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Design of bimodal pore Cu-Fe based catalyst with enhanced performances for higher alcohols synthesis

Mingyue Ding^a, Junling Tu^{a,b}, Noritatsu Tsubaki^c, Lungang Chen^a, Tiejun Wang^{*a}, Longlong Ma^a, Chenguang Wang^a

^a Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, PR China.

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China.

^c Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan.

Abstract

Bimodal support modified Cu-Fe based catalysts with different pore structures were prepared and tested for higher alcohols synthesis (HAS). It was found that the bimodal derived catalyst showed both higher catalytic activity and selectivity of C₂⁺OH compared to the traditional Cu-Fe based catalysts. In particular, both the activity and C₂⁺OH selectivity presented an increasing trend with the gradual decrease in bimodal support pore sizes. The characterization results indicated that decreasing support pore sizes resulted in the increase of BET surface area and dispersion of active Cu and Fe species inside the pore structures, which increased the bimetallic active sites and strengthened probably the synergistic effect of Cu-Fe via “confine effect” of bimodal pore structures, improving the HAS catalytic activity and shifting product distribution towards higher alcohols.

Keywords: Higher alcohols synthesis; bimodal support; Cu-Fe based catalyst;

1. Introduction

Higher alcohols synthesis (HAS), as an important technology in the production of clean and renewable fuels and chemicals from syngas derived from coal, natural gas and biomass, has drawn much attention for both industrial and academic applications. Compared to the other HAS catalysts, the use of Cu-Fe catalyst is more attractive for HAS with low H₂/CO ratio syngas derived from coal or biomass due to its higher water-gas shift activity and lower cost [1].

There are unabated attempts to improve the HAS performances of Cu-Fe based catalysts by the addition of chemical promoters such as basic and transition metals, as well as structure promoters, namely ZrO₂ and ZnO [2]. However, many byproducts such as carbon dioxide and hydrocarbons are still formed

* Corresponding author. Tel.: +0-20-87057790; fax: +0-20-87057789.

E-mail address: wangtj@ms.giec.ac.cn.

during HAS. Thus, how to improve the catalytic activity and selectivity of higher alcohols becomes the key of research for further development. The bimodal support where both large pore and small pore coexist has excellent advantages for improving the catalytic activity and selectivity of the target product because the large pores provide rapid transportations of reactant and product molecules, while the small pores simultaneously provide a large supported metal area [3]. Recently, the bimodal support is used widely in the fields of methanation of CO₂ and Fischer-Tropsch synthesis, which presents excellent performances in improving the catalytic activity and selectivity. The spatial and chemical characteristics of bimodal support provide us a new way to solve the above obstacle in HAS. However, an application of this kind of bimodal support to HAS is rarely reported. In the present study, the bimodal pore Cu-Fe based catalysts with different pore structures were prepared to investigate the effect of pore structure on the active Cu and Fe nanoparticles and catalytic performances (activity and selectivity) for higher alcohols synthesis.

2. Experimental

The bimodal support was prepared by incipient-wetness impregnation of commercially available silica gel (SG) with silica sol (SS). The weight percent of silica sol loading in the bimodal support is 5, 20, 40 and 80 wt%, which are labeled as M₅, M₂₀, M₄₀ and M₈₀, respectively. The Cu-Fe supported catalyst was prepared by incipient-wetness impregnation of different supports such as SG, SS or bimodal supports.

Textural properties of the catalysts were measured by N₂ physisorption at -196 °C using a Micromeritics ASAP 2010 instruments. Powder X-ray diffraction patterns (XRD) of the catalyst samples were measured on a D/max-RA X-ray diffractometer (Rigaku, Japan). Temperature program reduction of hydrogen (H₂-TPR) was carried out in a U-tube quartz reactor with a hydrogen-argon mixture (containing 5 vol % of hydrogen) as the reductive gas. The higher alcohols synthesis tests were conducted in a fixed-bed, stainless flow micro-reactor.

3. Results and discussion

3.1 Textural properties of the bimodal supports and bimodal derived catalysts

The pore size distributions of different supports are shown in Fig. 1(a). The pore size of SG and SS is 61 and 3 nm, respectively. As the silica sol is added into the silica gel, the obtained bimodal support M₂₀ contains 16 and 60 nm pores meantime, which indicates that combination of SG and SS results in the formation of bimodal pore structures. On the other hand, pore structures of the bimodal support may be adjusted effectively by varying the content of silica sol in the bimodal support. From Table 1 it is apparent that the BET surface area increases whereas pore volume presents a decreasing trend with gradual increasing of SS content, suggesting that the increase in SS content facilitates silica sol entering into the large pores of silica gel, resulting in the increase of BET surface area and decrease of pore volume.

