Short communication

Effect of the dimensions of carbon nanotube channels on copper–cobalt–cerium catalysts for higher alcohols synthesis

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ABSTRACT

A series of carbon nanotube (CNT)-supported copper–cobalt–cerium catalysts were prepared and investigated for higher alcohols synthesis. The superior selectivity for the formation of ethanol and C_{2+} alcohols achieved using the CuCoCe/CNT(8) catalyst was 39.0% and 67.9%, respectively. The diameters of CNTs considerably influence the distribution of metal particles and the electronic interaction between the tube surface and the active species. The electronic effect between the encapsulated Co species and the inner surface is greatly improved in the narrowest CNT channel, which is expected to facilitate the reduction of cobaltous oxide and promote the alcohols yield remarkably (291.9 mg/g_{cat}h).

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1. Introduction

Higher alcohols synthesis (HAS) from hydrogenation of carbon monoxide has attracted significant interest because of its potential application as a promising route for the production of fuel blends and hydrogen energy carriers or as value-added chemicals in fine chemical synthesis [1,2]. Typically, modified FT catalysts (e.g., Cu–Co) are regarded as one of the most promising candidates for HAS [3–6]. However, these catalytic systems produce a wide distribution of C_1–C_6 linear alcohols, which obeys the Anderson–Schulz–Flory (ASF) distribution, thus leading to the formation of methanol as the major product among the alcohols formed [7–9]. Therefore, development of catalysts with high efficiency and selectivity for the short chain alcohols (especially for ethanol) are highly desirable and challenging.

To narrow the alcohols distribution and improve the selectivity for short chain alcohols, a suitable promoter and support are necessary. Ceria exhibits interesting redox properties, and it has been reported that partially reduced CeO_2 is expected to create new sites for the adsorption of CO, thereby favoring the breaking of the C–O bond [10]. In particular, the Co–CeO_{2-x} interface could be beneficial for the formation of alcohols in FT reactions [11,12]. Therefore, cerium is chosen as the third component in the proposed Cu–Co–Ce catalyst. Carbon nanotubes (CNTs) have been drawing increasing attention since their discovery [13]. The confinement effects in catalysis have been systematically researched. Previous studies concluded that space restriction [14],

enrichment of reactants inside CNTs [15], and electronic interaction of the confined materials with CNTs [16] can be achieved. Furthermore, the properties of the active components can be tuned by varying the location on the exterior or interior surface of the CNTs, and the diameter of the CNT channels. To date, there are no reports and research on the influence of the diameters of CNTs on Cu–Co systems employed for HAS. Thus, CuCoCe/CNT catalysts with different CNT channel sizes were prepared and investigated, and the catalytic performance of the catalysts toward CO hydrogenation was examined in both a fixed bed and a slurry reactor.

2. Experimental

2.1. Materials

Analytical grade chemicals, including $Cu(NO_3)_2 \cdot 3H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Ce(NO_3)_3 \cdot 6H_2O$, were purchased from the Beijing Chemical Co., Ltd., and used without further purification. Three types of CNTs were used: CNT(8) (o.d.: <8 nm), CNT(20) (o.d.: 10–20 nm), CNT(30) (o.d.: 20–30 nm); they were purchased from Chengdu Organic Chemicals. HRTEM analysis shown that the average inner diameter of CNT(8), CNT(20) and CNT(30) was around 3.9, 6.3 and 7.4 nm respectively. The wall thickness of them was in range of 1.5–3 nm, 3–7 nm and 7–12 nm respectively. Raw CNTs were refluxed in 68 wt.% HNO_3 for 14 h at 140 °C in an oil bath to purify and cut the carbon tubes; in contrast, CNTs with closed caps were obtained by refluxing CNTs in 37 wt.% HNO_3 for 5 h at 100 °C. Then, the mixture was filtered and washed with deionized water, followed by drying at 60 °C for 12 h.

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Table 1
Catalytic performances of CuCoCe/CNT catalysts in carbon monoxide hydrogenation.

Samples	Reactor	CO conv.(%)	Total alc. STY (mg/g$_{cat}$h)	Carbon selectivity (C mol%)				Alcohol distribution (C mol%)				
				CH$_4$	C$_2$–C$_4$	ROH	CO$_2$	MeOH	EtOH	PrOH	BuOH	C$_5$OH
CuCoCe-out-CNT(8)	Fixed bed	17.6	191.7	28.3	39.3	29.7	2.7	43.6	32.6	15.1	7.3	1.4
CuCoCe/CNT(8)	Fixed bed	28.3	291.9	27.6	34.3	34.5	2.7	37.3	34.8	18.2	8.3	1.5
	Slurry reactor	26.1	272.6	22.5	34.1	38.8	4.5	32.1	39.0	18.0	9.0	1.9
CuCoCe/CNT(20)	Fixed bed	19.1	190.1	31.9	34.8	27.3	4.1	44.0	30.7	15.1	8.6	1.5
CuCoCe/CNT(30)	Fixed bed	18.0	185.0	33.0	33.7	26.6	5.2	48.3	25.5	16.3	8.0	2.0

Reaction conditions: 300 °C, 4.5 Mpa, 10,000 mL/g$_{cat}$h, 2:1 H$_2$: CO syngas ratio, TOS: 7 h for fixed bed, 12 h for slurry reactor.

2.2. Synthesis of Cu/Co/Ce-based catalysts

The CNTs were immersed in an ethanolic solution of precursor salts of Cu, Co, and Ce, and then subjected to ultrasonic treatment and stirring. The ultrasonic treatment and stirring facilitated the filling of the CNT channels with the precursor solution during impregnation. After 10 h of impregnation, the mixture was dried at 60 °C overnight, followed by heating to 110 °C for 10 h. After drying, the products were calcined in N$_2$ at 673 K for 4 h with a heating rate of 2 K/min. A series of catalysts were accordingly prepared using this method, i.e., CuCoCe/CNT(8), CuCoCe/CNT(20), CuCoCe/CNT(30), and the active components supported on CNT(8) with closed caps were denoted as CuCoCe-out-CNT(8). The loading of Cu, Co, and Ce was controlled at 10, 5, and 5 wt.% respectively.

