



## Structure and catalytic performance of alumina-supported copper–cobalt catalysts for carbon monoxide hydrogenation

Jingjuan Wang<sup>a,b</sup>, Petr A. Chernavskii<sup>c</sup>, Andrei Y. Khodakov<sup>b,\*</sup>, Ye Wang<sup>a</sup>

<sup>a</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

<sup>b</sup> Unité de Catalyse et de Chimie du Solide, UMR 8181 CNRS, Bât. C3, USTL-ENSCL-EC Lille, Cité Scientifique, 59655 Villeneuve d'Ascq, France

<sup>c</sup> Department of Chemistry, Moscow State University, 119992 Moscow, Russia

### ARTICLE INFO

#### Article history:

Received 2 May 2011

Revised 11 October 2011

Accepted 16 October 2011

Available online 20 November 2011

#### Keywords:

Co–Cu catalysts

Higher alcohols synthesis

Syngas conversion

*In situ* characterization

### ABSTRACT

The structure of alumina-supported copper–cobalt catalysts prepared by incipient co-impregnation was studied by using a combination of various characterization techniques including *in situ* XRD, XPS, TPR, XANES/EXAFS, *in situ* magnetic method, and TEM. The results suggest a much higher dispersion of copper than cobalt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and a stronger interaction between cobalt and copper oxide particles, leading to the formation of mixed copper–cobalt oxides in the calcined catalysts. Cobalt reduction was significantly enhanced in the presence of copper. Furthermore, our characterizations indicate the formation of bimetallic Cu–Co particles in the reduced catalysts and enrichment of the surface of bimetallic particles with Cu. The catalytic studies showed dramatic modifications of both the rate and selectivity in the hydrogenation of CO after addition of even small amounts of Cu to supported Co catalysts. The presence of Cu increased the selectivity to alcohols by an order of magnitude and decreased the overall carbon monoxide conversion. Structure–performance correlations suggest that the Cu–Co bimetallic particles may be involved in higher alcohol synthesis.

© 2011 Elsevier Inc. All rights reserved.

### 1. Introduction

The catalytic conversion of syngas derived from natural gas, coal, and biomass to valuable long-chain hydrocarbons and alcohols is one of the challenging and attractive subjects in the field of C1 chemistry [1–3]. The hydrocarbons and alcohols obtained from this process can be used as fuels, fuel additives for octane or cetane enhancement, and intermediates for value-added chemicals such as medicine, cosmetics, and polyester. The major challenge of carbon monoxide hydrogenation is the efficient control of the reaction selectivity to olefins, long-chain paraffins, or oxygenated products. Cobalt catalysts are the catalysts of choice for synthesis of long-chain paraffins using Fischer–Tropsch reaction, while copper-containing catalysts are selective in methanol synthesis from syngas. Both cobalt and copper catalysts are currently used in relevant large-scale industrial processes. It could be therefore expected that mixed copper–cobalt catalysts would have higher selectivity to C2+ alcohols.

It is known that the promotion of cobalt catalysts with different metals could lead to higher Fischer–Tropsch reaction rates and could also affect selectivity. The modifications of catalyst structure

and catalytic performance that are due to the promotion with the noble metals (Ru, Pt, Re, Pd) have been addressed in several reports [4–7]. The amount of promoting noble metal is usually very low, because of higher prices and rarity of these metals and sometimes their detrimental effects on the selectivity to long-chain hydrocarbons (e.g., Pt [4]). Recently, it was found [8,9] that addition of small amounts of Mn can enhance selectivity to higher hydrocarbons in Fischer–Tropsch synthesis. Promotion with Mn of carbon nanofibres and silica-supported catalysts resulted in higher C5+ selectivity that was accompanied with some smaller decrease in carbon monoxide conversion rate. The observed increase in C5+-selectivity for higher MnO loadings was attributed to the increase in the CH<sub>x</sub> coverage measured from SSITKA experiments [9].

Several attempts have been made in the past to design a viable industrial process for synthesis of higher alcohols from H<sub>2</sub>/CO/CO<sub>2</sub> mixtures (e.g., isobutanol synthesis, Synol process [10]). All these attempts, however, have not resulted in any major industrial manufacturing. The major difficulties include catalyst deactivation, low alcohol productivity, insufficient selectivity, and very complex mixture of reaction products [11,12].

