Direct Conversion of CO_2 into Methanol over Promoted Indium-based Catalysts

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Abstract: A strategy to enhance the selectivity over Indium oxide-based catalysts for direct conversion of CO_2 to methanol was investigated under mild reaction condition (528-573K, 40 bar). Surface reducibility, spectroscopic characteristics, and catalytic activity were correlated to catalyst composition. Promoted catalysts, especially Yttrium or Lanthanum-promoted indium oxide catalysts, showed much higher selectivity compared to the non-promoted catalyst.

Keywords: Methanol, Carbon dioxide hydrogenation, Indium oxide.

1. Introduction

CO_2 hydrogenation to methanol is potentially an important route to decrease CO_2 emissions: methanol is a versatile compound that can be used as fuel or as a precursor to many commodity chemicals. If a *green* (CO_2-free) H_2 source is used, the process is sustainable as demonstrated by the George Olah CO_2 to Renewable Methanol Plant in Iceland. This plant uses electricity, generated from hydro and geothermal energy, to make hydrogen. Although methanol synthesis from CO_2 and H_2 is exothermic, CO_2 conversion to methanol is kinetically limited at low temperatures and thermodynamically limited at high temperatures, resulting in a low theoretical methanol yield [12]. Cu-ZnO-Al_2O_3 (CZA) catalysts are currently employed for methanol synthesis from mixed syngas ($CO/CO_2/H_2$) in industry. However, these catalysts have low selectivity because of the competing reverse water–gas shift (RWGS) reaction, and limited stability, due to the sintering of the active surface. Recent DFT calculations have showed that the key intermediates involved in CH_3OH synthesis were more stable on a defective In_2O_3 surface than those on the Cu surface, strongly suppressing the formation of CO.[3] Supported indium oxide catalysts have been investigated as they are promising candidates for developing effective and stable catalyst with high selectivity towards methanol.

2. Experimental

In/ZrO_2, 0.15Sc-In/ZrO_2, 0.20Y-In/ZrO_2, and 0.20La-In/ZrO_2 were prepared from indium nitrate (Sigma-Aldrich, 99.99%), Scandium(III) nitrate (Sigma-Aldrich, 99.999%), Yttrium(III) nitrate tetrahydrate (Sigma-Aldrich, 99.99%), Lanthanum(III) nitrate hexahydrate (Sigma-Aldrich, 99.99%), and Zirconium(IV) oxide (Sigma-Aldrich, nanopowder, <100 nm particle size) via the wet impregnation method. A laboratory fixed-bed flow-reactor set-up consisting of mass flow controllers to feed H_2, CO_2, and He (Keen, ≥ 99.99%), a stainless steel reactor heated in a furnace and a back pressure regulator. Online gas chromatograph (Agilent, MicroGC 490) was used to monitoring the outlet gas composition.

3. Results and discussion

Figure 1 shows H_2-TPR profiles reduction peaks of In/ZrO_2, 0.15Y-In/ZrO_2, 0.20Y-In/ZrO_2, 0.25Y-In/ZrO_2 from 350K-800K: all dopants increase the reduction temperature (470K, 481K, 495K, and 505K, respectively). The higher loading of Yttrium oxide leads to the highest surface reduction temperature. Scandium and Lanthanum were also evaluated due to their similar ionic radius sizes and oxidation states. The catalytic selectivity of CO_2 to methanol reaction over In/ZrO_2, 0.15Sc-In/ZrO_2, 0.20Y-In/ZrO_2, and 0.20La-In/ZrO_2 (**Table 1**) generally decreased at higher temperature due to the competing RWGS reaction for all the catalysts. The selectivity of the non-promoted In/ZrO_2 at 573 K was 53%. Remarkably, by tuning the reducibility of the catalysts, ~15-20% higher selectivity toward methanol at all temperatures (528K-573K) is demonstrated over 0.20Y-In/ZrO_2 and 0.20La-In/ZrO_2. Lanthanum-incorporated catalyst also showed comparable methanol production rate: these appear to be promising candidates for practical use in the future.

