

# ZnO-In<sub>2</sub>O<sub>3</sub> solid solution hollow tube with different ZnO location improved CO<sub>2</sub> hydrogenation to methanol via the formate route

Yuchen Shi<sup>1</sup>, Weiguang Su<sup>1\*</sup>, Xinyu Wei<sup>1</sup>, Xudong Song<sup>1</sup>, Yonghui Bai<sup>1</sup>,  
Peng Lv<sup>1</sup>, Jiaofei Wang<sup>1</sup>, Guangsuo Yu<sup>1,2\*</sup>

*1 State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, China; 2 Institute of Clean Coal Technology, East China University of Science and Technology, Shanghai 200237, China*

*\*Corresponding author: weiguangsu@nxu.edu.cn; gsyu@nxu.edu.cn*

## Highlights

- ZnO on the wall of In<sub>2</sub>O<sub>3</sub> hollow tube promoted the creation of ZnO-In<sub>2</sub>O<sub>3</sub> solid solution.
- The solid solution strengthened electron transfer from Zn<sup>2+</sup> to In<sup>3+</sup>, promoting localized electron imbalance.
- Formate was intermediate species for methanol formation on ZnO-In<sub>2</sub>O<sub>3</sub> solid solution.
- The highest STY of methanol could reach 1.12 g<sub>MeOH</sub>h<sup>-1</sup>g<sub>cat</sub><sup>-1</sup> on ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst.

## 1. Introduction

Converting CO<sub>2</sub> into methanol could alleviate the greenhouse effect and realize the utilization of CO<sub>2</sub>. In<sub>2</sub>O<sub>3</sub> catalysts with methanol selectivity close to 100% have attracted wide attention of researchers. However, only 3-4% CO<sub>2</sub> conversion was obtained with 80% methanol selectivity on most In<sub>2</sub>O<sub>3</sub>-based catalysts. While precious metals could greatly improve methanol formation activity of In<sub>2</sub>O<sub>3</sub>, they were more costly. The ZnO-ZrO<sub>2</sub> solid-solution catalyst exhibited outstanding methanol yields<sup>[1]</sup>. The doping of trace amounts of ZnO in In<sub>2</sub>O<sub>3</sub> hollow tubes could increase the methanol activity because of formed ZnO/In<sub>2</sub>O<sub>3</sub> quantum dots heterojunctions<sup>[2]</sup>. Therefore, increasing the content of ZnO might be beneficial to improve methanol formation activity of In<sub>2</sub>O<sub>3</sub> catalysts, but there were little reports on ZnO/In<sub>2</sub>O<sub>3</sub> composite catalysts for CO<sub>2</sub>-to-methanol. Herein, catalysts of In<sub>2</sub>O<sub>3</sub> hollow tube with ZnO at three different positions (inside, outside and on the wall) were synthesized. The role of ZnO and ZnO location in In<sub>2</sub>O<sub>3</sub> hollow tubes on the catalytic performance of CO<sub>2</sub> hydrogenation to methanol was detailedly investigated.

## 2. Methods

54.26 mg Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.99%, Macklin) was dissolved in 5 mL methanol to which 401 mg MIL-68(In) was added. The mixture was stirred for 15 min and then evaporated to dryness, followed by vacuum drying at 60 °C for 3 h to form MIL-68(In)@Zn(NO<sub>3</sub>)<sub>2</sub> precursors. The catalyst of ZnO doped in the wall of In<sub>2</sub>O<sub>3</sub> hollow tube was synthesized by calcining the MIL-68(In)@Zn(NO<sub>3</sub>)<sub>2</sub> precursor at 500 °C for 2 h in air, named as ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall. The mass fraction of ZnO was 8%.

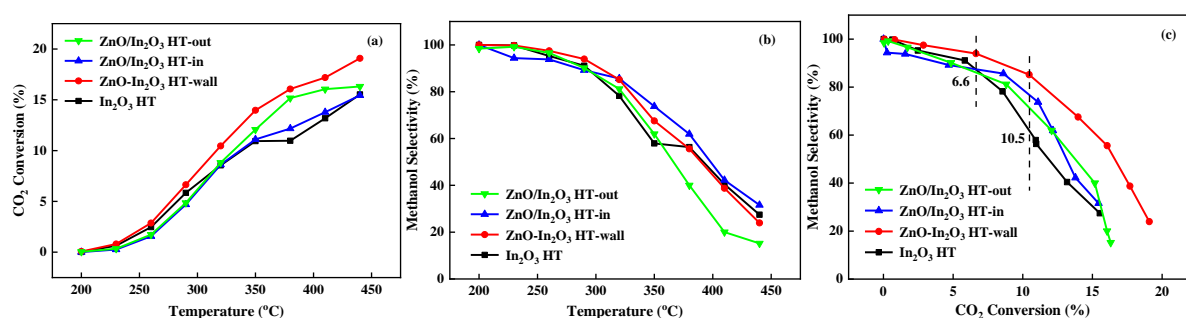
Temperature-programmed reduction of hydrogen (H<sub>2</sub>-TPR) and temperature-programmed desorption of CO<sub>2</sub> or H<sub>2</sub> (CO<sub>2</sub>-TPD or H<sub>2</sub>-TPD) were performed on a chemisorber (Micromeritics AutoChem II 2920). The morphology, mapping and high-resolution transmission electron microscopy (HRTEM) data was measured on a Talos F200X.