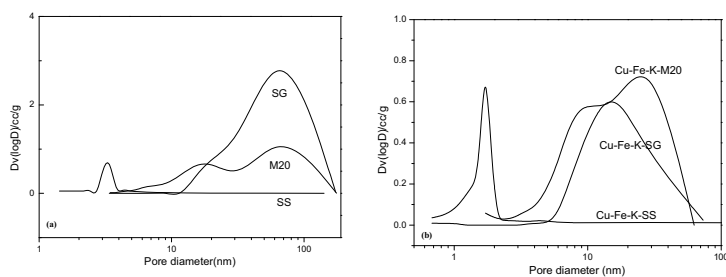


Fig. 1 The pore size distributions of different supports and catalysts: (a) SS, SG and bimodal support M20; (b) Cu-Fe-K-SS, Cu-Fe-K-SG and Cu-Fe-K-M20

Table 1 Textural properties of the silica-silica bimodal supports

Support	Support content (wt %)		BET surface area (m ² /g)	Pore volume (ml/g)	Pore diameter (nm)	
	Silica sol	Silica gel			Small pore	Large pore
SG	-	100	95	1.32	-	61
M ₅	5	95	101	0.84	22	60
M ₂₀	20	80	107	0.64	16	59
M ₄₀	40	60	113	0.55	9	58
M ₈₀	80	20	127	0.49	8	51
SS	100	-	737	0.32	3	-

Both the Cu and Fe active species are added into the different supports. The pore size distribution of the SG, SS and bimodal support M₂₀ derived catalysts is presented in Fig. 1(b). It is clear that both the SG and SS derived catalysts present a single pore structure, while the M₂₀ derived catalyst contains two pore sizes, indicating that incorporation of copper and iron species do not block the entrance of pore structures over the bimodal support. In addition, the textural properties of the bimodal support derived catalysts are shown in Table 2.

Table 2 Textural properties of the Cu-Fe supported bimodal catalysts

Catalysts	BET surface area (m ² /g)	Pore volume (ml/g)	Pore diameter (nm)		d _{XRD} (nm)	
			Small pore	Large pore	d _{CuO}	d _{Fe₂O₃}
Cu-Fe-K-SG	38	0.36	-	14.8	29.8	18.5
Cu-Fe-K-M ₅	73	0.48	8.4	30.6	19.9	14.1
Cu-Fe-K-M ₂₀	80	0.40	8.2	25.4	21.2	15.4
Cu-Fe-K-M ₄₀	84	0.30	8.1	24.8	22.8	16.3
Cu-Fe-K-M ₈₀	89	0.25	7.7	24.2	23.1	17.6
Cu-Fe-K-SS	110	0.12	1.7	-	7.5	6.7

Compared to the pore sizes of bimodal supports, both the large pore and small pore sizes of the bimodal modified catalysts decrease slightly, indicating that both the Cu and Fe active elements have entered into the pore structures of the bimodal supports. Especially, with the gradual increase of SS content in the bimodal derived catalysts, both the large pore and small pore sizes present a decreasing trend, which are consistent with the variation trend of pore sizes for the bimodal supports. Accompanied with the gradual increase of SS content from 5 to 80 wt% for the bimodal derived catalyst, the CuO and Fe₂O₃ crystallite sizes increase slowly from 19.9 and 14.1 nm to 23.1 and 17.6 nm, respectively. It is possible that both the copper and iron elements are well dispersed inside the large and small pores of the bimodal support as the support pore sizes are larger (such as the M₅ derived catalyst), resulting in the decrease of metal particle sizes. With the gradual decrease of support pore sizes, the metal nanoparticles may be aggregated slowly under the confinement of the pore walls, increasing the nanoparticle sizes.

