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ScienceDirect

Journal of Catalysis 244 (2006) 24–32

JOURNAL OF CATALYSIS

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CO hydrogenation over cobalt and iron catalysts supported over multiwall carbon nanotubes: Effect of preparation

László Guczi [a], G. Stefler [b], O. Geszti [a], Zs. Koppány [a], Z. Kónya [c,*], É. Molnár [c], M. Urbán [c], I. Kiricsi [c]

[a] *Institute of Isotopes, Hungarian Academy of Sciences, P.O. Box 77, H-1525 Budapest, Hungary*
[b] *Research Institute for Technical Physics and Materials Sciences, P.O. Box 49, H-1525 Budapest, Hungary*
[c] *Applied and Environmental Chemistry Department, University of Szeged, Rerrich Béla tér 1, H-6723 Szeged, Hungary*

Received 20 June 2006; revised 9 August 2006; accepted 16 August 2006

Abstract

CO hydrogenation was investigated over Co or Fe catalysts supported on multiwall carbon nanotubes (MWNTs). Two types of catalysts were prepared. For the simple impregnation method, metal acetate precursors were deposited onto the surface of MWNTs. These catalysts were denoted as “I-samples.” The second family of catalysts was prepared by deposition of preprepared metal oxide nanoparticles onto the MWNT support. These samples were labeled “P-samples.” All of the samples were characterized by TPR and TEM measurements and tested in CO hydrogenation. TPR measurements showed easy reducibility of the metal ions in the I-Co and I-Fe samples. TEM images generally pointed to a rather uniform particle size both before and after the reaction. The highest catalytic activity and high selectivity toward C_2–C_4 and C_{5+} fractions, as well as for olefin formation, were found for I-Fe. Catalytic activity was lower for P-Co and P-Fe. It can be established that these novel catalyst systems have high activity with high olefin selectivity and high fractions of larger hydrocarbons.

Keywords: Multiwall carbon nanotubes; Co and Fe on carbon nanotubes; CO hydrogenation; Electron microscopy; TPR

1. Introduction

Research activity focusing on the development of Fischer–Tropsch catalysts covers a widening field, even encompassing support materials. After the exhaustively investigated silica, alumina, titania, and mixed oxides, a new, challenging material, carbon nanotubes (CNTs), appeared as a possible support for various catalytic applications [1,2]. Studies comparing the catalytic activity of metal catalysts supported on various oxides, amorphous carbon, and CNTs showed that catalytic performance was generally the best on CNTs. For example, a multiwall CNT (MWNT)-supported platinum catalyst showed superior activity in catalytic wet air oxidation of nitrogen-containing compounds [3], and CNT-supported platinum catalyst did so in the oxidation of environmentally harmful organic compounds to CO_2 [4]. Yin et al. showed that CNT-supported metals are active in hydrogen generation from ammonia and that the CNT-supported Ru exhibited the highest efficiency in the reaction [5]. Chen et al. found that potassium-doped ruthenium supported on MWNTs gave the highest yield in ammonia synthesis among the potassium-doped ruthenium catalysts supported on various carbon materials [6]. Similar observations were published by Niesz et al., who reported that purified MWNT-supported platinum catalyst showed the highest turnover frequency in isopropanol dehydrogenation [7]. A recent review article discusses the development of the role of CNTs in heterogeneous catalysis between 1990 and 2003 [8].

The deposition of catalytic components onto CNTs—in most cases, onto MWNTs—is also an intriguing problem, as can be seen in the relevant literature. It is well known that the purification of catalytically made MWNTs is mainly performed in two steps; the first step is to remove the catalyst, where the

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[*] Corresponding author.
E-mail address: konya@chem.u-szeged.hu (Z. Kónya).

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doi:10.1016/j.jcat.2006.08.012

second step uses a strong oxidative media to remove amorphous carbon [9]. Generally, these treatments result in nanotube samples free of amorphous carbon and nontubular carbon nanostructures. This process also involves the generation of oxygen-containing functional groups on the outer shells of the nanotubes, however. These functional groups can help bond metal nanoparticles onto the nanotube surface [10,11]. Electrochemical deposition of metal particles with uniform size distribution has also been reported [12–14].

