

# Cobalt nanoparticles supported on graphene for Fischer-Tropsch Synthesis

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## Introduction

Fischer-Tropsch synthesis consists in the catalytic conversion of synthesis gas (H<sub>2</sub> and CO) and it is a promising alternative to produce high quality hydrocarbon fuels.

Although several studies around the Fischer-Tropsch synthesis (FTS), making the process viable economically is still a challenge. Aspects such as activity, selectivity, especially for heavier hydrocarbons, and the cost of the catalysts currently employed should be further studied in order to facilitate the process on a profitable industrial scale<sup>1</sup>. Since early works, it is widely accepted that Group VIII metals are very active in CO hydrogenation, mainly Co and Fe<sup>1,2</sup>. Co-based catalysts are preferred, since it is more active than Fe-based ones and require lower reaction temperature<sup>1</sup>. Recent studies also indicate that in catalysis metal nanoparticles supported on carbon nanomaterials used in FTS showed high activities for C<sub>5+</sub>, as well as low selectivity for the formation of methane and CO<sub>2</sub><sup>3-5</sup>. In this context, graphene has attracted the attention of the scientific community due to its unique properties, such as high mechanical and thermal resistance, high electron mobility, high surface area and availability of sites<sup>5,6</sup>. High surface graphene as a support for cobalt allow a better nanoparticles dispersion and its surface defects may be sites for adsorption of active species for catalysis process.

In this work, graphene was synthesized and cobalt nanoparticles were deposited on its surface. The materials were characterized by different techniques to verify if the synthesis method was capable to produced CoO highly monodisperse under the graphene leaves surface.

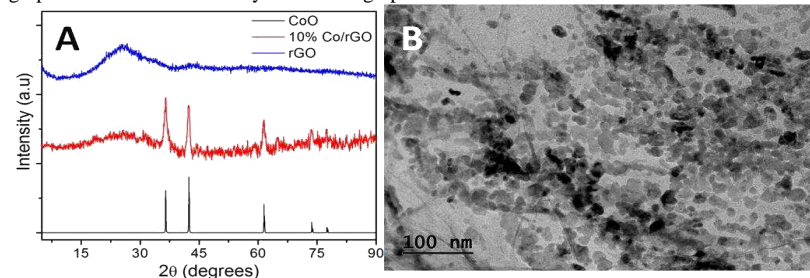
## Materials and Methods

Graphene synthesis process was an adaptation of improved Hummer's method<sup>7</sup>. Graphite flakes were chemically oxidized with sulfuric acid, phosphoric acid and potassium permanganate for 8 h. The graphite oxide (GO) obtained was purified and subsequently exfoliated and thermally reduced. The final support was denoted as reduced graphene oxide (rGO). Graphene-supported cobalt catalyst was prepared with a cobalt loading of 10 wt%. and was synthesized by deposition precipitation method, using Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O diluted in ethanol as precursor solution and ammonium hydroxide as precipitating agent. The catalyst was dried and calcined at 450 °C for 3 hours under Ar flow. The final product was named as 10% Co/rGO. Graphite oxide, rGO and 10% Co/rGO were characterized by XRD, Raman spectroscopy, BET, TGA and TEM techniques, as well as TPD analysis in order to verify H<sub>2</sub> consumption and reduction degree.

## Results and Discussion

To confirm the purity of the cobalt phase in the composite, XRD patterns of the samples were recorded. Figure 1A presents the pattern of the rGO, 10% Co/rGO and pure CoO. The peaks in the sample 10% Co/rGO can be related to the CoO and graphene.

The morphology of 10% Co/rGO nanocomposite was examine using transmission electron microscopy. A typical micrograph is presented in Figure 1B. The figure shows a thin graphene sheet embedded with Co nanoparticles (higher electron density portions on the graphene leaves). The weak contrast demonstrates that rGO sheet is very thin. The shape of the Co nanoparticles are spherical and highly disperse on the graphene surface. The cobalt oxide nanoparticles shows the diameter sizes around 17 nm. Raman spectroscopy results suggest that graphite oxide was efficiently reduced to graphene.



**Figure 1.** A-) XRD patterns of rGO and 10% Co/rGO compared to CoO profile. B-) TEM image of 10% Co/rGO sample.

The nitrogen adsorption/desorption isotherms confirmed the mesoporous structure of the synthesized rGO and 10% Co/rGO materials and the surface area of the materials were around 400 m<sup>2</sup>g<sup>-1</sup>. The Raman spectroscopy shows that the graphite oxide was efficiently reduced to graphene by thermal reduction method.

## Significance

The development of a high performance catalyst for FTS, mainly with high activity and selectivity for high-chained hydrocarbons, is essential for economic feasibility of this technology compared to tradition fuel production. The characterization results confirm that both rGO and 10% Co/rGO were successfully prepared by the proposed synthesis methods. The catalysts will be tested in Fischer-Tropsch synthesis.

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