

CHEMICAL KINETICS
AND CATALYSIS

Synthesis of Higher Alcohols via Syngas on Cu/Zn/Si Catalysts. Effect of Polyethylene Glycol Content¹

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Abstract—Cu/Zn/Si catalysts with different polyethylene glycol (PEG) content were prepared by a complete liquid-phase method, and characterized by XRD, H₂-TPR, N₂-adsorption, and XPS. The influence of PEG content on the higher alcohols synthesis from syngas was investigated. The results showed that addition of PEG can influence the texture and surface properties of the catalysts, and therefore affect their activity and product distribution. With an increase in PEG content, BET surface area, Cu crystallite size and surface active ingredient content of the catalysts first increased and then decreased, the CO conversion had similar variation tendency. However, the pore volume and pore diameter of the catalyst increased, and the binding energy of the active component and the content of Cu₂O decreased, which resulted in higher catalyst selectivity towards higher alcohols. The highest C₂₊OH selectivity in total alcohols was 60.6 wt %.

Keywords: higher alcohols, syngas, Cu/Zn/Si catalysts, CO hydrogenation, PEG

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1. INTRODUCTION

Environmental pollution and growing demand for energy force researchers to dedicate to the utilization of fossil fuels in more clean ways [1–4]. Higher alcohols synthesis from syngas has been paid much attention because they can be used as fuel additives and alternative transportation fuel [5–7]. However, low selectivity towards higher alcohols and poor stability of the catalysts make this process difficult to commercialize [8, 9]. Therefore, developing an efficient and highly selective catalyst is an actual problem.

Nowadays, the catalysts applied in higher alcohol synthesis from syngas include modified Fischer–Tropsch (F–T) catalysts, modified methanol synthesis catalysts, Mo and Rh based catalysts. Modified F–T catalysts, mainly including Cu–Co and Cu–Fe based ones, are regarded as the most promising for this process [10]. Huang suggested a novel preparation method of slurry catalysts for slurry reactor, named it complete liquid-phase method. Its main innovative thought lied in preparing the catalysts directly from solution to slurry. It is expected that the stability of catalysts can be improved, because the catalytic materials can be used in the same environment as its forma-

tion [11]. In our previous study, the ethanol selectivity of Cu based catalysts without alkalis or F–T elements could reach an unexpected point via complete liquid-phase technology; this was discovered accidentally, but it was difficult to repeat this result [12]. Fan et al. prepared a series of Cu/Zn/Al catalysts via complete liquid-phase technology with different surfactants used as the modifiers. The result showed that non-ionic surfactant can promote performance of the catalyst via adjusting its specific surface area, pore structure, phase composition and crystallite size [13]. Meanwhile, it was reported that polyethylene glycol (PEG) used to modify the silica surface, provides effective stabilization and immobilization of metal nanoparticles [14]. Therefore, in this paper, the Cu/Zn/Si catalysts were prepared via complete liquid-phase method, and the influence of PEG content on the higher alcohols formation was clarified.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Cu/Zn/Si catalysts with Cu : Zn : Si molar ratio 2 : 1 : 0.8 with various PEG content were prepared by a complete liquid-phase method. A certain amount of tetraethyl orthosilicate (TEOS) was dissolved in anhy-

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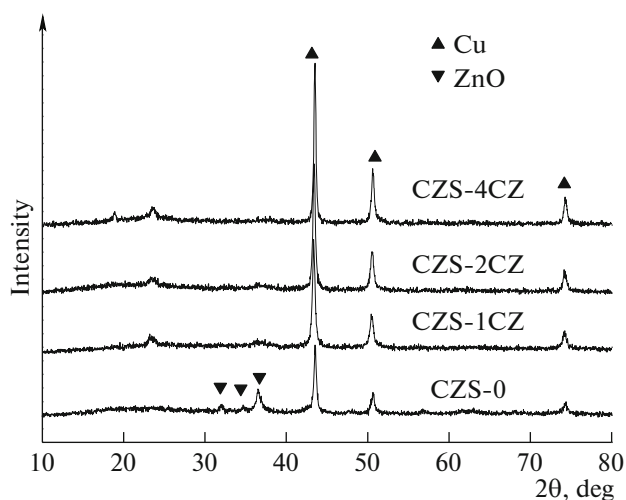


