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# Enhancement of performance and stability of Graphene nano sheets supported cobalt catalyst in Fischer–Tropsch synthesis using Graphene functionalization

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## ABSTRACT

Graphene nano sheets (GNS) were functionalized and used as cobalt Fischer–Tropsch synthesis (FTS) catalyst support. The effects of nitrogen functional groups on graphene surface on the activity, selectivity and stability of cobalt catalyst in FTS was investigated using a fixed bed micro-reactor. 15 wt.% of cobalt was loaded on the supports by impregnation method. Physico-chemical properties of pure and functionalized graphene, calcined fresh and used catalysts were studied by Raman spectroscopy, FTIR, BET, XRD, TEM, TPR and H<sub>2</sub>chemisorption techniques. According to the TEM and H<sub>2</sub>chemisorption tests, 480 hrs continuous FT synthesis increased the average cobalt particle size from about 7.8 to 8.8 nm for Co/GNS catalyst and from about 6.8 to 7.2 nm for Co/N-GNS catalyst. The proposed cobalt catalyst supported on functionalized GNS increased the initial %CO conversion from 70.6 to 74.5. The CO conversion over the Co/N-GNS after 480 hrs on stream decreased by 4.3% and that for Co/GNS decreased by 6.2%. For the Co/N-GNS catalyst 0.6% of total activity loss and for the Co/GNS catalyst 3.1% of total activity loss cannot be recovered after regeneration of the catalyst at the same conditions of the first regeneration step. Catalysts supported on functionalized GNS showed better stability.

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## 1. Introduction

Sustainable and efficient processing of fossil fuels is one of the key solutions for decrement of harmful environmental effects of greenhouse gasses emission (Shimizu et al., 2015; Olewski et al., 2015; Norouzi et al., 2016). Liquid fuels synthesized from natural gas by means of Fischer–Tropsch can play a promising role as a clean alternative fuel (Sherry and Fürstner, 2008; Dreyer and Bielawski, 2011; Su and Loh, 2012; Pyun, 2011). These fuels have several distinguished beneficial properties, as an alternative clean diesel fuel compared to conventional fossil diesel including virtually zero sulfur, negligible amounts of aromatics and hetero atomic species like sulfur and nitrogen. Higher

cetane number and the absence of polycyclic aromatic hydrocarbon (PAH) content, which are the principal properties of gas to liquid (GTL) fuels, have potential to reduce particulate matter (PM) emissions (Dhakshinamoorthy et al., 2012; Titirici and Antonietti, 2010).

Cobalt catalysts are widely used for the low-temperature FTS because of their economically high activity and selectivity to linear paraffins, low water–gas shift (WGS) activity and relatively low cost (Schulz, 1999; Reuel and Bartholomew, 1984; Schulz and Claeys, 1999). Improving catalyst activity, selectivity and stability is a major focus among technology providers and plant operators. It follows logically that a basic understanding of the mechanisms involved in the deactivation process is vital to improving catalyst stability. The potential causes of cobalt-based FT synthesis catalyst deactivation include (a) sintering; (b) re-oxidation of cobalt, including surface oxidation; (c) formation of

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stable compounds between cobalt and the support, e.g., cobalt aluminate; (d) surface reconstruction; (e) formation of carbon species on the cobalt surface; (g) carbiding; (h) poisoning (Rytter and Holmen, 2015).

Carbon nano materials have been considered for use as support materials due to their tensile strength, large surface area, promising thermal stability, ease of recovery and recyclability which in turn is important in adhering to sustainable chemistry protocol (Bachiller-Baeza et al., 2000; Lepró et al., 2008). The unique properties of two-dimensional structure, great intrinsic carrier, well developed porosity, active surface area, outstanding electronic properties and promising mechanical and thermal stability makes graphene as the current support key material in the heterogeneous catalyst system.

For application of a material as support of metal nano particles (NPs), one crucial point is the interaction between the surface of the material and the supported NP. The major properties of graphene are its hydrophobic and inert nature. Strong metal-support interactions can lead to stabilization of the supported NP, but they can also modulate the catalytic activity. Poor interaction with the metal particles causes further agglomeration and sintering. Also, in this application of graphene, the presence of dopant elements on graphene should play an important role as predicted by theory (Das et al., 2011; Lazar et al., 2013; Tavasoli et al., 2008a). For N-doped graphene, it was found that the interaction energy between metallic elements should be higher, indicating the most probably location of the metallic element, on top of N atoms present in graphene rather than on the carbons (Ning et al., 2015). The interaction between dopant N atoms with metal atoms, being much stronger than that between metal atoms and carbon, is presumed to contribute also to the stabilization of cobalt NPs on N-doped graphene during the catalytic cycle, with respect to undoped graphene. It seems that, formation of functional groups on graphene surface, not only will decrease the sintering of cobalt, but also will accelerate the hydrogen spill-over effect in the reduction process. This in turn will increase percentage dispersion, reduction degree, stability and performance of these catalysts simultaneously.

