Raising the activity and selectivity of cobalt catalysts for Fischer-Tropsch synthesis with a novel carbon nanotubes support in a CSTR

Mariane.T[1], Ahmad.T[2]*, Reza.M.A[1], Ajay.K.D[1] and Nicolas.A[3]

[1] Catalysis & Chemical Reaction Engineering Laboratories, Department of Chemical Engineering., University of Saskatchewan, Saskatoon, SK, S7N5C5 Canada
[2] Research Institute of Petroleum Industry, Tehran, Iran, P.O.Box 14665-1998
[3] Department of Chemical Engineering, Université de Sherbrooke, Sherbrooke, Qc, J1K 2R1
* tavassolia@ripi.ir

Introduction

The Fischer–Tropsch synthesis (FTS) process has shown to be catalyzed by certain transition metals, with Co, Fe, and Ru presenting the highest activity [1-3] .Among them, cobalt catalysts are the preferred catalysts for FTS based on natural gas because of their high activity for FTS, high selectivity to linear hydrocarbons, low activity for the water–gas shift (WGS) reaction, more stable toward deactivation by water (a by-product of the FTS reaction), and low cost compared to Ru [2-3]. In order to achieve high surface active sites ($Co°$), cobalt precursors are dispersed on porous carriers, with SiO_2, Al_2O_3, and to a lesser extent TiO_2 being the most frequently used. A drawback of these support materials is their reactivity toward cobalt, which during preparation or catalysis results in the formation of mixed compounds that are reducible only at high reduction temperatures [2-3]. Our previous works have shown that to avoid these problems, carbon nanotubes (CNT) can be used as a heterogeneous catalysis support [4].Their unique structural properties (mesoporous, high surface area) are quite suitable for use as catalytic support materials [4]. The present work was undertaken with the aim of exploiting the beneficial effects of carbon nanotubes support for Co catalyst prepared by the sequential aqueous incipient wetness impregnation method. The physico-chemical characteristics and catalytic performance of the catalysts are evaluated and the results are compared with the results of an alumina-supported cobalt catalyst.

Materials and Methods

Mknano-MWCNT (purity>95%) was used as support materials for the preparation of FTS catalysts. All catalysts were prepared with incipient wetness impregnation of cobalt nitrate ($Co(NO_3)_2.6H_2O$ 99.0%, Merck) solution on CNTs. Using sequential impregnation method C_1, C_2, C_3 and C_4 catalysts were prepared with cobalt loadings of 15, 25, 35 and 40wt.%. Also one γ–alumina supported (Conndea Vista Catalox B γ–alumina) catalyst (A_1) with cobalt loading of 15 wt.% was prepared just for comparison purpose. The catalysts were characterized by BET, SEM, TEM, XRD, TPR, and H_2 chemisorption. The catalysts were evaluated in terms of their FTS activity (g HC produced/g cat./h) and selectivity (the percentage of the converted CO that appears as a hydrocarbon product) in a continuous stirred tank reactor (CSTR). Prior to the activity tests, the catalyst (50 g) was reduced in situ in the CSTR with pure hydrogen at a flow rate of 60 NL/h and a temperature of 400 °C for 24 h. After the activation period, pure melted C_{28} paraffin wax was used as start-up media. C_{28} paraffin wax was degassed at degasser vessel with nitrogen at 120 °C for 1 h and transferred to the CSTR to mix with catalyst. A lead oxide-alumina containing the vessel was used to remove carbonyls before gas entering to the reactor at 180°C.The mixed gases (H_2 and CO) entered through a dip tube from the bottom of the CSTR below the stirrer with a flow rate of 90 NL/h (H_2/CO ratio of 2), a pressure of 2.5 MPa and a temperature of 220°C. The CSTR was operated at 750 rpm. Liquid products were removed from a cold (0°C) or hot trap (100°C) every 12h.

Results and Discussion

According to TEM picture, most of the cobalt particles were homogeneously distributed inside the tubes and the rest on the outer of the CNTs (Fig.1a). Carbon nanotubes as cobalt catalyst support was found to shift the reduction temperature of cobalt oxide species to lower temperatures. The strong metal–support interactions are reduced to a large extent and the reducibility of the catalysts improved significantly. CNT aided in well dispersion of metal clusters and average cobalt clusters size decreased. Cobalt catalyst supported on CNT significantly enhances the CO conversion and FT synthesis rate (Fig.1b).The hydrocarbon yield in the FT process obtained by CNT-supported cobalt catalyst is about 75% more than that obtained using cobalt on alumina supports. The maximum concentration of active surface $Co°$ sites and FTS activity for CNT-supported catalysts are achieved at 40 wt.% cobalt loading. CNT caused a slight decrease in FTS product distribution to lower molecular weight hydrocarbons.
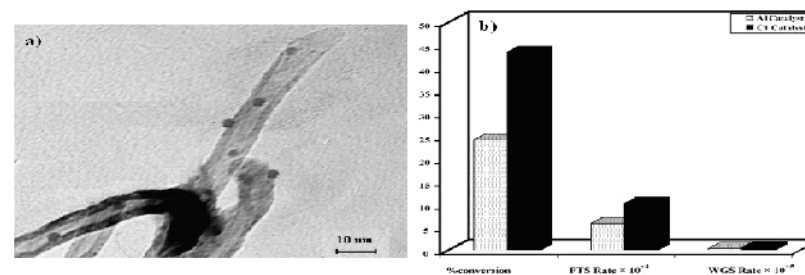

Figure 1: (a) TEM pictures of C_1; (b) FTS rate, %CO conversion, WGS rate and product selectivity of the A_1 and C_1 catalysts (T = 220 °C, P = 2.5 MPa and H_2/CO = 2).

Significance

This work is part of a world endeavor to evaluate the techno-economic feasibility of using FTS with new nanocatalyst formulations to convert fossil-derived or renewable gaseous fuels into green diesel.

References

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