Fig. 1. XRD patterns of the catalysts with different PEG content.

drous ethanol, followed by addition of the mixed solution containing anhydrous ethanol, distilled water and concentrated nitric acid and stirred for 2 h and then kept for 12 h to obtain a silica sol. Then, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and PEG-600, in turn, were dissolved in anhydrous ethanol and the resulting solution was slowly added to the silica sol. A homogeneous gel was obtained after stirring at 313 K for 4 h, and aging at room temperature for 7 days. The gel was dispersed in liquid paraffin and heated from 323 to 533 K at a heating rate of 5 K/min and then kept for 7 h at 533 K. To remove paraffin, the catalysts were extracted with petroleum ether in a Soxhlet apparatus for 24 h, and then dried in air. The catalysts were named as CZS- x CZ ($x = 0, 1, 2, 4$), where $x = 16n(\text{PEG-600})/n(\text{Cu}^{2+})$.

2.2. Characterization of the Catalysts

XRD patterns of the catalysts were recorded on Rigaku D/MAX-2500 diffractometer with $\text{CuK}\alpha$ radiation (40 kV, 100 mA) in 2θ range from 5° to 85° . The crystallite size of Cu was estimated from selected Cu(111) reflections using the Scherrer equation.

Table 1. Textural properties and crystallite size of Cu particles of different catalysts

Catalyst	BET surface area, m^2/g	Pore volume, cm^3/g	Pore diameter, nm	Cu crystallite size, nm
CZS-0	98.3	0.170	6.9	25.0
CZS-1CZ	113.9	0.235	8.3	23.2
CZS-2CZ	82.8	0.264	12.7	23.9
CZS-4CZ	79.8	0.349	17.5	28.0

Textual properties of the catalysts were studied by a nitrogen adsorption method using a Micromeritics Quantachrome instrument at 77 K. Pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method, and the specific surface areas were calculated from the isotherms using the Brunauer–Emmett–Teller (BET) method.

X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) with $\text{AlK}\alpha$ radiation ($h\nu = 1486.6$ eV) under ultrahigh vacuum (7×10^{-8} Pa).

H_2 -TPR tests (10 K/min) were performed to investigate the reducibility of the catalysts using a chemisorption instrument; the sweep gas was detected using an OmniStar instrument. The catalyst (50 mg) was pre-treated to remove physically adsorbed water and other impurities at 573 K under a flow of N_2 (32 mL/min) for 1 h and then cooled to 323 K; after cooling, the gas was changed to a $\text{H}_2/\text{N}_2 = 0.05$ mixture (35 mL/min).

2.3. Catalytic Activity Test

The activity of the catalyst was evaluated in a 500 mL slurry reactor. We added the slurry catalyst (30 g) into the reactor, and added liquid paraffin to total volume of 300 mL. Prior to reaction, the catalysts were reduced at 523 K in a flow of 20 vol % $\text{H}_2 + \text{N}_2$ for 4 h. After cooling to room temperature, the syngas ($\text{H}_2/\text{CO} = 2$) was introduced into the reactor at a feed flow rate of 150 mL/min at 523 K and 4 MPa. The steady-state activity of the catalyst was estimated from gas chromatographic analysis of the gaseous products (online) and analyzing the liquid products (offline).

3. RESULTS AND DISCUSSION

3.1. XRD Characterization

The XRD patterns of the catalysts with different PEG content are presented in Fig. 1; the crystallite size of Cu particles in different catalysts are shown in Table 1. The diffraction peaks of Cu and ZnO could be found in the CZS-0 catalyst, but the ZnO diffraction peaks gradually weakened to disappear in XRD pattern with the increasing PEG content in the catalyst, indicating that ZnO is well dispersed in it.

The ether oxygen atom of PEG can form coordination bond with Cu^{2+} and Zn^{2+} ions, so PEG can promote the dispersion of species by scattering Cu^{2+} and Zn^{2+} ions around its chain [13]. In addition, no crystalline silica species were detected by XRD. As shown in Table 1, the average crystallite size of Cu first decreased and then increased with further increase in PEG content, implying that a suitable amount of PEG improves the dispersion of copper species, but an excess of PEG is unfavorable. Firstly, PEG would intertwine with the excessive amount of PEG added,

so that the gel microspheres mutually reunited, leading to aggregation of the copper. Secondly, the strong reducibility of PEG can accelerate the reduction of CuO with the formation of Cu particles with larger crystallite size during heat treatment [15].

