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Fe-Ru small particle bimetallic catalysts supported on carbon nanotubes for use in Fischer–Tröpsch synthesis

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Abstract

Fe-Ru bimetallic catalysts for Fischer–Tröpsch (FT) synthesis were prepared by co-impregnation of Fe nitrate and Ru acetate salts on purified carbon nanotube (CNT) supports. The Fe-Ru/CNT catalysts were promoted with potassium and/or copper using an incipient wetness procedure in which the promoter was added at the same time as the Fe-Ru. The structures of the CNTs and sizes of the Fe-Ru metal particles (on average 2.1 nm) were determined by high-resolution TEM and HAADF-STEM. The reducibility of the catalysts was studied by temperature-programmed reduction (TPR) and the expected promoter effects (K, Cu on Fe) were observed. All the catalysts were used for the FT synthesis in a fixed-bed microreactor (275 °C, 8 bar, $H_2/CO = 2/1$). The effect of Cu and K on CO conversion, product selectivity and FT synthesis activity was investigated. The observed behaviour of the small particles obtained in this study followed similar trends to what has been observed before for Fe promoted catalysts suggesting that support interactions do not strongly affect the promoter properties of the metals. All the catalysts were found to be stable in the FT reaction (ca. 120 h) indicating that the Fe-Ru clusters possess remarkable stability in the FT reaction when supported on carbon nanotubes. This resistance to sintering is attributed to the metal support interaction characteristic of CNT supports.

Keywords: Fischer–Tröpsch; Fe-Ru bimetallic catalysts; Carbon nanotubes; Promotion

1. Introduction

Bimetallic catalysts play an important role in many industrial catalytic processes and represent an area of intense research activity. The addition of a second metal component to a catalyst allows for the possibility of systematically altering the size and/or the electronic structure of a catalyst. The presence of a second metal component can also make its influence felt by modifying the absorption characteristics of the catalyst surface, changing the reducibility of the catalyst or in certain cases altering the catalyst deactivation behavior. This has proven to be beneficial in bimetallic reforming catalysts [1].

Among the various bimetallic systems investigated, those of iron with noble metals such as Ru have drawn considerable attention over the decades because of their possible importance in the Fischer–Tröpsch (FT) synthesis [2]. Alloying iron with ruthenium results in a significant improvement in the stability of the catalytic system in FT synthesis compared with a one-component iron catalyst [3,4]. Further, supported iron-ruthenium catalysts are assumed to combine the benefits of high metal dispersion and alloying [3]. Supported alloys of these two metals are also known to possess unique catalytic properties in hydrocarbon synthesis, particularly giving a high selectivity to propylene [4]. The hydrocarbon product distribution in CO hydrogenation reactions over Fe-Ru bimetallic catalysts has been found to vary dramatically with the relative proportions of the two component metals [5]. Numerous studies of different bimetallic Fe-Ru combinations have been reported in the literature, but a comparison of the reported results is difficult,

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since different authors have used different supports, methods of preparation, and metal loadings [6].

In many heterogeneous reactions, the active phase is spread on a support. A catalyst support is not merely a carrier but it may also contribute to the activity of the catalyst. Earlier studies have indicated that using carbon as a support to provide an inert, poorly interacting surface could moderate the catalytic behavior of metals such as iron and ruthenium [7–12]. In particular, it has been noted that carbon nanotubes (CNTs) provide a relatively inert support, suggesting that this is a unique system for the study of the catalytic behaviour of metals since it provides reduced support interactions. This also suggests the use of CNTs as an alternative to amorphous carbon.

Tubular carbon, as a support, exists in a number of forms including plates [13], fishbone structures (both filled and unfilled, usually referred to as carbon nanofibres (CNFs)) [13,14] and classical nanotubes both as single-walled (SWCNTs) and multi-walled (MWCNTs) types [8,15]. These materials have been used as supports in FT studies. Both Fe and Co have been supported on these materials [7,8,15–19]. The relationship between results obtained from these different forms of carbon has not been elucidated in this study and will be discussed elsewhere.

In a previous study, we have reported the use of carbon nanotubes as a support for iron catalysts in the Fischer–Tröpsch synthesis [8]. The use of the tubular carbon as a support was found to stabilize highly dispersed iron particles formed from an aqueous impregnation technique using $Fe(NO_3)_3$ [7]. In addition, van Steen and Prinsloo [19] have studied Fe/CNF for FT synthesis and more recently Guczi et al. [15] have compared the activity of Co and Fe/CNTs for FT synthesis.

