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Bi-metal Cu–Co from $LaCo_{1-x}Cu_xO_3$ perovskite supported on zirconia for the synthesis of higher alcohols

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ABSTRACT

A new scheme for designing and preparing the catalyst for higher alcohol synthesis was presented in this work. According to the scheme, a series of zirconia-supported $LaCo_{1-x}Cu_xO_3$ catalysts were prepared by impregnating ZrO_2 with a mixed solution composed of ions of copper, cobalt and lanthanum and citric acid. The catalysts were characterized by using XRD, TEM, BET, H_2-TPR and XPS techniques. After reduction, the catalyst precursor favored to form nanoparticles of Co–Cu alloy highly dispersed on ZrO_2 and modified with La_2O_3. The metal nanoparticles of Cu–Co alloy together with ZrO_2 modified with La_2O_3 contributed to the excellent selectivity of higher alcohols as well as the very good stability.

1. Introduction

Higher alcohols, which refer to the alcohols with carbon atoms in a molecule higher than methanol, can be used as fuels, gasoline additives, chemicals and chemical raw materials [1–4]. Currently, the catalysts reported for higher alcohol synthesis (HAS) include mainly four types, which are modified methanol catalysts, Mo-based catalysts, Cu-modified Fischer–Tropsch (F–T) catalysts and Rh-based catalysts. Modified methanol catalysts are active and preferentially selective for the formation of methanol and isobutanol. As promoted with alkali, the selectivity for higher alcohols can be improved [5]. The Mo-based catalysts contain molybdenum sulfide and molybdenum carbide-based catalysts and show good selectivity towards C_1–C_5 straight chain alcohols, but the side reactions towards hydrocarbons especially CH_4 prevail at the same time, which have a negative effect on the alcohol productivity [6]. By the way, sulfur element may be brought into the alcohols as a contaminant. Rh-based catalysts have shown relatively high selectivity for the synthesis of C_{2+} oxygenates. However, the limited availability and the high cost restrict their application to industrial application [7,8].

Among the four types of the catalysts, Cu-modified FT catalysts are considered to be one of the most promising catalyst systems owing to its higher activity and higher C_{2+} alcohol selectivity [1,4]. However, the selectivities to methanol and methane are still too high for commercialization [9–12]. Bimetallic catalysts have been used in some reactions to balance the selectivity and activity [13]. For the synthesis of higher alcohols, it is accepted that the formation of Cu–Co bimetallic sites which favors the synergy between metallic copper and cobalt is really important [14,15]. On copper sites methanol is formed via CO hydrogenation, and on Co sites the bond of C – O can be broken while the bond of C – C can be formed. Thus, higher alcohols can be generated under the synergy of Cu and Co sites. On the other side, methanol is produced on Cu sites and CH_4 and other hydrocarbons are produced on Co sites. This suggests that the synergy between Cu and Co is critical [15,16]. So how to improve the distribution of copper and cobalt species to make them in interaction or to form alloy is the focus [17,18].

Tien-Thao and coworkers prepared $Cu_2O/LaCoO_3$ and $LaCo_{1-x}Cu_xO_3$ by a mechano-synthesis process known as reactive grinding, and studied their catalytic performance for HAS, and found that the copper outside the perovskite lattice favors the production of methanol and methane, while the copper in the perovskite lattice is advantageous to C_{2+} alcohol generation. In addition, the existence of strong cobalt–copper interaction in perovskites can enhance the metallic dispersion of cobalt and copper. After reduction of $LaCo_{1-x}Cu_xO_3$, nano-particles of copper and cobalt alloy supported on La_2O_3 was formed, which contributed to the good performance for HAS [10,19,20].

In our early study, Cu@–Co and Cu–Co alloy nanoparticles supported on a perovskite-type oxide of $LaFeO_3$ have been obtained by reducing $Co_3O_4/LaFe_{0.7}Cu_{0.3}O_3$. During the reaction, Cu–Co nano-particles generated copper-modified Co_2C species under the promotion of La_2O_3 which

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Table 1
BET surface areas and the mean particle size of $LaCo_{1-x}Cu_xO_3$.

