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Co-decorated carbon nanotubes as a promoter of Co–Mo–K oxide catalyst for synthesis of higher alcohols from syngas

Xiao-Man Wu, Yan-Yan Guo, Jin-Mei Zhou, Guo-Dong Lin, Xin Dong, Hong-Bin Zhang *

Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry for Solid Surfaces, Xiamen University, Xiamen 361005, China

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Abstract

A metal cobalt-decorated multi-walled carbon nanotube (MWCNT)-promoted Co–Mo–K oxide-based catalyst was developed, with excellent performance for the selective formation of C_{2-9}-alcohols from syngas. Under reaction condition of 5.0 MPa and 593 K, the space–time-yield of C_{2-9}-alcohols reached 628 mg/(g h) over the $Co_1Mo_1K_{0.05}$–12%(4.2% Co/MWCNT) catalyst. The addition of a minor amount of the Co-decorated MWCNTs into the $Co_1Mo_1K_{0.05}$ host catalyst caused little change in the apparent activation energy for the higher alcohol synthesis (HAS), but led to an increase of surface concentration of the two kinds of catalytically active species, CoO(OH)/Co_3O_4 and Mo^{4+}, both closely associated with the alcohol generation. Addition of 5% CO_2 in the feed gas at properly elevated reaction temperature (593 K) could further enhance the surface concentration of those active Mo and Co species. An excellent adsorption performance of the Co-decorated MWCNTs as promoter for H_2 would be conducive to generating a surface micro-environment with a high concentration of H-adspecies on the functioning catalyst, thus increasing the rate of surface hydrogenation reactions in the HAS. In addition, high concentration of H-adspecies on the catalyst would, through synergistic action with the CO_2 in the feed gas, greatly inhibit the water–gas-shift side-reaction. All these factors contribute to an increase in the yield of alcohols.

Keywords: Co-decorated carbon nanotubes; Co–Mo–K catalyst; Higher alcohol synthesis

1. Introduction

The higher alcohols (C_{2+}-alcohols), together with methanol and dimethyl ether (DME), have been considered as the most important species among coal-based clean synthetic fuels and chemical feedstocks. The higher alcohols have been confirmed to be a better and cleaner automobile fuel. They feature high octane numbers, and lower emissions of NO_x, ozone, CO and aromatic vapors [1]. Recently, use of methyl *tert*-butyl ether (MTBE) has been prohibited in some countries or regions as additive of oil-based fuel due to the new legal requirements in environment protection; this change has greatly renewed interest in hydrogenation of syngas to the C_{2+}-oxygenates as gasoline blends. Higher alcohol syntheses (HAS) on modified methanol catalysts [2,3], modified Fischer–Tropsch catalysts [4,5], alkali-promoted MoS_2 catalysts [6,7] and catalysts containing Mo, Group VIII metals and alkali [8–11], have been extensively studied since 1980s. Progress in this field has considerably contributed to the growing understanding of the nature of those catalytic reaction systems. Nevertheless, the existing technology of HAS is still on a small scale. The single-pass-conversion of the feed syngas and selectivity to C_{2+}-alcohols were both relatively low. Most systems produce methanol (over alkali-promoted MoS_2 catalysts) or hydrocarbons (over modified Fischer–Tropsch catalysts) as the main product instead of C_{2+}-alcohols [12–14]. Development of catalysts with high efficiency and selectivity for C_{2+}-alcohols has been one of the key objectives for research and development efforts.

Multi-walled carbon-nanotubes (MWCNTs) [15], as novel nanocarbon supports or promoters of catalysts, have drawn increasing attention recently [16–18]. The catalytic applications range from selective hydrogenation [19], hydrofomylation [20], ammonia synthesis [21], Fischer–Tropsch synthesis [22], methanol and higher alcohol synthesis [23–25], to selective dehydrogenation [26], selective oxidation [27] and electrocatalysis [28]. The catalytic studies conducted so far on MWCNT-based systems have shown promising results in terms

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* Corresponding author. Tel.: +86 592 2184591; fax: +86 592 2086116.
E-mail address: hbzhang@xmu.edu.cn (H.-B. Zhang).

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of activity and selectivity. From a chemical catalysis point of view, the excellent performance of MWCNTs in adsorption–activation of hydrogen and in promoting spillover of adsorbed H-species is very attractive, in addition to its high-mechanical strength, nanosize channels, sp^2-C constructed surfaces, graphite-like tube-walls and high-thermal/electrical conductivity; modification of some transition-metals to MWCNTs might further improve their performance for adsorbing and activating hydrogen, as well as promoting H-adspecies spillover [29].

