined by TGA on the two catalysts after reduction at a maximum temperature dictated by the TPR profiles, are listed in Table 2 along with H₂ uptakes and dispersions. A substantially lower EOR (61%) but higher dispersion is associated with the lower reduction temperature (290°C) for the consecutive deposition. Further H₂ uptake and EOR measurements are underway for the consecutively-deposited, given that the EOR is lower than desired.

Table 2. Extents of reduction, H₂ uptakes, and dispersions for Co/Ru/La-Al₂O₃ catalysts

Preparation Method	T _{redn} (°C) ^a	Extent of Reduction (%) ^b	H ₂ uptake (μmol/g _{cat}) ^c	Co Dispersion (%) ^c
Co-deposition	400	91	288	15
Consecutive deposition	290	61	279	22

^a Catalyst calcined at 250°C in air for 8 h and reduced at 1°C/min to T_{redn} and held for 16 h.

^b Extent of reduction at 400°C measured by TGA and corrected for Ru and La.

^c H₂ chemisorption at 100°C; following purge at -84°C; desorbed H₂ measured while heating to 450°C with TCD; data include mean for 3 measurements %D = 1.18X/EOR/w. [2]

Activity and selectivity to test on the two catalysts are currently being run in a fixed bed microreactor. The lower average pore diameter and lower extent of reduction predict that the activity and C₂₊ selectivity [4] of the consecutive-deposited catalyst will both be lower than those of the co-deposited catalyst.

Significance

This study is expected to provide insight into the influence of deposition order on Co FT catalysis and indicate how to increase efficiency of the noble metal promoter.

References

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