Supplementary materials

Hydrogen production via steam reforming of methanol on $Cu/ZnO/Al_2O_3$ catalysts: Effect of TiO_2 addition mode

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Figure captions

Fig. S1 - The effect of TiO_2 content on (a) methanol conversion, (b) H_2 time-space yield and CO selectivity for fresh CZAT-x catalysts.

Fig. S2 - The comparison of methanol conversion between catalysts before and after thermal treatment.

Table S1 - Information on the composition of catalysts.

Table S2 - H_2-TPR parameters for catalysts.

Table S3 - Methanol conversion before and after thermal treatment.

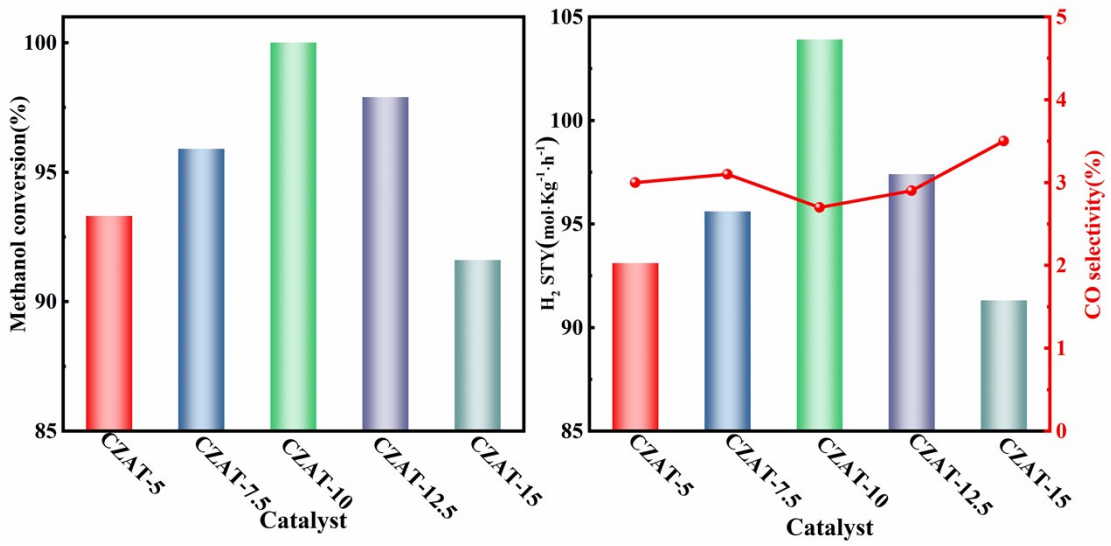

Fig. S1 - The effect of TiO_2 content on (a) methanol conversion, (b) H_2 time-space yield and CO selectivity for fresh CZAT-x catalysts.

Reaction conditions: 493 K, H_2O/CH_3OH= 1.2, $WHSV_{total}$ = 2 h^{-1}

From the experimental results, we can find that the activity of the catalyst shows a volcanic trend with the increase of TiO_2 content, in which CZAT-10 has the best catalytic activity. Therefore, the optimum TiO_2 incorporation in this work was found to be 10 w% of the total CZA catalyst.

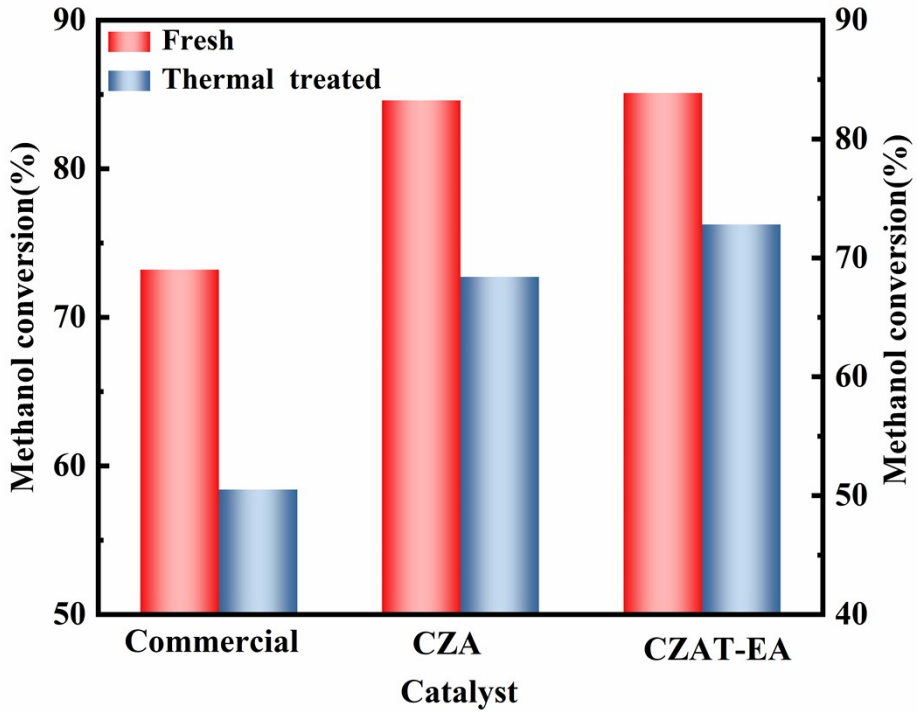

Fig. S2 -The comparison of methanol conversion between catalysts before and after thermal treatment.