Sample	S_{BET} ($m^2\ g^{-1}$)	$D_{perovskite}$ (nm)[a]
ZrO_2	92.2	
$LaCoO_3/ZrO_2$	61.2	12.3
$LaCo_{0.9}Cu_{0.1}O_3/ZrO_2$	59.5	13.1
$LaCo_{0.8}Cu_{0.2}O_3/ZrO_2$	56.9	13.1
$LaCo_{0.7}Cu_{0.3}O_3/ZrO_2$	58.8	14.3

[a] Calculated from XRD results with Scherrer formula: $D = k\lambda/(\beta\cos\theta)$.

were highly dispersed on the $LaFeO_3$ surface, the resultant catalyst is highly active and selective for HAS [21]. However, there is a defect for this preparation method, that is, whatever using La_2O_3 or $LaFeO_3$ as the catalyst support, the content of catalyst support is limited, leading to a small surface area of the support, and hence sintering of Cu–Co active species is inevitable.

An effective way of improving the dispersion of a catalyst is to load it on a support which has a high specific surface area. For example, it was reported that zirconium oxide can be used as the support for $LaCoO_3$, $LaFeO_3$ and $LaMnO_3$ by using impregnation method, applied to the reactions of oxidative reforming of diesel, CO oxidation and catalytic combustion of methane, respectively [22–24].

As a support for HAS catalysts, zirconia has shown a relatively better selectivity to higher alcohols compared with other supports according to literatures [25,26]. It was reported that ZrO_2 with a tetragonal crystal phase showed high selectivity towards ethanol, while the ZrO_2 with a monoclinic crystal phase exhibited high selectivity towards isobutanol [27]. For supporting bimetallic Cu–Co on ZrO_2, the reported methods include co-precipitation and ordinary impregnation [25,28], while the method by loading zirconia with perovskite-type oxides as the precursor of the bimetallic Cu–Co has not been reported up to now.

In this work, $LaCo_{1-x}Cu_xO_3$ was loaded on ZrO_2 and used as the catalyst precursor for HAS under the consideration listed as follows. (1) A crystalline of $LaCo_{1-x}Cu_xO_3$ likes a much large molecule in which the elements are uniformly dispersed at the atomic level including copper and cobalt. As a result, after reduction copper and cobalt tend to be in interaction or forming alloy. Similarly, as another result, La_2O_3 can also act as a promoter for HAS. (2) The support of ZrO_2 can possess a high specific surface area. (3) ZrO_2 is a promising support for Cu–Co for HAS and can be stabilized by La_2O_3.

2. Experimental

2.1. Catalyst preparation

ZrO_2 support was prepared according to the precipitation method as reported in the literature [29]. The aqueous solution of 0.3 M $ZrOCl_2$ was added to a 0.3 M NH_4OH solution at pH = 9–10 under stirring at a drop speed of 1 mL min^{-1}. The hydrous zirconia, after staying in its mother solution for 24 h, was filtered, washed with deionized water until no Cl^- could be detected by using the $AgNO_3$ test, then washed with ethanol, dried overnight at 110 °C and finally calcined at 700 °C for 5 h.

The loading of $LaCo_{1-x}Cu_xO_3$ on the ZrO_2 support was performed according to the citrate complexing method, for details see [30]. The support of ZrO_2 was impregnated with the aqueous solution of lanthanum, cobalt and copper nitrate at a La/Co/Cu molar ratio of 1:1 − x:x, in which citric acid in 120% mol of the total cations and glycol in 20% molar amount of the citrate acid were added. After staying overnight, the resulting sample was dried at 120 °C for 24 h and subsequently calcined at 300 °C and 700 °C for 2 h and 5 h, respectively, at a heating rate of 2 °C min^{-1}. Then the loading process above was repeated in order to obtain a higher $LaCo_{1-x}Cu_xO_3$ loading amount. The amount of $LaCo_{1-x}Cu_xO_3$ in the calcined sample is 16 wt.%. Four samples at a Co/Cu molar ratio of 1 − x:x (x = 0, 0.1, 0.2, 0.3) were prepared. For comparison, unsupported $LaCo_{0.7}Cu_{0.3}O_3$ was prepared according to the citrate method.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8-Focus X-ray diffractometer with Ni-filtered Cu K_α radiation (λ = 0.15406 nm). The spectra were obtained between the 2θ range of 20° to 52.5° at a scanning speed of 5° min^{-1}. The Scherrer equation was used to calculate the crystal size of the perovskite particles from the X-ray patterns.