Besides, it was reported [16] that the surface of large copper particles has higher CH_x and CO coverage and lower H coverage.

3.2. Textural Properties

The textural properties of the catalysts are listed in Table 1. The BET surface areas first increased and then decreased with the increasing PEG content, suggesting that a suitable amount of PEG allows obtaining higher surface areas. The pore diameters and pore volumes increase with increasing PEG content, indicating the PEG role in pore formation. Fan et al. [17] suggested that the catalyst pore size affects the catalytic activity as well as the products distribution because of the differences in the diffusion of both reactants and products.

3.3. H_2 -TPR Characterization

The reduction of the catalysts with different PEG content was studied using H_2 -TPR method. As shown in Fig. 2, all catalysts demonstrated the peak of H_2 consumption which can be attributed to the reduction of Cu_2O , which was not detected by XRD [18]. With the increasing PEG content, the position of the hydrogen consumption peak shifted towards the lower temperature showing that Cu_2O reduction proceeds more easily. This may be due to different dispersities of Cu_2O [19]. Moreover, the area of the hydrogen consumption peak decreased with increasing PEG content, indicating that the amount of reducible of Cu_2O was gradually reduced. Possibly, PEG in the heat treatment process facilitates the reduction of copper species, which is consistent with XRD result.

3.4. XPS Characterization

The surface chemical state of the components of the catalysts with different PEG content were characterized by XPS. The binding energies (BE) for Cu $2p_{3/2}$, Zn $2p_{3/2}$, and Si $2p$ are presented in Table 2.

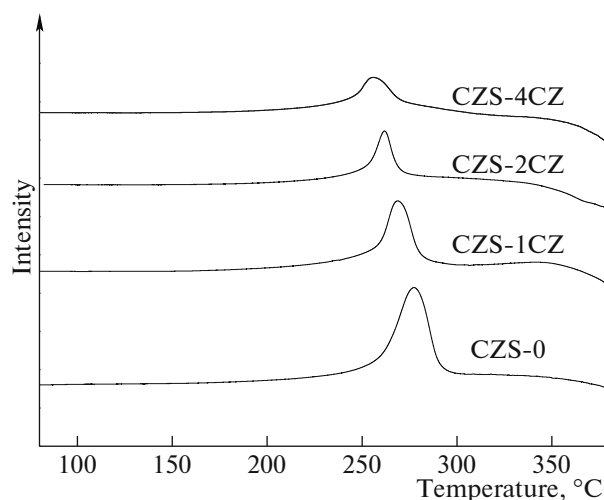


Fig. 2. H_2 -TPR spectra of catalysts with different PEG content.

For all the catalysts, the Cu XPS peaks were around 931.8–932.4 eV (BE); there are no shake-up satellite peaks in the range of 940–945 eV attributable to Cu^+ and Cu^0 species [20–22], which is in accordance with the XRD and H_2 -TPR results. Besides, with the addition of PEG, the Cu $2p$, Zn $2p$, and Si $2p$ peaks shifted toward lower BE proving the formation of Cu, Zn, and Si species with higher electron density. PEG molecules contain hydroxyl groups which can bind with metal ions, especially transition metal ions. As a strong electron-donating group, hydroxyl groups can share its lone pair of electrons with cation resulting in a higher electron density of Cu/Zn/Si catalysts containing PEG.

Surface compositions of the studied catalysts are listed in Table 2. Both the Cu/Zn and (Cu+Zn)/Si atomic ratios are far less than theoretical ones, indicating that the surface of the catalysts was enriched with Zn and Si; enrichment with Si is more significant. With an increase in PEG content, the content of Si on the catalyst surface gradually increases and the Zn content decreases, while the surface copper content shows an irregular trend. In addition, the (Cu + Zn)/Si atomic ratio first increased and then decreased with increasing PEG content. It is shown that the