Reaction conditions: 473 K, H_2O/CH_3OH= 1.2, $WHSV_{total}$ = 2 h^{-1}; thermal treatment conditions: 723 K, H_2O/CH_3OH= 1.2, $WHSV_{total}$ = 2 h^{-1},10 h.

Table S1 - Information on the composition of catalysts.

Catalysts	Mass fraction(%)							
	Theoretical composition(%)				Actual composition(%)[a]			
	CuO	ZnO	Al_2O_3	TiO_2	CuO	ZnO	Al_2O_3	TiO_2
CZA	65.0	22.0	13.0	-	64.8	21.7	13.5	-
CZAT-S	59.1	20.0	11.8	9.1	58.2	19.0	12.9	9.9
CZAT-D	59.1	20.0	11.8	9.1	57.8	18.9	12.9	10.4
CZAT-EA	59.1	20.0	11.8	9.1	58.6	19.0	12.6	9.8

[a]: Determined byXRF. $m_{(\text{Theoretical content of } TiO_2)} = m_{(CuO + ZnO + Al_2O_3)} \times 10\%$

The information of the chemical composition of CZAT-x catalysts, including the theoretical design values and the actual values obtained by XRF analysis, is listed in Table S1. The results of the XRF tests showed that the CuO, ZnO, Al_2O_3 and TiO_2 were very close to the theoretical design values. Minor differences in the values may come from mass loss during the preparation process and measurement errors.

Table S2 - H_2-TPR parameters for catalysts.

Sample	Temperature(℃)		H_2 consumption(mmol/g)		
	α	β	α	β	Total
CZA	230	254	3.10	4.98	8.08
CZAT-S	226	251	2.10	4.23	6.34
CZAT-D	223	250	1.98	4.35	6.33
CZAT-EA	212	239	1.85	4.61	6.46

As shown in Table S2, the hydrogen consumption of the catalysts followed the following order: CZA > CZAT-EA > CZAT-S ≈ CZAT-D. Among them, the CZA catalyst possessed the highest hydrogen consumption of 8.08 mmol/g, which indicated that it possessed more reducible oxygen species, which could be attributed to the higher CuO content of the CZA catalyst. The hydrogen consumption of the catalysts was positively correlated with the activity of the catalysts except for the CZA catalyst, in which the CZAT-EA had a higher hydrogen consumption, and its activity was better. The above results indicate that the TiO_2 effect is greater than the effect of CuO content when TiO_2 is introduced into in this system.

Table S3 - Methanol conversion before and after thermal treatment.

Catalysts	Fresh	Thermal treated	activity loss rates(%)
	X_{MeOH}(%)	X_{MeOH}(%)	
CZA	94.8	89.7	5.37
CZ	92.5	74.3	19.68

thermal treatment conditions: 723 K, H_2O/CH_3OH= 1.2, $WHSV_{total}$ = 2 h^{-1},10 h.
reaction conditions: 493 K, H_2O/CH_3OH= 1.2, $WHSV_{total}$ = 2 h^{-1}.

In our study, the focus was primarily on the influence of TiO_2 in a series of TiO_2-doped modified CZAT catalysts. In the corresponding characterizations, the absence of observable changes in aluminum-containing substances prevents us from directly concluding the role of Al_2O_3 in the CZAT system, while also acknowledging its potential impact.

To gain deeper insights into the influence of Al_2O_3, we conducted supplementary

experiments. In particular, we synthesized CZA and CZ catalysts and assessed their thermal stability by comparing methanol conversion before and after heat treatment under identical conditions (Table S3). The outcomes reveal that the CZA catalyst demonstrated notable thermal stability, exhibiting a lower rate of activity loss in comparison to the CZ catalyst.

The above results further indicate that Al_2O_3 plays an important role in improving the stability of the catalyst. This is consistent with the fact that in the $Cu/ZnO/Al_2O_3$ catalysts reported in the literature, Al_2O_3 is usually regarded as a structural additive due to its large specific surface area, and its presence can effectively inhibit the thermal sintering of the Cu particles during the reaction process, thus improving the stability of the catalytic materials[1, 2].

References

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[2] Behrens M, Zander S, Kurr P, et al. Performance Improvement of Nanocatalysts by Promoter-Induced Defects in the Support Material: Methanol Synthesis over Cu/ZnO:Al [J]. Journal of the American Chemical Society, 2013, 135(16): 6061-6068.