

Synthesis and characterization of niobium-promoted cobalt/iron catalysts supported on carbon nanotubes for the hydrogenation of carbon monoxide

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Abstract: Bimetallic Co/Fe catalysts supported on carbon nanotubes (CNTs) were prepared, and niobium (Nb) was added as promoter to the 70Co:30Fe/CNT catalyst. The physicochemical properties of the catalysts were characterized, and the catalytic performances were analyzed at the same operation conditions ($H_2:CO$ (volume ratio) = 2:1, $p = 1$ MPa, and $t = 260^\circ C$) in a tubular fixed-bed microreactor system. The addition of Nb to the bimetallic catalyst decreases the average size of the oxide nanoparticles and improves the reducibility of the bimetallic catalyst. Evaluation of the catalyst performance in a Fischer-Tropsch reaction shows that the catalyst results in high selectivity to methane, and the selectivity to C_{5+} increased slightly in the bimetallic catalyst unlike that in the monometallic catalysts. The addition of 1% Nb to the bimetallic catalyst increases CO conversion and selectivity to C_{5+} . Meanwhile, a decrease in methane selectivity is observed.

Keywords: Fischer-Tropsch synthesis; bimetallic catalyst; niobium promoter; carbon nanotubes

Conventional energy resources, such as coal, petroleum, and natural gas, are fulfilling the major energy demands; however, these resources are on the verge of being exhausted, and fossil oil sources are estimated to be depleted by 2050^[1]. The increasing population, economic development, and limited supplies of fossil fuels led to the development of new approaches to produce renewable liquid fuels^[2]. Fischer-Tropsch synthesis (FTS) gained popularity as an alternative approach to transform different non-petroleum carbon resources, such as coal, natural gas, and biomass, into valuable chemicals from syngas (H_2 and CO) or clean transportation fuels^[3]. FTS is a process that catalytically converts syngas into clean hydrocarbon fuels, whereas syngas can be derived from non-petroleum feedstock, such as coal, natural gas, or biomass. Increasing the quality of products by developing novel catalysts with high activity and selectivity is desirable in FTS reactions^[4]. In FTS reactions, syngas is transformed into liquid fuel through catalytic polymerization, which results in various products, such as paraffins, olefins,

alcohols, and aldehydes.

Some challenges still remain in catalyzing FTS reactions. From a fundamental perspective, one of the important difficulties is the control of selectivity. CO undergoes dissociative or hydrogen-assisted dissociative chemisorption on the surface of active metal phases to produce CH_x ($x = 0-3$) intermediates as monomers for polymerization. The connection between CH_x monomers results in chain growth and provides C_nH_m intermediates. C_nH_m intermediates with different carbon numbers can undergo hydrogenation or dehydrogenation to produce paraffins or olefins as final products^[5,6].

Ni, Fe, Co, and Ru are known to be the most active elements for FTS reactions^[7-9] because of their ability to dissociatively adsorb CO and H_2 ^[10]. One of the parameters that affect the activity of a catalyst is the chemical composition of the catalyst^[11-13]. However, other parameters, including appropriate physical properties and high surface area, are also important for the catalytic activity in FTS

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reactions^[13–15]. To overcome the problems associated with conventional metal oxide supports, researchers started using carbon as a catalyst support. Unlike other allotropes of carbon, carbon nanotubes (CNTs) have received significant attention because of their applications and fundamental properties. The presence of these micropores can reduce the full accessibility of reactant particles to active sites^[16]. CNTs are stable and inactive in many acidic and basic media. Traditional supports are rendered useless after a reaction. CNTs are more stable toward oxidation and hydrogenation than traditional carbon-based supports^[17,18].

The present work aimed to examine the performance of CNTs as monometallic Co and Fe and bimetallic Co-Fe catalysts supported on CNTs for FTS reactions. Moreover, niobium (Nb)-promoted bimetallic catalysts were prepared and characterized, and their performance in the FTS reaction was tested. In addition, the effect of increasing the H₂:CO volume ratio from 1:1 to 4:1 was studied.