Table 2. The binding energies (BE) for Cu $2p_{3/2}$, Zn $2p_{3/2}$, and Si $2p$

Catalysts	Binding energy, eV			Atomic composition, %			Atomic ratio	
	Cu $2p_{3/2}$	Zn $2p_{3/2}$	Si $2p$	Cu	Zn	Si	Cu/Zn	(Cu + Zn)/Si
CZS-0	932.3	1022.1	103.0	1.21	3.13	5.99	0.39	0.72
CZS-1CZ	932.4	1022.2	103.1	1.32	2.83	5.61	0.47	0.74
CZS-2CZ	932.3	1021.9	102.8	1.15	2.81	6.53	0.41	0.61
CZS-4CZ	931.8	1021.2	102.3	1.21	2.76	7.77	0.46	0.52

Table 3. Performance of the catalysts with different PEG content

Catalysts	CO conversion, %	Selectivity, mol %				C ₂₊ OH/ROH, %
		ROH	HC	DME	CO ₂	
CZS-0	17.0	71.6	1.5	14.2	12.7	0.3
CZS-1CZ	20.0	71.0	0.8	16.2	12.0	1.8
CZS-2CZ	9.9	64.5	3.4	15.8	16.3	11.2
CZS-4CZ	3.5	47.9	22.0	0.5	29.6	60.6

Reaction conditions: $T = 523$ K, $P = 4$ MPa, $H_2/CO = 2$, feed flow rate = 150 mL/min, ROH for total alcohols and HC for hydrocarbons.

Table 4. Product distributions for catalysts with different PEG content

Catalysts	ROH, wt %				HC, wt %				
	MeOH	EtOH	PrOH	BuOH	C1	C2	C3	C4	C5+
CZS-0	99.7	0.2	0.1	0.0	24.7	16.9	13.9	18.7	25.8
CZS-1CZ	98.2	1.0	0.3	0.5	15.9	11.5	8.3	23.0	41.3
CZS-2CZ	88.8	6.0	2.2	3.0	9.4	19.0	7.2	20.6	43.8
CZS-4CZ	39.4	49.6	3.5	7.5	8.1	19.5	11.6	11.2	49.6

higher (Cu + Zn)/Si atomic ratio can favor the catalytic activity.

3.5. Catalytic Performance

The catalytic performance of different catalysts in CO hydrogenation is summarized in Tables 3 and 4. One can see that higher alcohols formation on the CZS-0 catalyst without PEG is insignificant and the main product is methanol.

The catalytic performance of CZS-1CZ catalyst prepared with a small amount of PEG was not significantly different from that of CZS-0 catalyst except higher CO conversion, which corresponds to larger specific surface area of this the catalyst, smaller Cu grain size and higher active component content of the catalyst surface. With further increase in PEG content the CO conversion and total alcohols selectivity decreased, and the selectivity towards hydrocarbons and carbon dioxide increased. The mass fractions of higher alcohols in resulting alcohol mixture increased, as well as the fraction of long-chain hydrocarbons. When $n(\text{PEG-600})/n(\text{Cu}^{2+}) = 4/16$, C₂₊ alcohol fraction reached 60.6 wt %, and C₂₊ hydrocarbon fraction reached 91.9 wt %. We can suggest that the addition of a sufficient amount of PEG promotes carbon chain growth; these results are consistent with the data reported in [23]. Assuming the results of the catalysts characterization, we can conclude that a decrease in CO conversion is attributed to a decrease in the specific surface area and to an increase in Cu particle size. The formation capacity of higher alcohols and long-chain hydrocarbons is related to a decrease in the binding energy of Cu, the growth of Cu grains size and the increase in pore size of the catalyst. Zhang et al.

reported that CO hydrogen-assisted dissociation to form CH₂ and then CO insertion into CH₂ to form C₂ oxygenates were two important reactions of the higher alcohols formation [24]. Therefore, the synthesis of higher alcohols required both dissociated and non-dissociated CO molecules. Besides, Chen et al. suggested that the activity of the catalyst depends on the rate of CO hydrogenation, but excessive reaction rates at this step tend to promote the formation of methanol. The reaction rate of CO insertion affects the selectivity towards higher alcohols. So the higher selectivity towards higher alcohols requires a balance between CO hydrogenation and CO insertion capacities of the catalyst [25]. It was generally believed that Cu₂O has a stronger ability to adsorb and dissociate CO, and metallic Cu is a non-dissociative adsorption site for CO in Cu-based catalysts. In CZS-2CZ and CZS-4CZ catalysts, a decrease in the binding energy of Cu promoted non-dissociative adsorption of CO, and a decrease in Cu₂O concentration weakened the CO dissociation facilitating the CO insertion capacity of the catalyst simultaneously impairing its CO hydrogenation capacity. In addition, larger copper particle size and larger pore volume also provide an essential conditions for the carbon chain growth. An increase in selectivity towards CO₂ may be due to the fact that hydrocarbons and alcohols formation is always accompanied by the production of water, most of which appears to be converted to CO₂ through the water-gas-shift reaction [26].