The metal or metal oxide nanoparticles-decorated carbon nanostructures can be used as catalysts for various catalytic reactions because of the strong metal–support interaction due to the graphitic nature of CNTs [15]. Iijima et al. reported a direct route for deposition of Pd nanoclusters with an average diameter of 2.3 nm on single-walled carbon nanohorns in a one-step reaction [16,17]. Zhang et al. reported on palladium nanoparticles filling the CNTs and their application in hydrogenation of benzene [18]. Palladium nanoparticle–filled MWNTs were used as selective catalysts for hydrogenation of cinnamaldehyde to hydrocinnamaldehyde [19]. CNTs have high thermal stability [20,21] and, similar to graphite, high resistance against various corrosive chemicals. These characteristics make this type of nanoporous material a nanoreactor in which chemical reactions may take place; due to the restricted reactor volume, some sort of shape selectivity is expected. Nhut et al. gave a nice example of the use of CNTs as a nanoreactor [22]; they used the system for several interesting transformations, including the decomposition of H_2S and the production of one-dimensional zeolite crystals.

The catalytic activities, the stability of the catalysts and the product selectivity of a series of Fe/CNT catalysts in Fischer–Tropsch synthesis have been investigated [23]. Iron supported on CNTs produced a very stable and active catalyst. The addition of potassium led to decreased hydrogenation activity and increased chain growth during the Fischer–Tropsch reaction, producing higher-molecular weight products. The production of C_2 olefins also increased. Potassium also decreased methane production and increased water–gas shift activity. Copper, introduced to facilitate reduction of the iron, increased the Fischer–Tropsch synthesis reaction rate but had no major effect on the product spectrum.

The main goal of the present work is to prepare MWNT-supported cobalt and iron catalysts using two different preparation methods—a conventional impregnation–heat treatment reduction method and deposition of preprepared metal oxide nanoparticles followed by reduction—and to characterize them using TPR and TEM and study the catalytic activity as well as selectivity in CO hydrogenation.

2. Experimental

2.1. Synthesis of MWNTs

MWNTs were produced by catalytic chemical vapor deposition (CCVD) of acetylene over alumina-supported iron–cobalt bimetallic catalyst [9]. The catalyst was placed onto a quartz boat positioned in the heating part of the quartz reactor tube, and nitrogen was introduced into the reactor while the temperature was increased up to 700 °C. At this temperature, 30 cm^3/min acetylene was mixed into the nitrogen stream (270 cm^3/min). The chemical decomposition of acetylene took place under these conditions. After 30 min, the generation of MWNTs was completed; the acetylene stream was shut off, and the reactor was cooled in nitrogen flow. The raw product was suspended in NaOH solution to remove the alumina, followed by washing with distilled water. The metal catalyst particles formed at the beginning of the synthesis procedure were dissolved in diluted acid solution. The amorphous carbon species generally accompanying CNT generation was oxidized using potassium permanganate in acidic media as described elsewhere [9]. Finally, the sample was washed with distilled water until neutral pH was reached and dried in air. The sample prepared by this procedure comprised high-grade CNTs containing only traces of metal impurities occluded inside the tubes. The specific surface area of the MWNT sample was 170 m^2/g. It is noteworthy that the surface area of the samples did not change significantly during TPR and catalytic treatments

2.2. Preparation of the metal/MWNT catalysts

Two types of catalysts were prepared using MWNTs as support. For the first group of samples, a simple impregnation method was used to deposit the metal precursors (iron and cobalt acetates) onto the MWNT support. The predetermined amount of metal salts was dissolved in distilled water, and a precalculated amount of MWNTs was added to the solutions during sonication. After 15 min of sonication, the solvent was removed, and the product was dried and crushed carefully in an agate mortar. These samples are labeled I-Co and I-Fe. The nominal compositions of these samples are summarized in Table 1.

The second family of the MWNT-supported metal catalysts was prepared in two steps, with the samples denoted as P-Co and P-Fe. First, the metal nanoparticles were synthesized using the oleate method described previously [24]. In short, this preparation method involves the following steps: Metal chloride is transformed to metal oleate in a reaction with sodium oleate. Metal oleate is decomposed in a high-boiling point solvent such as 1-octadecene. After the metal oxide nanoparticles are separated and redispersed in ethanol, they are deposited onto the MWNT support from the suspension. Cobalt and iron oxide nanoparticles were prepared. The nominal compositions of the samples are given in Table 1.

Table 1
Composition of supported metal oxide catalyst precursor samples

Sample	Precursor metal salt	Amount of metal salt (g)	Amount of MWNT (g)	Nominal metal concentration (w%)
I-Co	Co-acetate	0.422	1.9	5
I-Fe	Fe-acetate	0.311	1.9	5
P-Co	Co-oleate	0.471	1.0	2.5
P-Fe	Fe-oleate	0.447	1.0	2.5