While Ru has been supported on CNTs and the materials have been investigated in many catalytic reactions [20] (for example, NH_3 synthesis [21] and the hydrogenation of cinnamaldehyde [22]) the use of Ru on CNTs in the FT reaction has not previously been described. In this paper we report on the role of Ru as a co-catalyst for a Fe-Ru catalyst supported on MWCNTs for use in the FT reaction. The small particle Fe-Ru catalysts were also promoted with Cu and K, and the influence of these classical Fe FT promoters is described.

2. Experimental

2.1. Catalyst preparation

CNTs were synthesized by the catalytic decomposition of C_2H_2 at 700 °C over iron supported on $CaCO_3$, as described elsewhere [7,8,23]. To avoid confusion with the catalyst used in the FT study, this catalyst will be referred to as the CNT production catalyst. Approximately 2.5 g of the nanotubes and some amorphous material were formed for every 1 g of CNT production catalyst used. A 30% HNO_3 solution was used to purify the CNT product [8,24]. The recovered nanotube material was then washed with distilled water until neutral before being dried overnight at 120 °C.

The carbon products of twelve CNT synthesis reactions were combined and thoroughly mixed to provide a homogeneous support material. Catalysts containing 10% iron supported on carbon nanotubes and promoted by 0.25% Ru were prepared by the incipient wetness (IW) impregnation process. In this method, $Fe(NO_3)_3{\cdot}9H_2O$ (7.21 g) and $C_8H_{12}O_8Ru_2$ (0.07 g), which was prepared in our laboratory according to the method described elsewhere [25], were dissolved in de-ionized water (18 mL) and added to 10 g of the carbon nanotube support. Three promoted catalysts (10FeRuCu, 10FeRuK and 10FeRuCuK) were similarly prepared by adding Cu, K or Cu and K to the 10% Fe catalyst. Thus, KNO_3 (0.052 g; 0.2% K) and/or $Cu(NO_3)_2{\cdot}3H_2O$ (0.228 g; 0.6% Cu) were added to an iron-ruthenium solution prepared as above and the mixture added drop-wise to 10 g of carbon nanotube support.

Keeping the Fe:Ru molar ratio the same, at 7.24, two other catalysts containing 5 and 2.5% Fe, i.e. 0.125 and 0.0625% Ru (5Fe/0.125Ru and 2.5Fe/0.0625Ru) were also prepared by the incipient wetness (IW) impregnation method. For the preparation of these catalysts, $Fe(NO_3)_3{\cdot}9H_2O$ (3.605 and 1.8035 g) and ruthenium acetate $C_8H_{12}O_8Ru_2$ (0.07, 0.35 and 0.175 g) were successively dissolved in de-ionized water (18 mL) and added to 10 g of the carbon nanotube support. Finally a 5% Fe catalyst loaded with 0.25% Ru (5Fe/0.25Ru) was also synthesized by the same procedures.

All the samples prepared were further dried in an oven (120 °C, in static air overnight) and then heated in nitrogen at 220 °C for 2.5 h.

ICP Optical Emission Spectroscopy (ICPOES) analysis of the catalysts revealed that the metal ratios obtained on the CNT support are very close to those predicted from the catalyst preparation procedure (Table 1).

2.2. Catalyst characterization

A JEOL 2010F scanning transmission electron microscope was used to obtain scanning and high-resolution transmission electron microscope (STEM and HRTEM) images. To measure the particle size distribution of catalyst particles on the CNTs, high-angle annular dark-field STEM operating at 200 kV was used. A Du Pont 951 thermogravimetric analyser (TGA) and a temperature-programmed reduction (TPR) apparatus, constructed in our laboratory, were used to characterize the CNT and the FT catalysts supported on carbon nanotubes. All characterization analyses were performed according to standard procedures as described previously [8].

Table 1
Actual metal content of various catalysts as determined by ICPOES

Catalysts composition	Notation	%Fe	%Ru	%K	%Cu
5% Fe/0.25% Ru/CNT	5Fe/0.25Ru	5.6	0.3	0	0
10% Fe/0.25% Ru/CNT	10Fe/0.25Ru	11.8	0.4	0	0
10% Fe/0.25% Ru/0.2% K/CNT	10FeRuK	9.8	0.2	0.4	0
10% Fe/0.25% Ru/0.6% CuCNT	10FeRuCu	10.9	0.5	0	0.6
10% Fe/0.25% Ru/CNT/0.2% K/0.6% Cu	10FeRuCuK	10.7	0.3	0.6	0.7
5% Fe/0.125% Ru/CNT	5Fe/0.125Ru	4.9	0.13	0	0
2.5% Fe/0.0625% Ru/CNT	2.5Fe/0.0625Ru	2.8	0.06	0	0