3.2 Temperature program reduction of the catalysts

The H₂-TPR profiles of the bimodal support derived catalysts are shown in Fig. 2. One main peak with one shoulder peak appeared at 150-280 °C correspond to the reduction of CuO → Cu and Fe₂O₃ → Fe₃O₄ for all of the catalysts, respectively, except for the M80 derived catalysts, which presents one main peaks corresponding to the reduction of Cu-Fe solid solution. In addition, a tail peak appeared at 400-650 °C for all of the catalysts in the H₂-TPR profiles, which could be attributed to the reduction of Fe₃O₄.¹⁵ It can be found that the intensity of CuO reduction peak presents a decreasing trend with the gradual decrease of support pore sizes, and disappears completely for the M₈₀ derived catalyst, which indicates that the decrease of support pore sizes results in possibly the decrease in CuO content whereas promotes the formation of Cu-Fe solid solution.

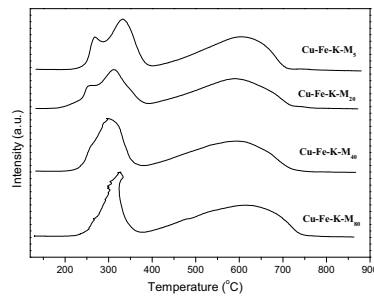


Fig.2 H₂-TPR profiles of the Cu-Fe supported bimodal catalysts

3.3 Phase structures of the fresh and used catalysts

The XRD patterns of the fresh and used Cu-Fe supported bimodal catalysts are shown in Fig. 3. From Fig. 3a it can be found that the XRD patterns of all the fresh bimodal support derived catalysts show the mainly diffraction peaks at 2θ values of 35.5, 38.7, 48.7 ° and 24.1, 33.2, 49.5, 54.1 °, corresponding to CuO (JCPDS card No.48-1548) and α-Fe₂O₃ (JCPDS card No.33-0664), respectively. This indicates that the fresh Cu-Fe supported bimodal catalysts are composed mainly of CuO and α-Fe₂O₃. In addition, the peak appeared about 35.6 ° is attributed to CuFe₂O₄, indicating that both the copper and iron species could be combined to form the Cu-Fe solid solution. The peak intensity of CuFe₂O₄ increases slightly with the decrease of bimodal support pore sizes, suggesting that decreasing pore sizes of bimodal support promote the formation of Cu-Fe solid solution via strengthening the interaction of Cu and Fe species in the confinement of support pore structures.

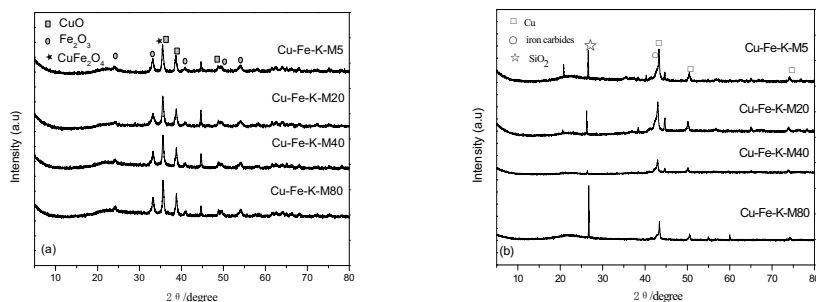


Fig. 3 The XRD patterns of the fresh and used catalysts: (a) the fresh catalysts; (b) the used catalysts

From Fig. 3b it can be found that some new diffraction peaks in the used bimodal support derived catalysts appeared at 2θ values of 43.3, 50.4 and 74.1 °, which is ascribed to metallic Cu. In addition, a

broad peak appeared at about 43.0 ° may be attributed to the formation of iron carbides. The peak intensity of both the metallic Cu and iron carbides decreases gradually with the decrease of support pore sizes, implying that decreasing pore sizes of bimodal support facilitate the dispersion of both the metallic Cu and iron carbides inside the pore walls. According to the BET results mentioned above, the BET surface area of the bimodal modified catalyst presents an increasing trend with the decrease in support pore sizes. Therefore, the bimodal support derived catalyst with smaller pore sizes provides higher BET surface area, promoting possibly the dispersion of both the metallic Cu and iron carbides inside the pore structures.