Catalytic systems based on rhodium, copper–zinc, molybdenum oxide, sulfide-based catalysts, and copper–cobalt precipitated catalysts have been investigated for higher alcohol synthesis [1,2,11]. Rhodium-based catalysts have shown so far the best selectivity for

\* Corresponding author.

E-mail address: [andrei.khodakov@univ-lille1.fr](mailto:andrei.khodakov@univ-lille1.fr) (A.Y. Khodakov).

higher alcohol synthesis [1,13–17]. However, the limited availability and high price of rhodium restrict industrial application of these catalysts. Several recent reviews have addressed modified copper–zinc methanol synthesis catalysts and molybdenum-based catalysts for the higher alcohol synthesis [1–3].

It is expected that the efficient control of selectivity either to hydrocarbons or to oxygenates may be achieved by using supported bimetallic cobalt–copper catalysts. The copper–cobalt catalysts for higher alcohol synthesis were first designed in 1970s in the IFP [18]. A large number of patent applications and papers, which focused on promoted Co–Cu-based catalysts for higher alcohol synthesis from syngas, appeared afterward [1,19–23]. The catalysts were typically prepared by either coprecipitation of metal nitrates with alkali carbonates or by pyrolysis, in which an organic acid, such as citric acid [24], was added to the mixture of metal nitrates before calcination [25]. Most of the catalyst preparation details have not been, however, disclosed in the open literature. In addition, several authors [26,27] have reported difficult reproducibility of the synthesis of copper–cobalt catalysts via coprecipitation or pyrolysis. Indeed, all preparation steps in the catalyst syntheses should be controlled with a great efficiency to obtain high and reproducible alcohol productivities.

Two major concepts about the nature of the active sites in copper–cobalt catalysts for higher alcohol synthesis have been developed. First, it has been suggested that the formation of higher alcohols may involve CuCo bimetallic sites [18,28,29]. Second, the formation of alcohols has been attributed to a synergy between metallic copper and partially reduced cobalt species [30–33]. To provide further insights into the active sites for alcohol synthesis, Subramanian et al. [34] investigated unsupported Cu–Co mixed nanoparticle model catalysts for alcohol synthesis from syngas and found that the Cu–Co mixed nanoparticles were more selective to ethanol than core–shell structured counterparts containing Co-core and Cu-shell. Though unsupported nanoparticles seem to be a good model system to study the active sites and mechanisms of carbon monoxide hydrogenation, the catalyst handling (e.g., pyrophoricity) and catalyst stability are problematic for long-term and large-scale operations. Insufficient stability is also one of the major problems relevant to the industrial use of the precipitated copper–cobalt catalysts [35].

It has been demonstrated recently that porous structure of the support may efficiently control the metal dispersion [36–39]. In the catalysts supported by porous oxides, the sizes of metal particles are typically limited by pore sizes of the support [39,40]. In contrast to the catalysts prepared by coprecipitation, in supported catalysts, the support texture may prevent sintering of metal particles [39,40] or limit sintering to the maximum pore diameter [41,42]. The support (e.g., alumina) can also strengthen the mechanical stability of a catalyst, which is particularly important for fluidized bed and slurry bubble column applications. However, it can be expected that the interactions between copper and cobalt might be different in the supported catalysts compared to the catalysts prepared by coprecipitation, which may lead to different structure of active phases and different catalytic performances.

In this paper, a series of alumina-supported Cu–Co catalysts are prepared by incipient wetness impregnation and are characterized by a wide range of spectroscopic techniques. Higher copper contents are used in this work in contrast to the cobalt catalysts promoted with noble metals. The catalytic performances of the promoted catalysts in carbon monoxide hydrogenation are examined in a fixed bed microreactor. The correlations between the catalyst structure and catalytic performance are discussed to gain insights into the probable active sites for the hydrogenation of carbon monoxide over the bimetallic catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