CONCLUSIONS

The PEG content had a significant influence on the surface properties and catalytic performance of the

catalysts prepared via complete liquid-phase method. A suitable amount of PEG favors an increase in BET surface area and the wide dispersion of the active ingredient, thus improving the CO conversion. Higher amounts of PEG provide the reduction of the binding energy of the active component, the pore volume and diameter increase, leading to the formation of higher alcohols and C₂₊ hydrocarbons.

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REFERENCES

- J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang, and X. Ma, *J. Am. Chem. Soc.* **134**, 13922 (2012).
- R. Zhang, G. Wang, and B. Wang, *J. Catal.* **305**, 238 (2013).
- I. Wender, *Fuel Process. Technol.* **48**, 189 (1996).
- N. Ak and A. Demirbas, *Energy Sources, Part A* **38**, 1730 (2016).
- K. J. Smith and R. B. Anderson, *J. Catal.* **85**, 428 (1984).
- X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo, and X. Bao, *Nat. Mater.* **6**, 507 (2007).
- V. Subramani and S. K. Gangwal, *Energy Fuel.* **22**, 814 (2008).
- J. J. Spivey and A. Egbibi, *Chem. Soc. Rev.* **36**, 1514 (2007).
- Y. Zhu, Y. Zhu, G. Ding, S. Zhu, H. Zheng, and Y. Li, *Appl. Catal., A* **468**, 296 (2013).
- K. Fang, D. Li, M. Lin, M. Xiang, W. Wei, and Y. Sun, *Catal. Today* **147**, 133 (2009).
- Z.-h. Gao, L.-f. Hao, W. Huang, and K.-c. Xie, *Catal. Lett.* **102**, 139 (2005).
- W. Huang, L. Yu, W. Li, and Z. Ma, *Front. Chem. Eng. China* **4**, 472 (2010).
- J. C. Fan, H. Wu, W. Huang, and K. C. Xie, *Chem. J. Chin. Univ.* **29**, 993 (2008).
- Z. S. Hou, N. Theyssen, and W. Leitner, *Green Chem.* **9**, 127 (2007).
- Z. Li, Z. Zuo, W. Huang, and K. Xie, *Appl. Surf. Sci.* **257**, 2180 (2011).
- J. P. den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen, and K. P. de Jong, *J. Am. Chem. Soc.* **131**, 7197 (2009).
- L. Fan, K. Yokota, and K. Fujimoto, *AIChE J.* **38**, 1639 (1992).
- Y. J. Liu, C. B. Liu, C. Li, and W. Huang, *Catal. Commun.* **76**, 29 (2016).
- A. Yin, X. Guo, W.-L. Dai, H. Li, and K. Fan, *Appl. Catal., A* **349**, 91 (2008).
- R. T. Figueiredo, A. Martínez-Arias, M. L. Granados, and J. L. G. Fierro, *J. Catal.* **178**, 146 (1998).
- Y.-W. Suh, S.-H. Moon, and H.-K. Rhee, *Catal. Today* **63**, 447 (2000).
- W. Gao, Y. Zhao, J. Liu, Q. Huang, S. He, C. Li, J. Zhao, and M. Wei, *Catal. Sci. Technol.* **3**, 1324 (2013).
- C. Xiaofan, W. Baoshan, X. Hongwei, and L. Yongwang, *Chin. J. Catal.* **34**, 808 (2010).
- R. Zhang, X. Sun and B. Wang, *J. Phys. Chem. C* **117**, 6594 (2013).
- W. Chen, Y. Ding, D. Jiang, G. Jiao, H. Zhu, Z. Pan, and H. Luo, *Chin. J. Catal.* **27**, 999 (2006).
- N. Tien-Thao, M. H. Zahedi-Niaki, H. Alamdari, and S. Kaliaguine, *Appl. Catal., A* **326**, 152 (2007).