1 Experimental

1.1 Catalyst preparation

Prior to catalyst preparation, the commercial MWCNT (Nanostructured and Amorphous Materials Inc. USA, >95%) supports underwent concentrated acid treatment and thermal treatments. MWCNTs were first treated with HNO₃ (65%, Merck) at 120°C for 14 h, washed with deionized water, and dried at 120°C for 6 h. The obtained MWCNT powders were subjected to thermal treatments at 900°C for 3 h with a heating rate of 5°C/min in an inert argon atmosphere. All catalysts were prepared using the co-impregnation of cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O >99%, Merck) and iron nitrate nanohydrate (Fe(NO₃)₃·9H₂O, 99%, Merck) as precursors, which were added to the support dropwise with constant stirring. After 24 h of stirring, all impregnates were dried at 120°C overnight. The impregnates were calcined at 350°C under flowing argon for 6 h with a heating rate of 5°C/min. Different catalysts containing a fixed amount of total metal (10%, by weight) were prepared and denoted as Co/CNT, and 70Co:30Fe/CNT, respectively. To prepare the promoted catalysts after drying the bimetallic catalysts, Nb (ammonium niobate (V) oxalate hydrate, 99.99%, Aldrich) was introduced to the bimetallic catalyst after drying by sequential impregnation at 1% under constant stirring for 24 h. The obtained powders were calcined at 350°C under argon for 6 h with a heating rate of 5°C/min.

1.2 Catalyst characterization

All the prepared catalysts were characterized by

Transmission Electron Microscopy (TEM). The samples for TEM studies were prepared by the ultrasonic dispersion of the catalysts in *n*-hexane. The suspensions were dropped onto a copper grid. TEM investigations were carried out using a Zeiss LIBRA 200 FE TEM (200 kV). The surface morphology of the prepared catalysts was studied using field emission scanning electron microscopy (FESEM-EDX) with the CARL Zeiss Supra 55VP instrument equipped with the Oxford INCA 400 EDX microanalysis system. X-ray photoelectron spectra were obtained from *K*-Alpha spectrometer (Thermo Scientific) at 50 eV pass energy. The reduction behavior of the catalysts was studied using a Thermo Finnigan TPD/R/O 1100 equipped with a thermal conductivity detector and mass spectrometer. Typically, 20 mg of catalyst was placed in the quartz tube. The catalyst samples were pretreated under nitrogen flow at 200°C to remove traces of water and impurities from the catalyst pores. H₂ temperature programmed reduction (H₂-TPR) was performed using 5% H₂/N₂ with a flow rate of 20 mL/min and heating from 40 to 800°C at 5°C/min.

1.3 Catalytic performance test

The catalytic activity of the prepared catalysts in FTS was evaluated in a tubular fixed-bed microreactor system (PID Eng&Tech). Typically, 35 mg of the catalyst was charged to the reactor. The catalyst was reduced in situ under 20 mL/min pure H₂ at 400°C for 3 h. The reactor temperature was reduced to 260°C, and the reaction was performed at 260°C, 1 MPa, H₂/CO (volume ratio) = 2, and space velocity (SV) = 51 L/(g·h). Online gas analysis was performed during the FTS reaction using a gas chromatograph (Agilent Technologies 7890) equipped with TCD and FID detectors. CO conversion, Hydrocarbon (HC) selectivity, and olefinitiy were calculated using Equations (1), (2), and (3), respectively.

$$\text{CO conversion (\%)} = \frac{(\text{moles of CO}_{\text{in}} - \text{moles of CO}_{\text{out}})}{(\text{moles of CO}_{\text{in}})} \times 100\% \quad (1)$$

$$\text{HC selectivity (\%)} = \frac{(\text{moles of HC produced})}{(\text{total moles of HC})} \times 100\% \quad (2)$$

$$\text{Olefinitiy} = \frac{(\text{moles of olefin})}{(\text{moles of paraffin})} \quad (3)$$

2 Results and discussion

2.1 Characterization of catalysts

The particle morphology, shape, and size of the prepared catalysts were characterized by FESEM-EDX. The representative images are shown in Figure 1. This figure indicates that the metal oxide particles are distributed on the CNT support (Figures 1(b)–(d)). The EDX result of Co/CNT, 70Co:30Fe/CNT and 1Nb-70Co:30Fe/CNT catalysts are shown in Figure 2.

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