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Development of cobalt–copper nanoparticles as catalysts for higher alcohol synthesis from syngas

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ABSTRACT

The synthesis of higher alcohols from syngas has been studied over different types of Cu-based catalysts. In order to provide control over the catalyst composition at the scale of a few nanometers, we have synthesized two sets of Co–Cu nanoparticles with novel structures by wet chemical methods, namely, (a) cobalt core–copper shell (Co@Cu) and (b) cobalt–copper mixed (synthesized by simultaneous reduction of metal precursors) nanoparticles. These catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (TPR). The catalysts were tested for CO hydrogenation at temperatures ranging from 230 °C to 300 °C, 20 bar and 18,000 scc/(hr.gcat). It was observed that the Co–Cu mixed nanoparticles with higher Cu concentration exhibit a greater selectivity towards ethanol and C_{2+} oxygenates. The highest ethanol selectivity achieved was 11.4% with corresponding methane selectivity of 17.2% at 270 °C and 20 bar.

1. Introduction

With today's increasing oil prices and declining fossil fuel resources, there is a need to look for alternative commercially viable energy sources. Bio-based fuel resources, particularly ethanol, have been studied extensively in the recent years as clean, sustainable and transportable fuel alternatives [1]. One promising process for bio-fuel production involves the conversion of bio-derived synthesis gas (syngas) to fuels and oxygenates. Syngas derived from biomass or coal is particularly interesting since both sources are abundant, and biomass is a renewable feedstock [2]. It is well known that syngas conversion to C_{2+} oxygenates is often limited by the formation of methane and methanol. However, C_{2+} alcohols are more desirable products, both as neat fuels [3–5], fuel additives or as a carrier for hydrogen to supply fuel cells. In addition to its potential application as a transportation fuel, ethanol has been considered as a feedstock for the synthesis of variety of chemicals, fuels and polymers [6,7]. It is estimated that ethanol could replace as much as one-third of the domestic petroleum use in the near future [8]. Hence, the development of a suitable and efficient catalyst to produce higher alcohols from syngas, coupled with an understanding of the underlying reaction mechanism, is clearly important.

The general mechanism of C_2 oxygenate formation from syngas has been extensively studied and the main steps are believed to be: (a) dissociative adsorption of CO and H_2, (b) formation of surface hydrocarbon $(CH_x)_{ads}$ and hydroxyl $(OH)_{ads}$ species and (c) CO insertion to form the C–C bond [9]. Ethanol formation is favored by a catalyst that selectively promotes the CO insertion reaction instead of the hydrogenation of the $(CH_x)_{ads}$ surface species, since hydrogenation of $(CH_x)_{ads}$ species leads to hydrocarbon formation [10].

The catalysts that have been studied for this reaction include Rh-based catalysts and alkali-promoted Cu-based catalysts [10]. Rh-based catalysts have been found, so far, to be the most selective catalysts for the synthesis of higher alcohols from CO hydrogenation [10]. The activity and selectivity of C_2^+ oxygenate synthesis on Rh catalysts has been attributed to their ability to catalyze both CO dissociation and CO insertion [11]. However, CO dissociation on surfaces such as fcc Rh(1 1 1) is almost impossible or very slow and the presence of steps/kinks are necessary to enhance the CO dissociation rate [12]. This is in agreement with the catalytic behavior of Rh in CO hydrogenation since it has been suggested that metals which adsorb CO strong enough to activate the molecule but do not dissociate it readily are active catalysts for the formation of oxygenates [13]. However, the high cost and limited availability of the precious Rh metal catalysts [14] have led to the

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development of base metal catalysts such as modified Cu-based catalysts for this application. The advantage of having mixed metals (either alloy, core–shell or physical mixture) is that they can be used to prepare catalysts with different metal-promoter morphologies and to control atomic-level interactions. This may lead to further improvement in the selectivity to desired products.

The study of catalysis with nanoparticle surfaces is growing rapidly. Nanometer-sized metal/alloy particles are receiving great attention in modern chemical research because of their unique properties that are different from the corresponding bulk materials [15]. These unique properties affect the electronic, magnetic, optical and chemical properties which are applicable in such diverse fields as photochemistry, electrochemistry, optics, and catalysis [15]. The origin of their intriguing behavior is attributed to high surface-to-volume ratios which lead to large fractions of metal atoms available at the surface for catalysis [16].

Cobalt nanoparticles are expected to possess excellent magnetic, hardness and impact resistance properties. Recently cobalt nanoparticles have been used as catalysts as well [16]. Surfactants play a vital role in controlling the particle size and shape of nanoparticles synthesized using wet-chemical methods. De Silva et al. [17] have reported that the surfactants influence the reaction pathways, prior to nucleation, leading to the formation of cobalt nanoparticles. However, the surfactants required during the synthesis are retained on the surfaces and thus may also lead to loss of catalytic activity. Recently, bimetallic/core–shell nanoparticles are also receiving much attention since they offer high surface area coupled with the ability to provide multiple surfaces for catalysis providing added efficiency [18]. These nanostructured bimetallic materials are of economic interest as well since precious materials can be deposited on inexpensive cores [18].

