Research paper

Effect of γ-alumina nanorods on CO hydrogenation to higher alcohols over lithium-promoted CuZn-based catalysts

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ABSTRACT

To achieve high catalytic activities and long-term stability to produce higher alcohols via CO hydrogenation, the catalytic activities were tuned by controlling the loading amounts of γ-alumina nanorods and Al^{3+} ions added to modify Cu-Zn catalysts promoted with Li. The selectivity of higher alcohols and the CO conversion to higher alcohols over a Li-modified $Cu_{0.45}Zn_{0.45}Al_{0.1}$ catalyst supported on 10% nanorods were 1.8 and 2.7 times higher than those with a Cu-Zn catalyst without nanorods and Al^{3+} ions, respectively. The introduction of the thermally and chemically stable γ-Al_2O_3 nanorod support and of Al^{3+} to the modified catalysts improves the catalytic activities by decreasing the crystalline size of CuO and increasing the total basicity. Along with the nanorods, a refractory $CuAl_2O_4$ formed by the thermal reaction of CuO and Al^{3+} enhances the long-term stability by increasing the resistance to sintering of the catalyst.

1. Introduction

Global warming and environmental pollution have led researchers to devote much attention to the synthesis of higher alcohols. To mitigate the strong dependence on natural oil, alternative fuels such as coal, natural gas, biomass, and shale gas have attracted enormous interest [1–3]. Higher alcohols ($C_{2+}OH$), which are converted to carbon-based feedstocks (biomass, coal, natural gas) [3–5], have been used as alternative fuels and chemical feedstocks [6–10]. To synthesize higher alcohols, many researchers have experimented using different types of catalysts, which are classified as Rh-based catalysts [9,11,12], Mo-based catalysts [9,13,14], and Cu-based catalysts such as modified Fischer-Tropsch (FT) catalysts [9,15] and alkali-promoted methanol catalysts [9,16–18].

Catalysts containing Rh have a high selectivity to synthesize higher alcohols using syngas, but they are too expensive for industrial application [11,19]. Mo-based catalysts (MoS_2, Mo_2C) [20,21] are resistant to sulfur and less sensitive to CO_2, but the catalytic process requires high pressure and high temperature; they also require a long reaction time to reach a stable state [14].

Cu-based catalysts are relatively inexpensive compared to Rh- or Mo-based catalysts and are of interest because of their ability to synthesize higher alcohols by a simple method that involves doping alkali into the Cu-based catalysts [16,17]. Modified FT catalysts (Cu-Co, Cu-

Fe, and Cu-Ni) are promising with respect to higher alcohol synthesis using syngas [22,23]. However, since the Cu-Co catalyst has a low catalytic stability in long-term operation and a low total alcohol selectivity, it is unsuitable for use in industrial processes [15,24]. The Cu-Fe catalyst has a phase change between Cu and Fe, which weakens or interrupts the interaction between the two transition metals, which adversely affects the CO hydrogenation reaction [25]. The Cu-Ni catalyst is more suitable for methanol synthesis than higher alcohol synthesis due to the formation of the binary metal alloy [26]. All the modified FT catalysts are inappropriate because hydrocarbons are produced in large amounts, which decrease the content of higher alcohols during FT reactions.

Cu-Zn-based methanol catalysts promoted with alkali metals have been widely used because they are highly effective in the synthesis of higher alcohols due to their high activity in mild environments. However, since the catalysts tend to be sintered at high temperature and high pressure, the catalytic activities tend to drop sharply [16,17]. Thus, to prevent deactivation from sintering of the catalysts, metal additives such as Al, Cr, Ce, and Mn are added to the Cu-Zn catalysts [16,26,27]. Addition of these metals to the catalysts increases the specific surface area to prevent aggregation, allowing the activity and selectivity of the catalyst to be improved. Cu-Zn-Cr and Cu-Zn-Ce catalysts operate at high pressure (up to 7.6 and 20 MPa, respectively) to synthesize alcohols [16,27]. Cu-Zn-Mn shows an increase in the

Table 1
Sample names, compositions of raw materials, and physicochemical properties of Li-promoted Cu-Zn-based catalysts.

Catalyst name	Li − Cu: Zn: Al		γ-Al$_2$O$_3$ nanorods/ (CuZnAl) (mol%)	*Phase	**BET Surface area (m^2/g)	**Pore Diameter (nm)	**Pore Volume (cc/g)	*Crystallite sizes (nm)		***Basicity (mmol/g)
	Li (wt %)	Cu:Zn:Al (mol %)						CuO	Cu$_2$O	
L-CZA(0)/0	0.5	50: 50: 0	0	A	20.54	40.12	0.20	11.42	8.99	0.45
L-CZA(0)/5	0.5	50: 50: 0	5	A + M	33.90	33.32	0.28	7.91	6.38	0.461
L-CZA(0)/10	0.5	50: 50: 0	10	A + M	35.32	36.57	0.32	6.96	6.12	0.47
L-CZA(0)/15	0.5	50: 50: 0	15	A + M	37.88	39.98	0.37	6.34	6.08	0.54
L-CZA(5)/10	0.5	47.5: 47.5: 5	10	A + M + H	40.92	42.08	0.28	3.66	6.81	0.60
L-CZA(10)/10	0.5	45: 45: 10	10	A + M + H	52.51	21.81	0.28	4.04	5.85	1.05
L-CZA(12)/10	0.5	44: 44: 12	10	H + A + M	54.87	26.19	0.35	4.74	3.72	1.52

*Phases were identified by XRD analysis. A: aurichalcite, M: malachite, and H: hydrotalcite.