In studies of preparation of MWCNT-based functionalized materials, a most straightforward route by melting the elements on MWCNT surfaces was earlier reported by Dujardin et al. [30]. However, research efforts by Ebbesen and coworkers [31] showed that only liquids with low surface tensions could wet MWCNT surfaces. Ang et al. [32] reported a so-called ‘‘two-step sensitization–activation method’’, where the surfaces of oxidized MWCNTs were activated by the introduction of catalytic nuclei, and then the activated MWCNTs catalyze metal deposition specifically onto their surfaces upon immersion in electroless plating baths. However, there might be a small concentration of some heterogeneous metal element such as Sn or Pd remaining in the sensitization–activation process in metal-decorated MWCNTs. Figlarz et al. [33–35] developed a so-called ‘‘polyol method’’ for synthesis of fine metallic powders of Co, Cu, Ni, Pb and Ag, in which the metal precursor(s) are suspended or dissolved in a polyol such as ethylene glycol. The resultant glycol–metal precursor mixture is then heated to reflux and the metallic moieties precipitated out of solution. This can be a viable catalyst-free method for the deposition of fine metallic powders. Metal-decorated MWCNTs could also be prepared by metal vapor deposition. Nevertheless, the dispersion of metal or metal compounds on MWCNTs by chemical means is still largely based on conventional catalyst preparation techniques, such as wet impregnation followed by chemical reduction.

In the present work, several metal cobalt-decorated MWCNTs, abbreviated as *x*% Co/MWCNT (where *x*% represents mass percentage), were prepared by an intermittent microwave irradiation-assisted polyol reduction–deposition method, and characterized through transmission electron microscope (TEM), scanning electron microscope (SEM)/energy dispersive spectrum (EDS), XRD and H_2-TPD (temperature-programmed desorption) measurements. Using the *x*% Co/MWCNT as promoter, we prepared several *x*% Co/MWCNT-promoted Co–Mo–K oxide-based catalysts by the combined co-precipitation and impregnation method. The catalysts displayed higher catalytic activity and selectivity for HAS from syngas, as compared to the MWCNT-free counterpart and to a reference catalyst promoted by the simple MWCNTs.

2. Experimental

2.1. Preparation of MWCNTs

The MWCNTs were prepared from catalytic decomposition of CH_4 by the method reported previously [36]. The prepared MWCNTs were a herringbone-type of multi-walled carbon nanotubes, with the outer diameters of 10–50 nm, inner diameters of 3–7 nm, and N_2-BET surface area of $\sim$140 m^2/g. Such nanotubes were constructed by a superposition of many graphene layer facets, which were tilted at a certain angle with respect to the axis of the central hollow nanofibre, as if a number of cones were placed one on top of the other [37]. The freshly prepared MWCNTs were purified with boiling concentrated nitric acid, followed by rinsing with deionized water, then drying at 383 K under dry N_2 atmosphere. Open-end MWCNTs with hydrophilic surface were thus obtained. In the purified MWCNTs, the contents of the total carbon and the graphitized carbon were $\geq$99.5% and $\geq$90% (mass percentage), as evidenced by elemental analysis and O_2-TPO (temperature-programmed oxidation) measurements, respectively. Tests of H_2-temperature-programmed hydrogenation (TPH) showed that the temperature needed for initiating the hydrogenation reaction of the MWCNTs with H_2 was $\geq$773 K, indicating that this type of MWCNTs was stable in H_2-atmosphere at the reaction temperatures for the HAS [25].

2.2. Preparation of Co-decorated MWCNTs

Each *x*% Co/MWCNT was prepared according to the following procedure in reference to the synthesis parameters used by Kurihara et al. [38]. In brief, 0.66 g of $Co(Ac)_2$ (of AR grade) was put into 50 mL ethylene glycol (of AR grade) in a 100-mL beaker, followed by agitating till the Co precursor salt was completely dissolved. 2.11 g of the purified MWCNTs were put into the above solution under agitating by ultrasonicating. The beaker was placed in the center of a household microwave oven (2450 MHz, 720 W). After microwave-heating for 2 min, the suspending mixture was agitated for 10 s, then put into the microwave oven and heated for 1 min. After another round of the agitating/microwave-heating process, the resulting suspension was filtered. The precipitate was then rinsed several times with deionized water, and finally dried at 373 K. A Co-decorated MWCNTs material was thus obtained. Element analysis showed that the cobalt content in the prepared material was at 4.2% (mass percentage). By changing the loading amounts of MWCNTs and $Co(Ac)_2$, one could prepare a series of *x*% Co/MWCNT with varying Co contents.

2.3. Preparation of Co/MWCNT-promoted Co–Mo–K oxide catalysts

A series of *x*% Co/MWCNT-promoted Co–Mo–K oxide-based catalysts, denoted as $Co_iMo_jK_k$–*y*%(*x*% Co/MWCNT) (where *y*% represented mass percentage), were prepared by the combined co-precipitation and impregnation method. Two aqueous solutions containing calculated amounts of $Co(NO_3)_2\cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (all of AR grade), respectively, were simultaneously added dropwise under vigorous stirring into a Pyrex flask containing a calculated amount of the *x*% Co/MWCNT at constant temperature of 353 K. The addition was adjusted to maintain a constant pH of $\sim$5. The precipitate was continuously stirred for 4 h at 353 K,