Generally, a catalyst active for higher oxygenate synthesis must contain both adsorbed molecular CO, and surface carbon species produced by dissociative adsorption of CO. So the catalyst must be able to dissociate only a portion of the CO molecules and must balance this with the hydrogenation of the intermediate to form alcohols. Hydrogenation of the $(CH_x)_{ads}$ intermediate produces undesirable methane [10]. Keeping this in mind, we choose the combination of Co and Cu for this study due to the following reasons [19]:

(a) Co—dissociates CO and hydrogenates the resulting surface carbon species into hydrocarbons, e.g., in F-T synthesis [19].
(b) Cu—assists in non-dissociative activation of CO, e.g., in methanol synthesis [19].

Thus a combination of Co and Cu might be expected to adsorb molecular CO on the Cu, which can then react preferentially with the carbon chains generated on the Co, thereby leading to higher alcohols.

We are aware of no literature reports that use Co–Cu bimetallic nanoparticles as catalysts for CO hydrogenation reaction. Herein, we report the synthesis, characterization and catalytic activity of Co–Cu nanoparticles in the conversion of syngas to higher alcohols. A series of cobalt–copper nanoparticles were synthesized by wet chemical methods to achieve either core–shell nanoparticles or mixed nanoparticles and then tested for CO hydrogenation reaction in a fixed bed microreactor system. The focus of the present research is to investigate the Co–Cu nanoparticle catalysts for the synthesis of C_{2+} oxygenates from syngas via CO hydrogenation and the impact of reaction temperature on their activity and selectivity.

2. Experimental

All the catalyst syntheses were carried out under inert atmospheric conditions using commercially available reagents. Cobalt chloride, dodecyl-N,N-dimethy-3-ammonio-1-propanesulfonate (sulfobetaine SB-12, 98%), tetrahydrofuran (THF), sodium borohydride, 1 M lithium hydrotriethylborate in THF, copper sulfate and sodium citrate hexahydrate were purchased from Aldrich Chemical Company and were used without further purification. Commercial cobalt nanoparticles, dispersed in toluene, were purchased from Strem chemicals. All the solvents used were degassed prior to use.

2.1. Synthesis of Co@Cu core–shell nanoparticles

2.1.1. Synthesis of cobalt (core) nanoparticles

Two sets of Co core nanoparticles were used—Co nanoparticles that were (1) commercially purchased from Strem chemicals (dispersed in toluene) and (2) chemically synthesized using water as the solvent and SB-12 as surfactant [18]. A mixture of cobalt chloride and SB-12 was placed in a three-necked flask which was evacuated and then filled with nitrogen three times. Degassed water was added to the flask under sonication and the contents were dissolved. Sodium borohydride was dissolved in water separately and this solution was added drop wise into the earlier $CoCl_2$ mixture over a period of 30 min. The pale pink solution turned black immediately upon addition, indicating the formation of cobalt nanoparticles. After the addition is complete, the reactants were stirred for an additional hour to ensure completion of the reaction, followed by the addition of 15 ml of acetone to destroy the excess reducing agent. The resulting cobalt nanoparticles were separated, washed thoroughly with degassed water followed by ethanol, and dried to obtain a fine powder.

2.1.2. Displacement formation of copper shell

The procedure as described by Guo et al. [18] was used to develop a shell around the two sets of cobalt nanoparticles. In a typical process, cobalt nanoparticles were added to a copper–citrate electrolyte, containing 0.25 M $CuSO_4·5H_2O$ and 0.3 M $C_6H_5Na_3O_7·2H_2O$ at a pH of 4.0. The reactants were sonicated for an hour under nitrogen environment. Fig. 1 illustrates this synthesis procedure. The particles were then separated using a magnet and washed thoroughly with degassed water followed by ethanol, then dried to obtain a fine powder. The final core–shell catalyst obtained from the commercial cobalt nanoparticles is designated as Co@Cu-1 and the one from water dispersible cobalt nanoparticles, synthesized in our lab using water as solvent, is designated as Co@Cu-2 in this paper.

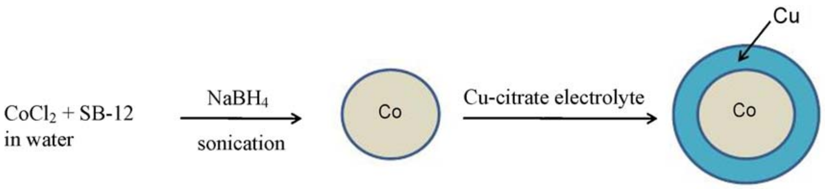

Fig. 1. Illustration of the synthesis of Co core @ Cu shell nanoparticles.