Specific surface areas of the catalysts were evaluated by N_2 adsorption according to the BET method using a Quantachrome QuadraSorb SI instrument. The samples were pretreated in vacuum at 300 °C for 4 h before experiments.

Transmission electron microscopy (TEM) experiments were conducted on a JEOL JEM-2100F microscope field-emission scanning electron microscope. After ultrasonic dispersion of the catalysts in

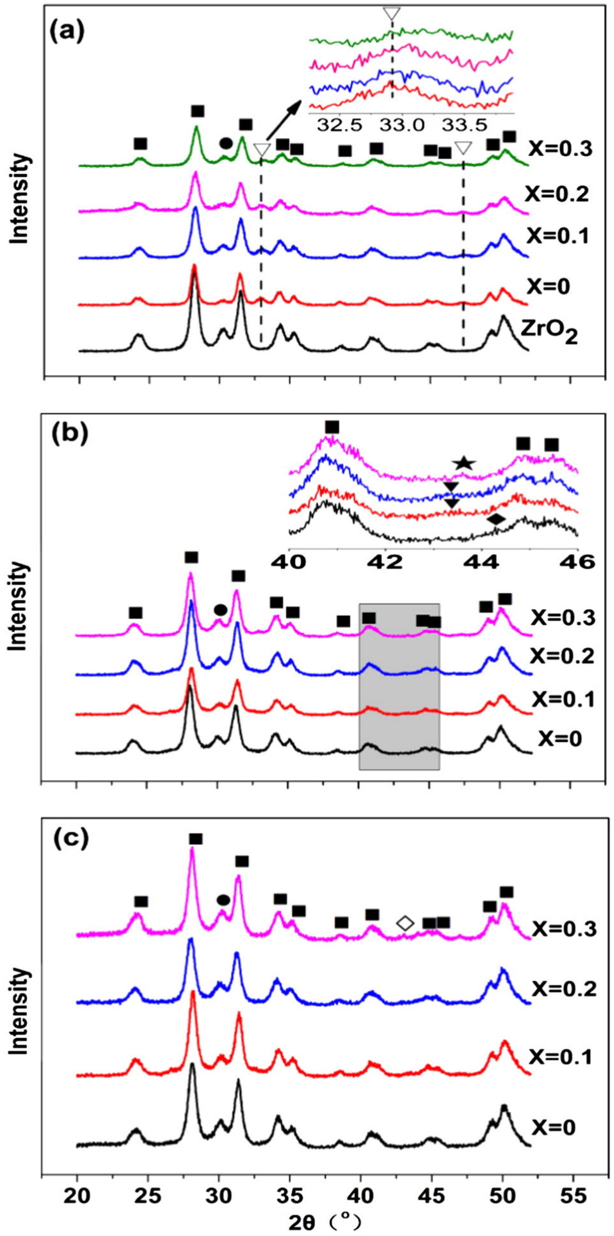

Fig. 1. XRD patterns of $LaCo_{1-x}Cu_xO_3/ZrO_2$ (a) the fresh catalysts; (b) catalysts after reduction at 650 °C for 3 h with H_2 flow rate of 30 mL min^{-1}; (c) catalysts after reaction at GHSV of 3900 h^{-1}, in temperature range of 280–350 °C, in the syngas mixture of $H_2/CO/N_2$ = 8/4/1 and at 3 MPa for 13.5 h. (■) m-ZrO_2; (●) t-ZrO_2; (▽) $LaCo_{1-x}Cu_xO_3$; (★) $Co_{0.52}Cu_{0.48}$; (▼) Cu; (◆) Co; (◇) Co_2C.