In present work, graphene was functionalized before loading of cobalt precursors. The performance and stability of Co/GNS and Co/N-GNS catalysts during 480 hrs continues FT synthesis in a fixed bed micro reactor was investigated. The major aim of the study is to investigate how the structure and properties of support affect the deactivation trends of cobalt catalyst. Furthermore, a number of characterization techniques are also employed to find out the main causes of Co/GNS and Co/N-GNS catalyst deactivation.

## 2. Experimental

### 2.1. Support preparation

#### 2.1.1. Preparation and purification of Graphene

Graphene was used as support material for preparation of cobalt catalysts. The support was prepared in Research Institute of Petroleum Industry, Tehran, Iran. The impurities in graphene are one of the factors preventing access to its significant features and need to be eliminated before the experiments. The purification procedure was done as follows: the pristine graphene was treated with 30% HNO<sub>3</sub> reflux at 120 °C overnight, washed with distilled water, dried at 120 °C for 6 hrs and in order to eliminate the amorphous carbons, the temperature was increased to 400 °C in air with a ramp rate of 10 °C/min and maintained at this temperature for 20 min (Rashidi et al., 2010; Naeimi et al., 2009). This support was named GNS.

#### 2.1.2. Functionalization of Graphene

It is known that graphene has a hydrophobic surface, which is prone to aggregation and precipitation in water in the absence of a dispersant/surfactant. Up to now, many efforts have been made to prepare hydrophilic graphene and numerous

methods for chemical functionalization of graphene. Among them, we have chosen one method for graphene functionalization. In order to introduce N-containing functional groups, graphene was treated at 400 °C for 6 hrs in flowing ammonia with a flow rate of 25 sccm (10 vol.% NH<sub>3</sub> in He) (Kundu et al., 2010). To neutralize the ammonia gas, it was imported to acetic acid solution. This support was named N-GNS.

### 2.2. Catalyst preparation

The above produced GNS and N-GNS were used as supports for preparation of catalysts. Purified graphene (GNS) and functionalized graphene (N-GNS) supported catalysts were prepared with loadings of 15 wt.% cobalt. The catalysts were prepared using an aqueous solution of cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 99.0%, Merck). The sequential impregnation method was used to add cobalt to the supports. After impregnation step, catalysts were dried at 120 °C and calcined under argon (Ar) flow at 450 °C for 3 h with a heating rate of 10 °C/min. The samples were carefully passivated at 150 °C using 1:200 (v/v) flow of O<sub>2</sub>/Ar gas mixture, during the cooling step.

### 2.3. Characterization

The FTIR absorption technique for confirming the formation of functional groups was conducted on a Bruker ISS-88 system. A smooth transparent pellet of 0.5–5% of supports were mixed with 95–99.5% potassium bromide (KBr), was made and the infrared beam passed through this pellet.

The Raman shift of the support materials was measured on a Confocal Raman Microscope Systems with a laser source of 785 nm.

The cobalt loadings of the calcined fresh and used catalysts were verified by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system. For this purpose, 0.02 g of sample was dispersed in 5 ml of nitric acid (Merck 65%) and 5 ml hydrochloric acid (Chem-Lab, 37%). The temperature of the mixture was kept at 40–50 °C for 2 hrs. The resulting mixture was filtered and washed several times with distilled water. The filtrate solution was diluted with deionized water up to 250 ml (acid digestion).

The surface area, pore volume, and average pore radius of the support; fresh and used catalysts, were measured by an ASAP-2010 system from Micromeritics. The samples were degassed at 200 °C for 4 hrs under 50 mTorr vacuum and their BET area, pore volume, and average pore radius were determined.

The morphology of the catalysts was studied by transmission electron microscopy (TEM) method. Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a carbon coated copper grid. TEM investigations were carried out using a Philips CM20 (100 kV) transmission electron microscope equipped with a NARON energy dispersive spectrometer with a germanium detector.

XRD patterns of the catalysts were conducted with a Philips PW1840 X-ray diffractometer with monochromatized Cu/K<sub>α</sub> radiation. Using Scherrer equation, the average size of the cobalt oxide crystallites in the catalysts were estimated from the line broadening of cobalt oxide peaks.

The H<sub>2</sub>-TPR profiles of the catalysts were performed in order to study the reducibility of the metal species in the catalysts. The calcined catalyst sample (0.05 g) was first purged in a flow of Helium at 140 °C to remove traces of water and gases

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