Effect of calcination and promotion with noble metals on the structure and catalytic performance of cobalt silica and alumina supported Fischer-Tropsch catalysts: A comparative study

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Introduction

In the 21st century, natural gas has expected to become an increasingly important raw material for manufacturing clean fuels and chemicals. Fischer-Tropsch (FT) synthesis is a major part of Gas-to-liquid (GTL) technology, which converts natural gas into liquid fuels. Cobalt catalysts are particularly suitable for production of diesel fuels, lubricants and waxes. For relatively large cobalt particles, FT activity of cobalt catalysts depends on the overall amount of exposed metal cobalt atoms [1, 2]. Thus, a highly active cobalt catalyst for FT synthesis should possess high cobalt dispersion, good cobalt reducibility and stable cobalt surface sites.

Two essential issues should be considered in the design of cobalt FT catalysts. First, preparation of cobalt catalysts involves several oxidative and reductive pretreatments. Secondly, cobalt catalysts are often promoted with noble metals. Silica and alumina supported cobalt systems are the most common catalysts for FT reaction. Silica supported cobalt catalysts have found their application in fixed bed reactors, while alumina supported catalysts are more suitable for slurry bubble columns. The objective of this paper is to compare the effect of oxidative pretreatments and promotion with noble metals (Pt, Ru, Re) on cobalt structure, reducibility and FT catalytic performance of cobalt silica and alumina supported catalysts.

Materials and Methods

Cobalt catalysts were synthesized via incipient wetness (co)impregnation using aqueous solutions of cobalt nitrate and promoters. Cab-o-sil M-5 fumed silica (S_{BET}=214 m^2/g) and Puralox 5/170 alumina (S_{BET}=163 m^2/g) were used as catalytic supports. The precursors of noble metal promoters were solutions of ruthenium nitrosyl nitrate in HNO_3, perrhenic acid and hexachloroplatinic(IV) acid. The contents of cobalt and promoting noble metal (Ru, Re or Pt) in the catalysts were respectively 10-15 wt.% and 0.1-0.2 wt.%. The impregnated catalysts were dried in an oven, oxidized in a flow of air at different temperatures (373-673 K) and then reduced in hydrogen at 673 K for 5 h. At different stages of preparation, the catalysts were characterized by X-ray diffraction, UV-visible spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, in situ X-ray absorption spectroscopy (XANES/EXAFS), DSC-TGA analysis, propene chemisorption and in situ magnetization measurements. The catalytic performance was evaluated in fixed bed microreactor at steady state conditions.

Results and Discussion

Cobalt dispersion. In both cobalt alumina and cobalt silica supported catalysts, the sizes of cobalt crystallites are strongly affected by pore sizes of the supports. Large cobalt particles are usually found in wider pore catalysts. In the monometallic silica catalysts, in addition to the support pore sizes, cobalt dispersion is also strongly affected by the temperature of catalyst calcination; cobalt particle sizes are smaller, when the catalysts have been calcined at lower temperature (423-473 K). In the alumina supported catalysts, temperature of catalyst calcination produces a much smaller effect on cobalt dispersion. In silica supported catalysts, promotion with noble metals significantly reduces the sizes of cobalt particles (<50%), while in alumina supported catalysts, noble metal promotion only slightly (<10%) affects cobalt dispersion. Calcination of both alumina and silica supported catalysts at temperatures higher than 673 K results respectively in barely reducible cobalt aluminate and cobalt silicate.

Cobalt reducibility. In the monometallic silica supported catalysts, cobalt reducibility primarily depends on cobalt particle size; lower reducibility is observed for smaller cobalt particles. Promotion with Re and especially Ru significantly enhances cobalt reducibility. Very poor cobalt reducibility was observed in monometallic alumina supported catalysts. Differently to the catalysts supported on silica, oxidative pretreatments of alumina based catalysts at moderate temperatures (<673 K) do not much modify cobalt reducibility. On other hand, the effect of promotion with noble metals on cobalt reducibility was much more significant with alumina than with silica supported catalysts.

Catalytic performance. Because of lower reducibility, monometallic alumina supported catalysts exhibit lower FT reaction rates than silica supported counterparts. Calcination of both monometallic silica and alumina catalysts at different temperatures only slightly modifies the catalytic performance. Promotion with noble metals results in considerable increase in FT reaction rates. The effect was more pronounced with alumina supported catalysts and silica supported catalysts, which were precalcined at lower temperatures. Hydrocarbon selectivities were only slightly affected by the promotion. Slightly higher C5+ selelctivities are observed for alumina supported catalysts At the 10 % carbon monoxide conversion level, C5+ selectivity varied respectively between 75-80 % and 60-70 % with alumina and silica supported catalysts.

Significance

The present paper show that oxidative pretreatments and promotion with noble metals have different effects on the structure and catalytic performance of silica and alumina supported cobalt FT catalysts. With silica supported catalysts, oxidative pretreatments and promotion improve both cobalt dispersion and reducibility. Higher concentration of active sites for FT reaction has been obtained for the silica supported catalysts, which contain noble metal promoters and were precalcined at lower temperatures. A much lower effect of oxidative pretreatments on cobalt dispersion and reducibility has been observed with alumina supported catalysts. Promotion with noble metal improves to a much lesser extent cobalt dispersion in alumina supported catalysts. In alumina supported catalysts, the enhancement of catalytic performance on promotion with noble metals is principally due to better cobalt reducibility.

References

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