3.4 HAS performances

HAS performances of the Cu-Fe supported bimodal catalysts are measured under reaction conditions of 320 °C, 5.0 MPa, 6000 h⁻¹ and H₂/CO = 2 (see Table 3). The traditional SG derived catalyst has the lowest surface area, which exhibits the lowest catalytic activity. In contrast, the bimodal support derived catalysts owning larger surface area and pore structures present higher HAS activity. Especially, the catalytic activity presents an increasing trend with the decreasing of support pore structures and increasing of BET surface area for the bimodal modified Cu-Fe based catalysts. In addition, the activity of the SS catalyst with the largest surface area is as high as that of the bimodal support derived catalysts. According to the above characteristic results, the bimodal derived catalyst with lower support pore sizes presents higher surface area and the well dispersion of bimetal species, providing more active sites. Furthermore, decreasing support pore sizes enhances the interaction of Cu-Fe and improves the stability of metal particles via the confinement of pore walls. Therefore, the increasing of active metal sites and strengthening of synergistic effect between Cu and Fe species promote the HAS catalytic activity. On the other hand, with the increase of surface area and decrease of bimodal support pore sizes, the active metal sites increase and synergistic effect of Cu-Fe enhances, which improve the formation of C₂⁺OH via the strengthening of carbon chain growth ability of methanol.

Table 3 HAS performances of the Cu-Fe supported bimodal catalysts

Catalysts	X _{co} (%)	Selectivity (%)			C ₂ ⁺ OH/C ₁ OH
		ROH	CO ₂	HC	
Cu-Fe-K-SG	31	49	36	15	1.26
Cu-Fe-K-M ₅	44	57	29	14	1.56
Cu-Fe-K-M ₂₀	53	61	28	11	1.64
Cu-Fe-K-M ₄₀	54	62	28	10	2.41
Cu-Fe-K-M ₈₀	56	63	28	9	2.61
Cu-Fe-K-SS	54	42	43	15	0.73

3.5 The reaction mechanism for higher alcohols synthesis

As we all known, for the Cu-Fe based HAS catalyst copper is known to be the major element for methanol synthesis, facilitating the dissociative chemisorption of H₂ and the associative adsorption of CO. Iron element, especially for iron carbides are the active sites of Fischer-Tropsch synthesis, serving as the dissociative of CO and associative adsorption of H₂. Therefore, the production of higher alcohols requires the synergetic functioning of iron and copper. The reaction mechanism scheme for higher alcohols synthesis from syngas over the Cu-Fe supported bimodal catalysts is shown in Fig. 4, where * represents a vacant site and *R or R* indicates a molecule adsorbed on a site. The dissociation of H₂ and association of CO* on the surface of active copper sites induce the formation of methanol. The dissociation of CO* and association of H₂ on the surface of active iron species result in the formation of *CH_x, which moves to an adsorbed CO* to form (CH_x)_nCO*, and then to produce mixed alcohols via the hydrogenation reaction. The increase of surface area and decrease of bimodal support pore sizes shorten the distance

between Cu and Fe species and strengthen the synergistic effect of Cu-Fe, facilitating the insertion of CO* into the *CH_x species and promoting the formation of C₂⁺OH.

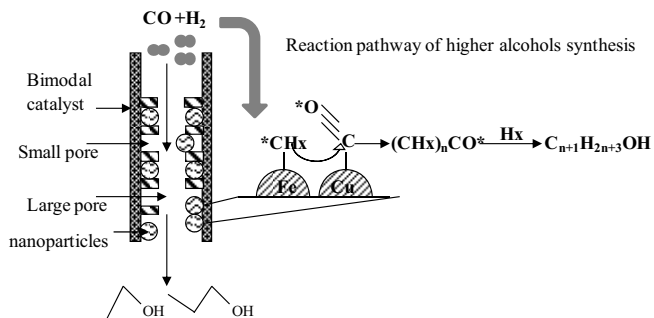


Fig. 4 The reaction mechanism scheme of HAS for the Cu-Fe supported bimodal catalysts

4. Conclusions

The Cu-Fe based catalyst prepared by the multi-functional silica-silica bimodal support exhibited excellent HAS performances due to the spatial and chemical effects of the bimodal support. The increase of BET surface area and decrease of bimodal support pore sizes improved the active bimetal dispersion and strengthened the Cu-Fe synergistic effect via the confinement of pore structures, promoting the catalytic activity for HAS and further shifting product distribution towards higher alcohols.

Acknowledgements

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Biography

Dr. Mingyue Ding, associate professor, Master Tutor, engaged in the study on the key technology of clean liquid fuels synthesis, system integration and engineering demonstration for biomass conversion into higher alcohols, ether and hydrocarbons.