2.3. Characterization

Powder X-ray diffraction patterns (XRD) were recorded on a Rigaku MiniFlex II X-ray diffractometer. H$_2$-temperature-programmed reduction mass spectrometry analysis (H$_2$-TPR-MS) was carried out to study reducibility of the catalysts with chemisorption instrument (TP-5080) and OmniStar instrument. X-ray photoelectron spectroscopy (XPS) was used to analyze the change of surface composition measured by AXIS ULTRA DLD equipment. The morphology and microstructure of the materials were observed on a high resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F).

2.4. Catalysis studies

Carbon monoxide hydrogenation reactions were performed both in a fixed bed stainless steel tubular microreactor (15.5 mm in diameter, 500 mm in length) and in a 0.5 L continuous slurry reactor with a mechanical agitator. The 30–40 mesh silica sand (SiO$_2$) was used to dilute the 1.5 g catalyst particles in the fixed bed. The liquid paraffin with the distill-off temperature at 340 °C was used as solvent in the slurry reactor. The reactions were run at temperature 573 K and pressure 4.5 MPa, using a feed gas of 2:1 H$_2$ and CO mixture at a space velocity of 10,000 mL/g$_{cat}$h. Catalysts were reduced with a 10% hydrogen-in-nitrogen mixture for 3 h at 673 K in the fixed bed or in a tube furnace. All experimental data were obtained under steady-state conditions that were invariably maintained for 7 h, and no deactivation was observed in 24 h. The products were analyzed by four online GCs during the reaction.

3. Results and discussion

3.1. The evaluation of the catalytic performance

The catalytic performance of CuCoCe/CNT(8) was studied and compared with that of CuCoCe/CNT(20), CuCoCe/CNT(30), and CuCoCe-out-CNT(8). The data are presented in Table 1. As observed, the total alcohols and ethanol selectivity gradually increased upon decreasing CNT channel diameter. However, CuCoCe/CNT(30) and CuCoCe/CNT(20)

displayed comparable space-time yield (STY). In contrast, CuCoCe/CNT(8) exhibited a much larger space-time yield (291.9 mg/g$_{cat}$h), and the C$_{2+}$ alcohols selectivity reached ~62.7%, which is considerably higher than that achieved over CuCoCe/CNT(30) and CuCoCe/CNT(20). It is also observed that CuCoCe-out-CNT(8) exhibited a remarkably lower catalytic performance than that of CuCoCe/CNT(8). The total alcohol STY decreased by 100 mg/g$_{cat}$h, and furthermore, the total alcohols selectivity and the alcohol distribution results showed that particles on the outside were not as effective for HAS as particles inside the CNTs.

The catalytic performance of CuCoCe/CNT(8) in a slurry reactor was also studied. As the results show, the catalyst tends to favor the formation of higher alcohols in a slurry reactor, the C$_{2+}$ alcohols selectivity increased to 67.9% and the ethanol selectivity reached ~39%, which were considerably higher than those achieved over other catalysts.
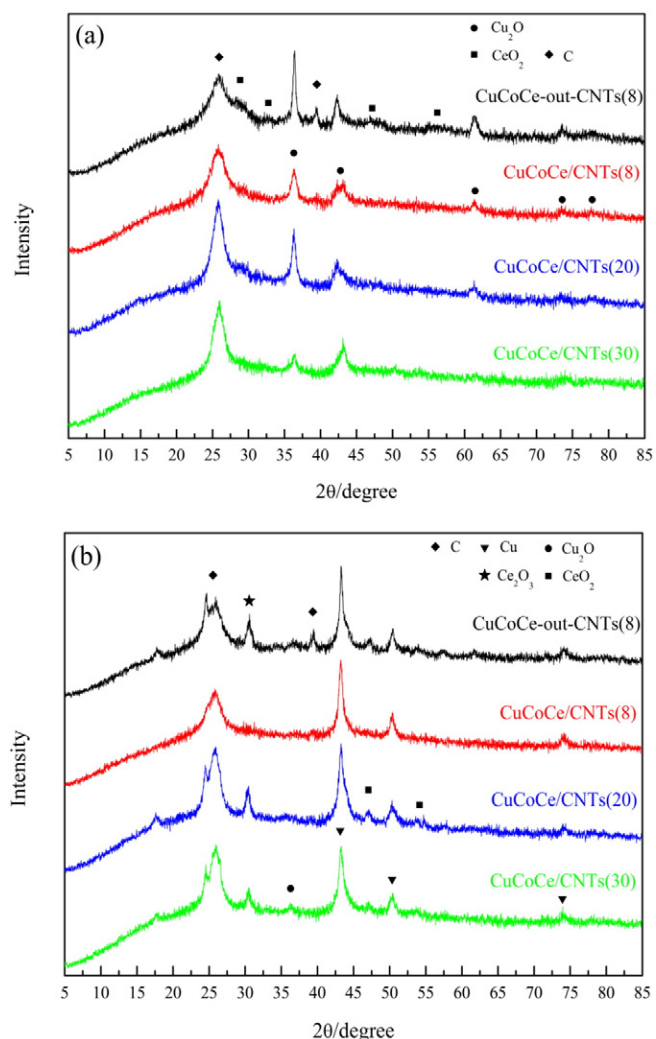
Fig. 1. XRD patterns of the (a) fresh and (b) used catalysts.