

CO₂ hydrogenation over indium based catalysts:

Investigation of the various reaction pathway and the effect of SMSI

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Highlights

- CO₂ hydrogenation over In_x/ZrO₂ catalysts was thoroughly studied.
- Methanol selectivity increased with indium loading.
- High efficient In/TiO₂ catalyst with CO selectivity of 100%.
- Operando-DRIFTS was employed to investigate the intermediate and mechanism.

1. Introduction

Catalytic conversion of CO₂ to valuable products is of great interest, especially to methanol, which is vital to downstream process to generate alkane, olefin, dimethyl ether and other products. In addition, methanol is ready to be integrated into the existing liquid fuel transportation infrastructure as a direct energy source. Hence, catalytic conversion of CO₂ to methanol is potentially to relieve the global warming and energy problem. Recently, indium based catalytic system for CO₂ hydrogenation has been coming into the spotlight. The CO₂ conversion and methanol selectivity over bulk In₂O₃ reached 7.1% and 39.7%, respectively. Especially, both ZrO₂ supported indium catalysts and pure In₂O₃ with a selectivity of about 100% was reported. However, besides methanol, the CO was also observed over indium based catalysts.

On the basis of previous study, CO₂ hydrogenation over indium based catalysts showed two reaction pathways, i.e. RWGS reaction (reverse-water-gas-shift reaction) and methanol synthesis. However, less effort has been contributed to the study the mechanism beneath two reaction pathways over indium based catalysts. In this study, multiple-techniques were performed to identify the surface indium species and the origin of different products over indium based catalysts.

2. Methods

In_x/ZrO₂ catalysts were prepared by incipient-impregnation method, where x was denoted to the mass fraction of indium. A certain amount of In(NO₃)₃ was dissolved in ethanol and impregnated into ZrO₂ support. The slurry was dried over night at 110 °C and then calcined in air at 600 °C for 2 h with a ramping rate of 5°C·min⁻¹. Catalytic performance was evaluated using a continuous stainless steel fixed-bed micro-reactor with a length of 450 mm, an inner diameter of 6 mm and an external diameter of 8 mm, respectively. The reactor was pressurized using mixed gas (H₂:CO₂:N₂=15:60:25, 60ml/min) to 5.0 MPa, then the temperature was increased to 290 °C with a ramping rate of 1 °C /min.

3. Results and discussion

The catalytic performance of In_x/ZrO₂ catalysts is displayed in Figure 1. When the loading amount increased from 1wt% to 10wt%, the selectivity of methanol initially increased with the Indium loading amount to a maximum value of 63% for In₅/ZrO₂, and then decreased with further rise of Indium content. However, the selectivity of CO showed a contrary tendency. Moreover, the performance of indium catalysts with different supports was also evaluated. Especially, exhibited a CO selectivity of 100% was observed over In/TiO₂.

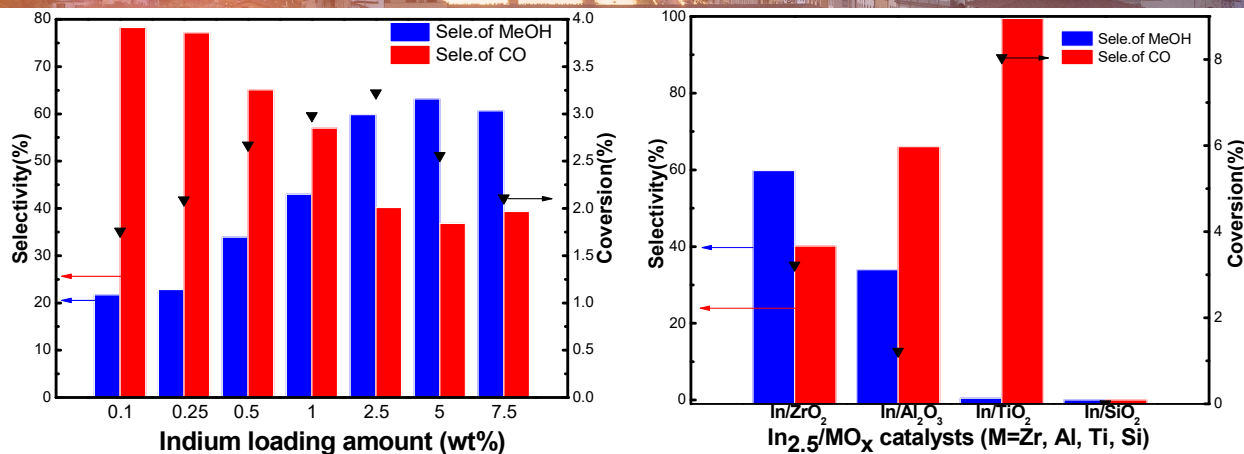


Figure 1. Catalytic performance of In_x/ZrO_2 catalysts with different loading amount (left), and indium catalysts with different supports (right).

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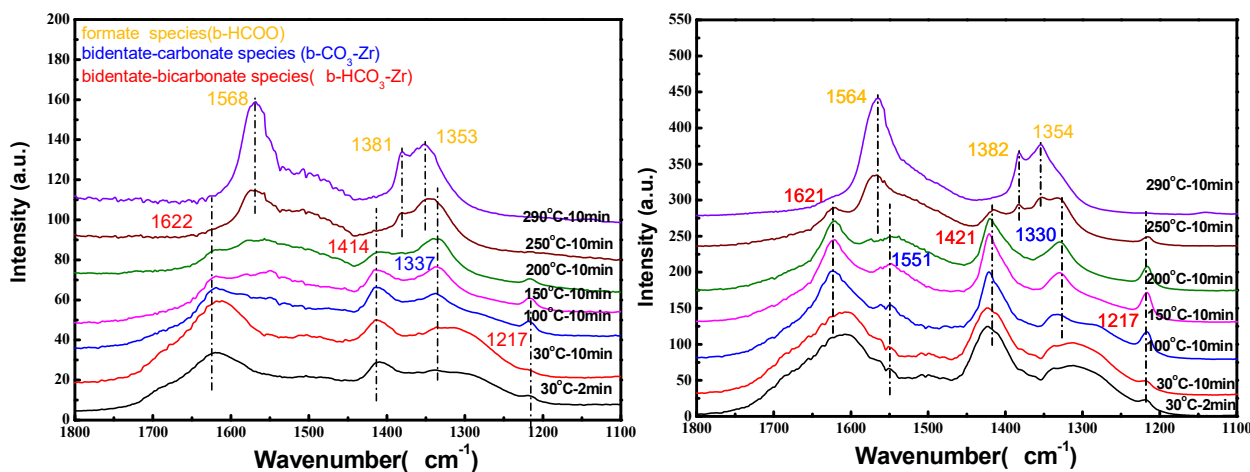


Figure 2. *in situ* DRIFTS spectra of $\text{In}_{2.5}/\text{ZrO}_2$ (left), and $\text{In}_{0.5}/\text{ZrO}_2$. Gas composition: 15% CO_2 , 60% H_2 and 25% N_2

4. Conclusions

On the basis of the characterization results, we believe that the surface indium species play important roles to manipulate product distribution in the CO_2 hydrogenation. Additionally, the interaction between support and indium is also a key factor to control the reaction pathway.

References

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Keywords

Indium; Operando-DRIFTS; SMSI; methanol