Investigation on the Promotional Role of Ga₂O₃ on CuO-ZnO/HZSM-5 Catalyst for

CO₂ Hydrogenation

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Supporting information

TEM

Catalyst characterization

The surface morphology of the catalyst was characterized by the transmission electron microscope (TEM). TEM images were collected on a Hitachi HT7800 with an accelerating voltage of 100 kV.

Results and discussion

In order to obtain insight into the morphology of the catalysts, transmission electron microscopy (TEM) was conducted on the representative CZG_0H and CZG_5H samples. From the two sets of comparative catalyst TEM photos in Figure S4, it can be seen intuitively that the components in the catalyst exist in the form of aggregates, and the interface between the particles in the aggregates is blurred¹. As shown in Figure S4a, catalyst consists of particles with large spherical shapes, and the majority of them are clustered together. In contrast, individual separated oxide particles are easier distinguished on the sample CZG_5H , and particles are spherical and uniformly distributed (Figure S4b). The average diameter of the particles in the CZG_5H catalyst is much smaller ². TEM test results show that the addition of Ga makes the catalyst form highly dispersed. The TEM observations are consistent with the findings from XRD.

References

- 1 F. Chena, P. P Zhang, Y. Zeng, R. Kosola, L. W. Xiao, X. B Feng, J. Li, G. B Liu, J.H. Wu, G. H. Yan, Y. Yoneyamaa, N. Tsubakia, *Appl. Catal., B*, 2020, **279**, 119382.
- 2 D. Kima, G. Parka, B. Choib, Y. B. Kim, Int. J. Hydrogen Energy, 2017, 42, 29210-29221.

Figures and tables



Figure S 1 Carbon dioxide conversion rate of catalysts with different ${\rm Ga_2O_3}$ content



Figure S 2 Selectivity of catalysts with different ${\sf Ga}_2{\sf O}_3$ content



Figure S 3 CO₂-TPD patterns of the catalysts: a-CZG0H, b-CZG₅H.



Figure S 4 TEM images of the catalysts: a - CZG_0H; b - CZG_5H.

Table S1. Three groups of test results of catalyst

Catalysts	Sample 1	Sample 2	Sample 3	Mean	Standard Deviation
CZG₀H	18.6	18.3	18.7	18.5	0.2
CZG_1H	19.9	20.1	19.8	19.9	0.2
CZG₃H	20.8	21.3	20.7	20.9	0.3
CZG₅H	22.3	22.6	22.4	22.5	0.2
CZG ₁₀ H	21.3	21.5	21.0	21.3	0.2

Table S2. Reproducibility experiment of catalyst

Catalysts	Operator 1	Operator 2	Operator 3	Mean	Standard Deviation
CZG₀H	18.5	17.9	18.7	18.4	0.4
CZG_1H	19.9	20.0	19.7	19.9	0.2
CZG₃H	20.9	21.3	20.8	21.0	0.3
CZG₅H	22.5	22.8	22.1	22.5	0.4
CZG ₁₀ H	21.3	21.0	21.3	21.2	0.2

Table S3. The experimental error and reproducibility of Cu dispersion									
	Catalysts	Sample 1	Sample 2	Sample 3	Mean	Standard Deviation	Reproducibility		
-	CZG₅H	15.3	15.5	15.6	15.5	0.15	3	_	

Table S4. Peak area and distribution ratio of $\rm H_{2}\mathchar`-TPR$

Catalysts	T_{α}	T_{β}	$A_{\alpha}+A_{\beta}$	$A_{\alpha}/(A_{\alpha}+A_{\beta})$ %
CZG₀H	236	269	6282	53
CZG_1H	238	264	14463	57
CZG ₃ H	241	270	15694	63
CZG₅H	246	272	15849	69
CZG ₁₀ H	248	277	8107	30

Table S5. Peak area, peak temperature and distribution ratio of $\rm CO_2\mathchar`-TPD^{[a]}$

_	Weak		Medium		Strong					
catalysts	Aα	T_{α}	A _α /(A _T) %	A_{β}	T_{β}	A _α /(A _τ) %	Aγ	T_{γ}	Α _γ /(Α _τ) %	A _T
CZG₀H	218	207	18	919	421	74	99	589	8	1235
CZG₅H	192	247	23	463	397	54	195	535	23	850

[a] $A_{\alpha},\,A_{\beta},\,A_{\gamma},$ represent area of the corresponding sites, A_T represent total peak area.