Catalysis Communications 22 (2012) 24–27

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Comparison of induction behavior of Co/CNT and Co/SiO_2 catalysts for the Fischer-Tropsch synthesis

Suli Bai, Chengdu Huang, Jing Lv, Zhenhua Li *

Key Lab for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Weijin Road 92, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 9 October 2011
Received in revised form 11 December 2011
Accepted 6 February 2012
Available online 19 February 2012

Keywords:
Cobalt
Carbon nanotubes
Induction period
Fischer-Tropsch synthesis

ABSTRACT

Carbon nanotubes and silica gel supported cobalt catalysts (Co/CNT and Co/SiO_2) for Fischer-Tropsch (FTS) synthesis with syngas as feedstock were prepared. The catalysts were characterized by TPR, BET, and TEM. Effect of support material on induction period of FTS was investigated. Results showed that, there was a remarkable induction period about 26 h and very fluctuating temperature at the initial reaction stage for Co/SiO_2 catalyst. The catalytic performances for FTS changed notably during the induction period. CNTs as supported material could remarkably shorten the time of induction period as well as promote the catalytic activity and stability for FTS.

1. Introduction

As a result of diminishing petroleum reserves, the FTS attracts greater interest. A lot of researches have been done to develop an efficient FTS catalyst or to exploit an economic FT process. Cobalt-based catalysts appear to provide the best compromise between performance and cost for the synthesis of hydrocarbon from syngas derived from coal, natural gas, or biomass [1–3].

For most of the supported catalysts, typically there exists an induction period, which could last from minutes to hours depending on their properties, before the steady state is achieved [4–6]. The activity data is reliable for catalyst evaluation only after the induction period. Many researchers pointed out that most of the supported Fe-based and Co catalysts have induction period for FTS reaction which lasts over 24 h [7–9]. For Fe catalyst, it has been confirmed that Fe phase was transformed from Fe_2O_3 to Fe_3O_4 and then to Fe_xC during the induction period. The extent of carburization increases with time on stream during the initial stage of FTS reaction. After Fe_2O_3 is converted to Fe_xC, the steady-state is reached [10]. Catalysts with more carbide species were often found in earlier studies to exhibit higher FTS activity [11,12]. There are many reports mentioned that Co/CNT having induction period, but it is usually to only start FTS investigations after the catalyst stabilizes. So, it is not very clear what changes occured on the catalyst surface in the induction period.

In this paper, Co/CNT and Co/SiO_2 were prepared and the induction behavior and performances for FTS were investigated. It was found that, the induction time could last for 26 h on Co/SiO_2 catalyst, which is in agreement with earlier reports [7,9], while on CNT supported Co catalyst, the induction time is less than 10 h. Furthermore, temperature fluctuated greate during the induction period for SiO_2 supported cobalt catalyst compared with Co/CNT catalyst. The activity for FTS was enhanced by using CNTs as support material.

2. Experimental details

2.1. Catalyst preparation

Commercial silica gel (Qingdao Yumingyuan Silica-Gel Reagent Factory, China) and carbon nanotubes (Chengdu Organic Chemicals Co.Ltd., Chinese Academy of Sciences) were used as support materials.

The silica gel (20–40 mesh) and CNTs (Outer Diameter: 20–30 nm, Inner Diameter: 5–10 nm, Length: 10–30 μm, Purity: >95 wt.%) were used as support materials. Raw CNTs were refluxed at 122 °C (azeotropic point) for 6 h in 65 wt.% HNO_3 in an electric heating unit, then filtered and washed with distilled water until neutral pH was reached, followed by drying at 120 °C for 8 h. Catalysts containing 20 wt.% Co were prepared using incipient wetness impregnation method with aqueous solution of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$). After impregnation, the samples were dried at 100 °C for 10 h and subsequently calcined at 200 °C for 5 h in argon atmosphere with a temperature ramp of 1 °C/min. The prepared catalysts were denoted as Co/SiO_2 and Co/CNT, respectively.

* Corresponding author at: Postal address: School of Chemical Engineering and Technology, Tianjin University, Weijin Road 92, Tianjin 300072, China. Tel.: +86 22 27405484; fax: +86 22 87401818.
E-mail address: lizhenhua001@gmail.com (Z. Li).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2012.02.006

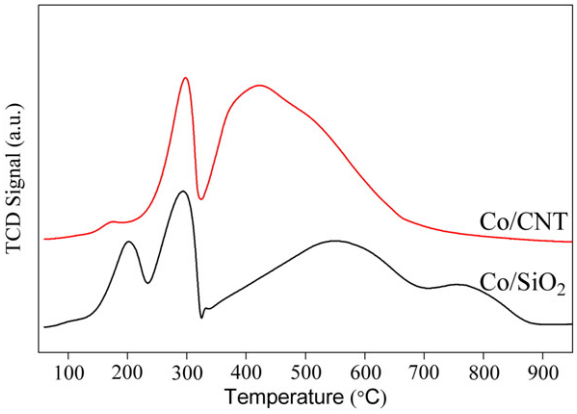

Fig. 1. TPR profiles of Co/SiO_2 and Co/CNT catalysts.

2.2. Catalyst caracterization

Temperature programmed reduction (TPR) was performed using a Micromeritics AutoChem 2910 system, equipped with a thermal conductivity detector (TCD). The sample was first purged in a flow of argon at 200 °C for 60 min to remove trace amount of water, and then cooled down to room temperature. A 10% H_2/Ar mixture (30 mL/min) was then introduced and the sample was heated to 900 °C with a ramp of 10 °C/min. TCD was used to record the hydrogen-consumed signal.

