

Sinergies between organic-matrix combustion synthesis and Pt-promotion on the performances of Co-based FT catalysts

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1 Introduction

Ninety years after its discovery, Fischer-Tropsch Synthesis (FTS) is recently receiving new interest as the key-process to convert synthesis gas derived from natural gas, coal and biomass, into high quality transportation fuels [1-5]. While most of the original FTS processes relied on high-temperature bulky Fe-based catalysts, the attention today has shifted toward low-temperature Co-based supported catalysts, which exhibit higher activity and selectivity [2]. Due to the constant turnover frequency of cobalt crystallites bigger than 6 nm [3], the activity of cobalt catalyst linearly depends on the number of metallic active sites located on the support. In turn, the number of Co-metal centers is determined by the Co particle size (i.e. cobalt dispersions), the Co loading, and the Co reduction degree [4,5]. Understanding the role of these parameters and controlling such parameters during the synthesis represent one of the most significant challenge in view of the development of highly active catalysts to be used within intensified FTS reactors [5]. The synthesis of highly active catalysts has been recently reported by both academic and industrial research groups [6,7]. With respect to conventional supported FTS catalysts, which are prepared by incipient wetness impregnation, highly active catalysts have been obtained either by adding PGM as promoters [8,9] or by adopting new synthesis routes, such as the organic matrix combustion, OM [6,10]. PGM have been found able to favor cobalt reduction, thus increasing the fraction of cobalt which takes part to the reaction [8,9]. OM, which consists in the addition of an organic material to the precursors-containing solution and in the combustion/decomposition of such compound during a fast calcination step, has been found effective in the synthesis of small and stable (with respect to sintering) Co-crystallites, at least in the case of SiO₂ supported catalysts [6]. However, small crystallites are known to be much more resilient to reduction than bigger Co-aggregates [7]. In this work, we investigated for the first time the synergies between the OM method, using urea as fuel, and the adoption of PGM, platinum in particular, as reduction promoter.

2 Experimental

Catalysts with a nominal Co-content of 18 wt.% were prepared using of Co(NO₃)₂·6H₂O (98%, Aldrich) as precursor and fumed SiO₂ (S) or stabilized alumina (AS) as supports. In the case of silica, a commercial material was used (Sigma Aldrich S5130), with the following properties SA^{BET}= 422m²/g, PV=1.96 cm³/g and dp= 19 nm. Stabilized alumina was prepared inhouse by forming a superficial CoAl₂O₄ spinel phase on commercial γ -Al₂O₃ powders (Sasol Puralox): the resulting material showed SA^{BET}=96 m²/g, PV=0.41 cm³/g and dp=15 nm.

18 wt.% Co/AS sample was prepared by using an aqueous solution of urea (99%, Aldrich, urea/Co molar ratio=4.1) and Co(NO₃)₂·6H₂O (98%, Aldrich). To the scope, such mixture (8.3 (g_{Co(NO₃)₂·6H₂O}+g_{urea})/mL_{H₂O}) was heated at 60°C under stirring to form a homogeneous slurry, then mixed with AS. Afterwards, the mixture was dried in static air at 110°C for 4 h and then combusted in static air at 500°C for 10 minutes. In order to reach the desired Co loading, the entire procedure has been repeated 3 times. The resulting catalyst was named AS-OM-18. 18 wt.% Co/S sample was prepared by following the same impregnation procedure adopted for Co/AS, but using an higher content of water (0.5 (g_{Co(NO₃)₂·6H₂O}+g_{urea})/mL_{H₂O}), drying in a rotary evaporator at 70°C for 4 h, and then calcining in static air at 500°C for 10 minutes. In this case, due to the higher pore volume of the support, the desired cobalt loading was obtained in a single impregnation step. The resulting catalyst was named S-OM-18.

Reference alumina and silica supported samples (named AS-IWI-18 and S-IWI-18, respectively) were also synthesized through the conventional incipient wetness impregnation (IWI) technique for comparison purposes. 0.1 wt.% platinum-containing samples were finally prepared starting from all the previous samples. Those samples have been named by adding the appendix -0.1Pt to the sample name (e.g. AS-OM-18-0.1Pt).

All the synthesized materials were characterized by elemental analysis, N₂ physisorption, X-ray diffraction, thermogravimetric analysis, differential scanning calorimetry and temperature-programmed reduction. Their catalytic performances were then assessed in a continuous flow reactor operating at 230°C and 1 atm by feeding 5 and 2.5 NL_{syngas}/h/g_{cat} with a stoichiometric H₂/CO molar ratio.