**Textural properties were studied using low temperature (77 K) N$_2$-physisooprtion using Moonsorp-1.

***Basicity was measured by CO$_2$-TPD method.

production of methanol and higher alcohol selectivity with lower overall activity [26]. Cu-Zn-Al catalysts, which can be used under milder conditions, show an optimum catalytic performance in the synthesis of higher alcohols [26].

To increase the catalytic activity of Cu-based catalysts, it is important to choose an appropriate alkali promoter for higher conversion and selectivity. The role of the alkali enhancer is to neutralize the surface acidity of the catalyst and/or support and to facilitate the adsorption of CO molecules on the catalyst surface [28]. However, if too much enhancer is used, the active sites are blocked, which lowers the catalytic activity [29]. In general, the alkali promoters used are mainly Na, K, Rb, Cs, and Li in Cu-based catalysts [30]. K mainly increases the selectivity to methanol and ethanol [23], and Na has the highest selectivity of higher alcohol at the beginning only because of its low stability [23]. Cs predominantly produces methanol [23]. Cu-based catalysts promoted with Li have lower activity than those with other promoters but have increased selectivity for higher alcohols around 300 $^\circ$C and are more stable during the reaction [23,31].

On the other hand, the catalytic activity and selectivity for higher alcohols are not solely dependent on the addition of alkaline ions but also depend on the counter anions of the salt and the support. The counter anion of the alkali salt chosen for alcohol selectivity should be easily removed by the alkali, and the alkali salt should be evenly distributed over the catalyst. For even dispersion of the catalyst, the alkali promoter with a relatively low pKa value was used such as LiNO$_3$; this is readily soluble in water [32].

In general, the support enhances the stabilization of the active species and promoters for the synthesis of higher alcohols; promotes the donation or exchange of hydrogen or oxygen; donates and receives electrons of metal particles; and controls the degree of reduction and dispersion [33]. Particularly in CO hydrogenation, strong interactions between supports and active metals have a significant influence on the synthesis of higher alcohols [34]. A strong metal-support interaction (SMSI) leads to changes of phase and morphology triggered by partial reduction of the active oxide or oxide supports. The formation of oxygen vacancy defects due to the reduction can cause strong bonding between the active metal and the surface of supports [35,36]. The shaping and sizing of active metals and supports can also exhibit strong SMSI due to their large surface-to-volume ratio [37]. In addition, doping small amounts of specific cations such as Li$^+$, Na$^+$, and Sr^{2+} to the catalyst affects the mutual solid–solid interactions between the components [38,39]. It indicates the necessity of a strong SMSIs catalyst, which provides a significant effect on the catalytic reaction.

Thus, we investigate the effect of alumina nanorods (ARs) as a support with a large surface-to-volume ratio on the activity of Cu-Zn-based catalysts promoted by Li and on the long-term thermal stability for effective conversion of syngas to higher alcohols.

2. Experimental section

2.1. Synthesis of γ-Al$_2$O$_3$ nanorods

All chemicals were analytical grade reagents and were used as received without further purification. All experiments were conducted in air. The γ-Al$_2$O$_3$ nanorods as a support were synthesized using a boehmite precursor (see Supplementary Fig. S1 and S2) by a hydrothermal route [40]. A 1.00 M solution of aluminum chloride hexahydrate (AlCl$_3$·6H$_2$O, Sigma Aldrich, 99%) was prepared with 100 ml distilled water under vigorous stirring at room temperature. Then, 1.00 M of 50 ml ammonia solution (28% NH$_3$ in water, Junsei) was added to 1.00 M of 50 ml sodium hydroxide (NaOH, Yukari, 96%) solution to prepare a mixed precipitant. The precipitant solution was added dropwise to the aluminum chloride solution, and the pH value was adjusted to 5 with ammonia solution. The mixture was transferred to a 330 ml Teflon-lined autoclave and kept at 200°C for 24 h. After the reaction, the resulting solution was centrifuged and washed three times with distilled water and ethanol then dried at 80°C in a vacuum oven. The dried boehmite powder was calcinated in a box furnace and heated to 500°C (3°C/min) for 2 h in air.

2.2. Fabrication of catalysts

For the catalyst preparation by co-precipitation (see Supplementary Fig. S3), solutions of nitrate and AR were prepared separately according to the molar ratio as shown in Table 1.

In order to investigate the effect of the introduction of ARs on Cu-Zn based catalysts, the catalysts containing with molar ratio of Cu:Zn = 5:5 and the amount of ARs was varied through co-precipitation as shown in Table 1 and Supplementary Table S1. The prepared ARs of 0 − 15 mol% were added to 125 ml of nitrate solutions according to the compositions of Table 1 and dispersed, and the catalysts were prepared by co-precipitation method. The nitrate precursors used were a 1.00 M solution of copper (II) nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, Junsei, 99%) and zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, Sigma Aldrich, 98%) (Cu:Zn = 5:5). 1.2 M Na$_2$CO$_3$ solution as a precipitant and the prepared solution added dropwise to hot distilled water (100 ml) at 65°C. During precipitation, the pH was kept at 6.5 − 7.5. After aging for 6 h, the precipitates were filtered and washed several times with distilled water and then dried at 80°C for 24 h in a vacuum oven. After grinding, the dried catalyst was calcined at 350°C (3°C/min) under air for 4 h. The lithium promoter (0.5 wt%, Li) was doped to the resulting solids by vacuum impregnation with an aqueous solution of lithium nitrate (LiNO$_3$, Junsei, 98%) followed by drying and final calcination in air for 4 h at 350°C. To investigate the synergistic effect of the Al^{3+} ions and the ARs, the catalyst was prepared with a Cu:Zn ratio of 5:5 with 5 − 15 mol% of ARs, and the amount of Al^{3+} was varied through co-