Specific surface area, pore volume, and average pore size of the catalysts were measured using a Micromeritics Tristar-3000 system. Prior to the experiment, the sample was outgassed at 300 °C for 4 h. Adsorption of N_2 was carried out at −196 °C to obtain adsorption–desorption isotherms. The BET surface area and pore size distribution are calculated with BET equation and BJH equation, respectively.

Morphologies of supports and catalysts were characterized by a transmission electron microscope (TEM) (Philips TECNAI G^2F20). Sample specimens for TEM studies were prepared by ultrasonic dispersion of the catalysts in ethanol, and the suspensions were dropped onto a Micro-mesh copper grid.

2.3. Catalyst evaluation

The FTS performance of catalyst was evaluated in a fixed-bed microreactor. Prior to the reaction, the catalyst was reduced in situ at 400 °C for 10 h in a hydrogen flow. A thermocouple was located inside a stainless-steel sheath in direct contact with the catalyst bed to ensure accurate temperature measurement. The average temperature of the catalyst bed was controlled at 230 °C. A temperature measuring software was used to get instant recording of hot spot temperature. The wax and water mixture product was collected in a hot trap (170 °C), and the oil and water were collected in a cold trap (−4 °C). Effluent gaseous phase products were passed through an Agilent 6820 GC equipped with TCD and FID for online analysis. The liquid product and solid wax analysis were performed on a SP 3420 GC equipped with a FID. The reaction conditions were as follows: $T = 230$ °C, $P = 2.0$ MPa, $H_2/CO = 2$, $GHSV = 1800\ h^{-1}$.

The catalytic activity (expressed as CO conversion) and hydrocarbon selectivity were calculated on carbon basis [9]. The chain growth probability (α value) was attained based on the Anderson–Schultz–Flory chain-length statistics equation [13,14].

Table 1
N_2 adsorption–desorption results of the supports and cobalt catalysts.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
SiO_2	609.2	0.934	4.8
Co/SiO_2	366.5	0.524	4.8
Raw CNT	108.1	0.556	17.7
CNT [a]	178.5	0.537	10.8
Co/CNT	146.3	0.295	7.2

[a] Carbon nanotubes after 65 wt.% HNO_3 treatment.

3. Results and discussion

Temperature programmed reduction (TPR) is an effective method to study the reduction behavior of metal on support. The H_2-TPR profiles of Co/SiO_2, Co/CNT and CNTs are shown in Fig. 1. In this figure, two distinguishable peaks are observed for Co/CNT catalyst. Peaks at 300 °C and 420 °C are attributed to the two reduction steps of Co_3O_4 to Co, via a medium of CoO. The second peak also includes the gasification of support which extends the TPR spectra to higher temperatures of 700 °C as indicated by TPR of CNTs [15,16]. The weak peak at around

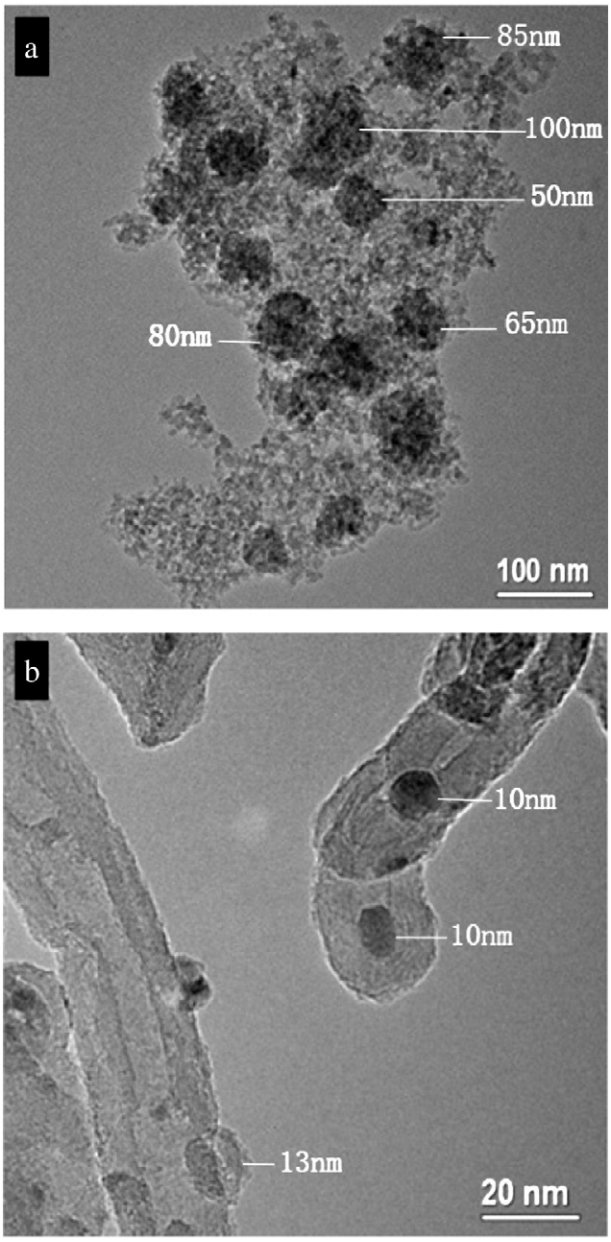

Fig. 2. TEM images of prepared catalysts. (a) Co/SiO_2, (b) Co/CNT.