Iron Catalyst Supported on Carbon Nanotubes for Fischer-Tropsch Catalysts – Deactivation Study

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Introduction

Carbon nanotubes (CNTs) have unique properties such as high thermal conductivity, high aspect ratio, meso-pore and macro-pore structures and straight pores. These properties suggest that CNTs can be ideal support for Iron catalyst in Fischer-topsch synthesis (FTS). In terms of FT synthesis, there are a few studies on the application of CNTs as support for Co and/or Fe catalysts [1-4]. However controversy encircles the stability of CNT supported FT catalysts. This research is a part of our comprehensive studies regarding activity, selectivity and stability of CNTs as support for FT catalysts indicating the major reason for deactivation of iron catalyst supported on carbon nanotubes.

Materials and Methods

Two type of catalysts (Fe/CNT1 and Fe/CNT2) were prepared using incipient wetness impregnation method with iron loading of 10wt%. For Fe/CNT2, before metal doping, the CNTs (180 m^2/g, inner pore diameter 5-10 nm and outer diameter of 15-20nm) were treated with 60wt% HNO_3 110^oC for 14 hours. The fresh and used catalysts were characterized by nitrogen adsorption, TPR, XRD, SEM, TEM, H_2 chemisorptions and Raman spectroscopy. The activity, selectivity and stability of the catalysts were assessed using H_2/CO =2:1 (molar) ratio in the feed, an overall pressure of 2 MPa and reaction temperatures of 275^oC within a reaction period of 480 h in a fixed bed micro reactor.

Results and Discussion

According to FT activity of the catalysts within a time pried of 480 hours, the Fe catalyst supported on CNTs pretreated in nitric acid at 110^oC was relatively stable (deactivation rate = 0.008 %CO conversion/h). The catalysts supported on as-grown CNTs experienced a rapid deactivation from CO conversion of 84 to 58 % within 480 h. Based on ICP analysis on fresh and used catalysts, the metal content of catalyst remained constant. Thus the metal lost or coking was not the important factor for catalyst deactivation. In the case of the catalysts supported on as-grown CNTs, XRD, TEM and H_2 chemisorption analyses on the fresh and used catalysts showed that the size of metal oxide increased form 8 to 35 nm, respectively (See Table 1 and Fig. 1). Thus, it can be concluded that the main reason for catalyst deactivation was the sintering of active metal sites. In the case of Fe/CNT1 catalyst, the regeneration of catalysts with reduction in H_2 atmosphere at 400^oC resulted in partial recovery of catalyst activity (25% restoration of activity). This also confirms that sintering of metal site which is an irreversible deactivation process has the main role in deactivation of the CNT supported catalysts. In comparison between Fe/CNT1 and Fe/CNT2, the results of Raman spectroscopy suggested that the stability of active metal sites for the hot-acid treated support is attributed to the interaction of metal cluster with the support due to the presence of defects created by treatment in hot nitric acid. Table 1 shows the characteristics and the FT activity and selectivity of the catalysts studied.

sample	Fe/CNT1	Fe/CNT2
Pretreatment	-	Nitric acid at 110 ^oC
Fe location	Exterior (close cap)	Interior (open cap)
Particle size (nm) (before reaction)	8	6
Particle size (nm) (after reaction)	35	9
%CO[a]	83 → 58	74→70
selectivity[a] (C5+ wt%)	44.2 → 40.2	52.8→50.1
%CO after regeneration[b]	64	73

Table 1. characteristics and FT performance of the Fe/CNT catalysts
Process conditions: 2 Nl/g-cat/h, 2MPa, H_2/CO = 2. All catalysts contain 10wt% Fe
a) Ranges in the data represent activity change with time on stream
b) %CO conversion after reduction in H_2 at 400^oC at the end of reaction period of 480 h.

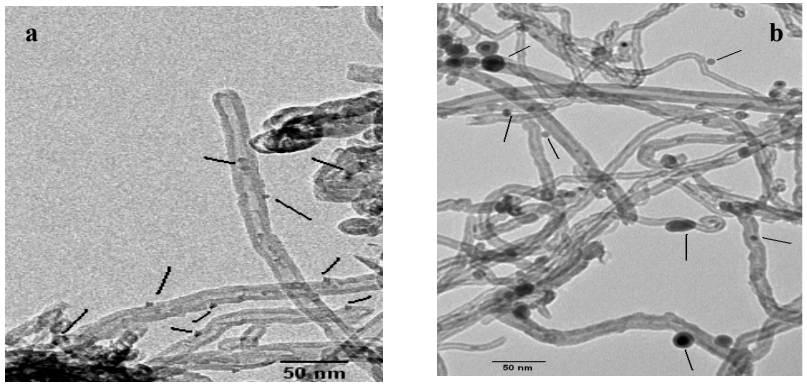

Fig. 1 TEM analysis of Fe/CNT1 a) before and b) after FTS (dots are iron oxide particles)

Significance

In commercial FT catalyst, metal precursors are dispersed on SiO_2 and Al_2O_3. A drawback of these support materials is their strong interaction with metal site resulting in catalyst deactivation [5]. To avoid these problems, the use of pretreated CNT supports with adequate functional groups is suggested.

References

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