Commercial  $\gamma$ - $\text{Al}_2\text{O}_3$  (Puralox SCCA 5/170 from Sasol, Germany) with BET surface areas of  $\sim 165 \text{ m}^2 \text{ g}^{-1}$ , pore volume of  $0.47 \text{ cm}^3 \text{ g}^{-1}$ , and pore diameter of 8 nm was used as support. The monometallic and bimetallic Cu–Co catalysts were prepared by incipient wetness co-impregnation of  $\gamma$ - $\text{Al}_2\text{O}_3$  using aqueous solutions of cobalt nitrate or copper nitrate. Co-impregnation was used instead of sequential impregnation, because it might provide better alcohol yields [43]. Aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and/or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was added dropwise into dry alumina powder with continuous stirring; the samples were aged at room temperature for about 4 h. The catalysts with 20 wt.% metal content were prepared by 2-step incipient wetness impregnation. Between and after the impregnations, the catalysts were calcined in air at 373 K for 2 h and at 623 K for 5 h (heating rate of  $1 \text{ K min}^{-1}$ ). The catalysts were labeled as  $x\text{Cu}y\text{Co}/\text{Al}_2\text{O}_3$ , where  $x$  and  $y$  stand for copper and cobalt weight contents.

### 2.2. Catalyst characterization

The X-ray powder diffraction (XRD) experiments were performed using a Siemens D5000 diffractometer using Cu  $K\alpha$  radiation for crystalline phase detection. The average sizes of cobalt and copper oxide crystallites were calculated using the  $\text{Co}_3\text{O}_4$  (311) diffraction peak at  $2\theta = 36.96^\circ$  and CuO (111) diffraction peak at  $2\theta = 35.5^\circ$ , respectively, according to the Scherrer equation [44]. The *in situ* XRD patterns were measured during catalyst reduction in hydrogen (3%  $\text{H}_2$  in Ar). The experiments were conducted by passing pure  $\text{H}_2$  through the catalyst while increasing the temperature at a linear rate.

The *ex situ* X-ray absorption spectra at both Co and Cu absorption K edges (7709 and 8.979 eV, respectively) were measured at SNBL BM01B beam line, ESRF, France. The X-ray absorption measurements were performed in transmission mode; two ionization chambers were used for X-ray detection. The Si (111) channel cut monochromator was calibrated by setting the first inflection point of K-edge spectrum of Co and Cu foils. The X-ray absorption data were analyzed using the conventional procedure using ATHENA package [45]. The XANES spectra after background correction were normalized by the edge height. After subtracting the metal atomic absorption, the  $k^2$ -weighted EXAFS signal was transformed without phase correction from  $k$  space to  $r$  space. Crystalline  $\text{Co}_3\text{O}_4$ , CuO, and  $\text{Cu}_2\text{O}$  were used as reference compounds for XANES and EXAFS analysis.

The reducibility of the catalysts was studied by temperature-programmed reduction (TPR). The TPR was carried out by AutoChem II 2920 apparatus from Micromeritics using 0.05 g of the sample in 5 vol.%  $\text{H}_2/\text{Ar}$  stream ( $50 \text{ cm}^3 \text{ min}^{-1}$ ). The temperature was increased from room temperature to 1173 K at a rate of  $3 \text{ K min}^{-1}$ .

Surface analyses were performed using a VG ESCALAB 220XL X-ray photoelectron spectrometer (XPS) equipped with Al  $K\alpha$  (1486.6 eV) non-monochromatized source that was used for excitation with a 300 W-applied power. The analyzer was operated in a constant pass energy mode ( $E_{\text{pass}} = 40 \text{ eV}$ ). Binding energies were referenced to the  $\text{Al}_{2p}$  core level (74.6 eV) of the support. The vacuum level during experiments was better than  $10^{-7} \text{ Pa}$ . The powdered catalyst was pressed as a thin pellet onto a steel block. The reproducibility was 0.2 eV for the  $\text{Co}2p$  binding energy. The *in situ* reduction was carried out in pure hydrogen at 673 K in the reactor cell of the preparation chamber attached to the analysis chamber of the spectrometer. Then, the reduced sample was trans-

Download English Version:

<https://daneshyari.com/en/article/6528178>

Download Persian Version:

<https://daneshyari.com/article/6528178>

[Daneshyari.com](https://daneshyari.com)