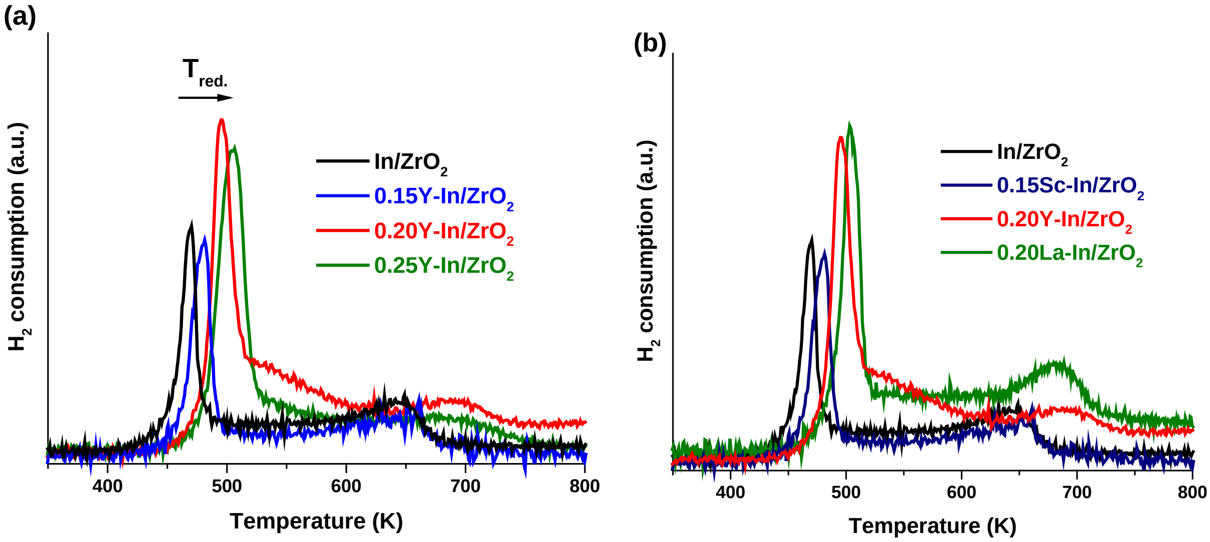

Figure 1. (a) H_2- TPR profiles of In/ZrO_2, $0.15Y\text{-}In/ZrO_2$, $0.20Y\text{-}In/ZrO_2$, $0.25Y\text{-}In/ZrO_2$ from 350K-800K. (b) H_2- TPR profiles of In/ZrO_2, $0.15Sc\text{-}In/ZrO_2$, $0.20Y\text{-}In/ZrO_2$, $0.20La\text{-}In/ZrO_2$ from 350K-800K.

Table 1. CO_2 conversion, methanol production rate, and methanol selectivity over In/ZrO_2, $0.15Sc\text{-}In/ZrO_2$, $0.20Y\text{-}In/ZrO_2$, $0.20La\text{-}In/ZrO_2$. Reaction conditions: P_{tot} = 40 bar, F_{tot} = 130 sccm, Catalyst loading = 0.15 g, GHSV = 4×10^4 $cm^3\,h^{-1}\,g_{cat.}^{-1}$.

Catalyst	Temperature (K)	CO_2 conversion (%)	MeOH selectivity (%)	MeOH production rate ($g_{MeOH}\,h^{-1}\,g_{cat.}^{-1}$)
In/ZrO_2	573	10.5	53	0.490
	558	6.0	65	0.385
	528	0.9	81	0.171
$0.15Sc\text{-}In/ZrO_2$	573	6.9	57	0.440
	558	3.4	66	0.313
	528	0.9	90	0.119
$0.20Y\text{-}In/ZrO_2$	573	6.0	72	0.370
	558	3.4	80	0.234
	528	1.2	100	0.072
$0.20La\text{-}In/ZrO_2$	573	9.0	66	0.400
	558	6.9	80	0.345
	528	1.7	100	0.147

4. Conclusions

A number of supported indium oxides with Scandium, Yttrium, or Lanthanum modifiers were synthesized and investigated. It was found that the reducibility of the indium oxide catalysts in a hydrogen atmosphere is correlated to methanol production rates and selectivity. The Y-promoted catalyst had higher surface reduction temperature compared to the supported indium oxide catalyst. Furthermore, the incorporation of Y and La increased the selectivity of methanol from CO_2 conversion significantly. A selectivity of nearly 100% can be achieved at 528K and 40 bar, a mild reaction condition compared to the commercial process (513-533K, 50-100 bar). These results show that this is a feasible method for the design of selective catalysts for sustainable methanol economy.

References

1. Porosoff, M. D., Yan, B. &Chen, J. G. *Energy Environ. Sci.* **9,** 62–73 (2016).
2. Goeppert, A., Czaun, M., Jones, J.-P., Surya Prakash, G. K. &Olah, G. A. *Chem. Soc. Rev.* **43,** 7995–8048 (2014).
3. Ye, J., Liu, C., Mei, D. &Ge, Q. *ACS Catal.* **3,** 1296–1306 (2013).