The reaction was operated in fixed bed reactor with 0.1 g catalyst. The catalyst was pretreated in N<sub>2</sub> at atmospheric pressure and purged for 1 h at 300 °C. The reaction gas (H<sub>2</sub>/CO<sub>2</sub> = 3/1) was fed into the reactor, at which time the reaction pressure, temperature and the gaseous hourly space velocity (GHSV) were 3 MPa, 200 °C and 33000 mL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, respectively.

## 3. Results and discussion

Figure 1 showed the catalytic performances of CO<sub>2</sub> hydrogenation on four In<sub>2</sub>O<sub>3</sub> catalysts. CO<sub>2</sub> conversion gradually increased with raising temperature, reaching 15.5% at 440 °C over In<sub>2</sub>O<sub>3</sub> HT catalyst. At the same temperature, CO<sub>2</sub> conversion on the three ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall, ZnO/In<sub>2</sub>O<sub>3</sub> HT-in and ZnO/In<sub>2</sub>O<sub>3</sub> HT-out solid solution catalysts was significantly enhanced compared to In<sub>2</sub>O<sub>3</sub> HT. Among them, the ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst had the highest CO<sub>2</sub> conversion, which could reach 19.2% at 440 °C. Methanol selectivity gradually decreased as the temperature increased. The methanol selectivity over ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall and ZnO/In<sub>2</sub>O<sub>3</sub> HT-in was slightly higher than that on In<sub>2</sub>O<sub>3</sub> HT at the same reaction temperature. The formation of ZnO-In<sub>2</sub>O<sub>3</sub> solid solution not only facilitated the adsorption and activation of CO<sub>2</sub>, but also promoted the conversion of CO<sub>2</sub> to methanol. The methanol selectivity diminished gradually with increasing CO<sub>2</sub> conversion. When the CO<sub>2</sub> conversion was higher than 6.6%, the variation trend of methanol selectivity was basically as follows: ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall > ZnO/In<sub>2</sub>O<sub>3</sub> HT-in > ZnO/In<sub>2</sub>O<sub>3</sub> HT-out > In<sub>2</sub>O<sub>3</sub> HT. The methanol selectivity on In<sub>2</sub>O<sub>3</sub> HT, ZnO/In<sub>2</sub>O<sub>3</sub> HT-out, ZnO/In<sub>2</sub>O<sub>3</sub> HT-in and ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalysts was 61%, 71%, 77% and 86% respectively at a CO<sub>2</sub> conversion of about 10.5%.

The ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst exhibited the highest methanol formation activity, because the structure of ZnO location on the wall of the In<sub>2</sub>O<sub>3</sub> hollow tube resulted in the highest electron density of oxygen vacancy on In<sub>2</sub>O<sub>3</sub> surface<sup>[3]</sup>, i.e., the best “quality” of oxygen vacancy, which was most conducive to CO<sub>2</sub> and H<sub>2</sub> activation. The formation of ZnO-In<sub>2</sub>O<sub>3</sub> solid solution enhanced the electron density of In<sub>2</sub>O<sub>3</sub> surface, and the electron transfer from Zn<sup>2+</sup> to In<sup>3+</sup> between ZnO and In<sub>2</sub>O<sub>3</sub> promote the local electron imbalance even more. ZnO boosted electron delocalization in surface lattice oxygen and increased the oxygen vacancy density. Hence, the formation of ZnO-In<sub>2</sub>O<sub>3</sub> solid solution was very beneficial to methanol generation.



**Figure 1.** Catalytic performances of CO<sub>2</sub> hydrogenation on In<sub>2</sub>O<sub>3</sub> catalysts. (200–440 °C, 3.0 MPa, and 33000 mL h<sup>-1</sup>g<sub>cat</sub><sup>-1</sup>)

#### 4. Conclusions

The effect of ZnO at three different positions (inside, outside and on the tube wall) on the catalytic performance of CO<sub>2</sub> hydrogenation to methanol over In<sub>2</sub>O<sub>3</sub> hollow tube was investigated. ZnO-In<sub>2</sub>O<sub>3</sub> solid solution could be further in-situ formed during reaction, especially the structure of ZnO on the wall of In<sub>2</sub>O<sub>3</sub> hollow tube was the most conducive to the generation of solid solution with Zn atom substituting In atom in In–O bonds. ZnO facilitated electron delocalization in surface lattice oxygen, which transferred and concentrated the electrons on surface oxygen vacancy to increase the electron density, especially for ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst. The “quality” of surface oxygen vacancy on ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst was greatly increased, which promoted the adsorption and activation of H<sub>2</sub> and CO<sub>2</sub>. CO<sub>2</sub>-to-methanol was produced via formate route, and formate was the intermediate species. ZnO-In<sub>2</sub>O<sub>3</sub> HT-wall catalyst exhibited the highest methanol formation activity with a methanol STY of 1.12 g<sub>MeOH</sub> h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>.

#### References

- [1] J. Wang, G. Li, Z. Li, C. Tang, Z. Feng, H. An, H. Liu, T. Liu, C. Li, *Sci. Adv.* 3 (2017) e1701290
- [2] Y.C. Shi, W.G. Su, X.Y. Wei, Y.H. Bai, X.D. Song, P. Lv, J.F. Wang, G.S. Yu, *J. Colloid Interf. Sci.* 636 (2023) 141–152
- [3] W. Wei, Z. Wei, R. Li, Z. Li, R. Shi, S. Ouyang, Y. Qi, *Nat. Commun.* 13 (2022) 3199

#### Keywords

CO<sub>2</sub> hydrogenation to methanol; ZnO-In<sub>2</sub>O<sub>3</sub> solid solution; ZnO location; formate species