3 Results and discussion

As a result of the different morphology of the two adopted supports, S-supported catalysts show SA between 250 and 320 m²/g, PV between 1.2 and 1.6 cm³/g and dp of 18-19 nm, while AS-supported catalysts have considerably lower surface areas (70-100 m²/g), along with lower pore volume (0.3-0.4 cm³/g) and smaller pore diameter (11-14 nm). After calcination, both S- and AS-supported catalysts contain cobalt as Co₃O₄ (or cobalt aluminates in the case of AS-based catalysts, Fig 1). Due to the very low Pt-content, negligible effects in catalyst morphology and phase composition can be attributed to the presence of Pt. On the contrary, both in the case of AS and S-supported samples, the preparation method strongly affects the aggregation of cobalt atoms. OM catalysts show broader Co₃O₄ diffraction peaks than IWI catalysts (cf., e.g., XRD patterns for AS-supported samples Fig. 1), indicating smaller crystallites: average cry-sizes calculated with the Scherrer equation for the AS-OM catalysts range indeed from 7 to 8 nm, roughly half of the diameter of Co-metal centers in the AS-IWI samples. Similarly, in the case of the S-supported samples, average cry-sizes are between 10 and 14 nm in the case of the OM samples, roughly 70% of the values calculated for the corresponding IWI catalysts. Interestingly, AS-supported catalysts present smaller Co crystallites with respect to S-supported catalysts, independently on the adopted synthesis method. This can be explained considering the effects of the strong metal support interaction (SMSI) occurring in the case of stabilized γ -Al₂O₃ supported samples. Nevertheless, H₂-TPR profiles of S- and AS-supported catalysts are similar, at least at temperatures relevant to industrial operations (Fig 2): a first H₂ consumption phase, observed between 200-300°C, and associated to Co₃O₄ reduction to CoO, is followed both in the case of S- and AS-samples by the further reduction of CoO to Co⁰ (between 400°C and 700°C). An additional reduction peak is detected at temperatures higher than 700°C in the case of AS-OM catalysts, likely related to the reduction of cobalt-aluminum mixed spinels present on the stabilized support. It is well evident that catalysts prepared via OM are more difficult to be reduced with respect to IWI catalysts, most probably due to the smaller size of cobalt oxide crystallites. However, the presence of Pt effectively promotes the reducibility of the cobalt species: this is particularly evident in the case of the OM catalysts, whose H₂-consumption profile in the presence of Pt is comparable to that of the Pt-promoted IWI sample. As expected, the higher dispersion and reducibility of OM catalysts promoted with Pt results in a higher catalyst activity in the

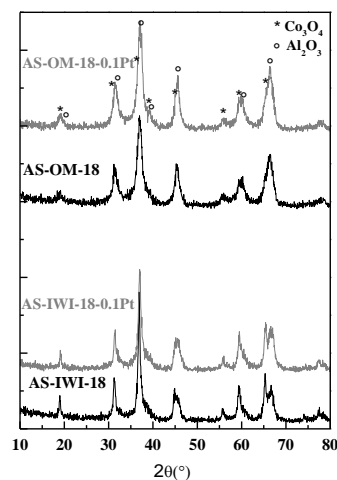


Fig.1. XRD spectra of OM and IWI AS catalysts, promoted and unpromoted with Pt

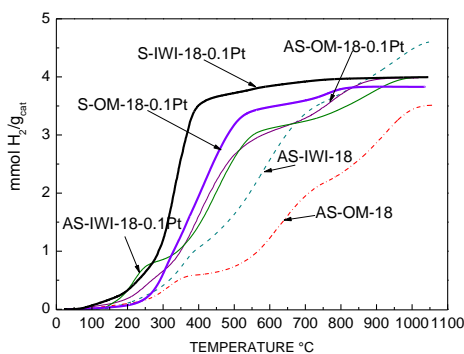


Fig.2. TPR: Integral curves of hydrogen consumption normalized by catalyst loading as a function of temperature

FTS: for example, CO conversions measured at atmospheric pressures for AS-supported samples range as follows: 10.5% AS-OM-18-0.1Pt, 5.6% AS-IWI-18-0.1Pt, 4.4% AS-IWI-18, 8.9% AS-OM-18. At the same time, AS samples were found to be more active than S-supported thanks to the smaller average cry-size.

4 Conclusions

Organic Matrix is a synthesis method much more effective than incipient wetness impregnation in obtaining highly dispersed cobalt-based FT catalysts, especially when stabilized γ -Al₂O₃ is used as support. However, small Co-crystallites are hardly reducible, which vanishes the benefits of the high dispersion in terms of catalytic performances. The adoption of small amount of platinum can overcome such an issue, by granting the complete reduction even of highly dispersed cobalt crystallites. As a result, the combined adoption of OM synthesis method and Pt-promotion brings to highly active catalysts, showing CO conversion 2 times higher than in the case of unpromoted IWI samples. Long term test under pressure are presently ongoing to evaluate the benefits associated with the combined OM and Pt-promotion in terms of product selectivity and the effects of crystal size on the catalyst stability.

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