Supported indium oxide as a selective catalyst for carbon dioxide to methanol hydrogenation

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Abstract: Approaching the challenge of trying to tackle the global warming issue, carbon dioxide utilization as a C1 building block appears as a promising solution. A series of novel supported In oxide catalysts was prepared and employed in the selective carbon dioxide hydrogenation to methanol. In contrast to the benchmark Cu-ZnO-Al_2O_3 catalyst, In_2O_3 provides a high selectivity and less stability issues. The catalysts were prepared by different methods, including incipient wetness impregnation and dry ball milling. The influence of the support is thoroughly investigated.

Keywords: indium, carbon dioxide, methanol

1. Introduction

Carbon dioxide hydrogenation into a valuable feedstock carries a two-fold positive effect: i) reducing amount of CO_2 emitted into the atmosphere and ii) producing fine chemicals from an abundantly available C1 building block. Methanol is a chemical of a current high importance and demand. Traditionally it is synthesized using the benchmark Cu-ZnO-Al_2O_3 catalyst which faces selectivity limitations.[1] Recently, the group of Perez-Ramirez reported on In_2O_3 as a catalyst that features high selectivities to methanol and outstanding activity under industrially relevant conditions. [2] Herein we report on different oxides as carriers for In_2O_3, the influence of the support and preparation method on the reaction activity and selectivity is thoroughly discussed.

2. Experimental

A series of In_2O_3 supported on CeO_2, ZrO_2, V_2O_5 and Nb_2O_5 was prepared by incipient wetness impregnation (IWI) method using a Chemspeed robotic platform. A 0.5 M aqueous solution of $In(NO_3)_3$ was prepared and added dropwise into 1 g of a carrier in three steps, each of 0.38 ml. The powders were mixed after every solution addition, shaken and heated at 60°C during every step. IWI was followed by the calcination step at 450°C, static air for 7h.

Ball milled samples were prepared using planetary mill using 1 g of metal oxide, 90 mg of $In(NO_3)_3$ under the following conditions: 400 rpm, reverse mode for 12h, using 20g of zirconia beads.

Catalysts with loadings of 9 and 20% were prepared, which was confirmed by ICP-OES.

Carbon dioxide hydrogenation was performed on Flowrence® reactor system, using undiluted catalysts. The catalysts are first activated in N_2 at 300°C for one hour, then the reaction starts by supplying 50 bar of CO_2/H_2 (1:4) mixture.

3. Results and discussion

When zirconia was employed as a support for In_2O_3 ($In_2O_3@ZrO_2$) , the highest selectivity to methanol was achieved (ca. 60%) which is in the line with previous findings (Figure 1).[2] In_2O_3 supported on vanadium oxide gives the highest conversion of approximately 3.5%, although the main detected product is carbon monoxide. Three of the studied catalysts – $In_2O_3@CeO_2$, $In_2O_3@ZrO_2$ and $In_2O_3@Nb_2O_5$ – outperform the benchmark catalyst Cu-ZnO-Al_2O_3 which shows 2.1% conversion and 10.9% selectivity towards methanol.[2] Higher methanol selectivity over In_2O_3-based catalysts was attributed to the suppression of water gas shift reaction which is the major reaction over Cu based catalyst. In case of In_2O_3 catalysts, the drastic dependence of catalyst performance is the result of changes in both electronic and geometric properties due to different metal-support interactions.

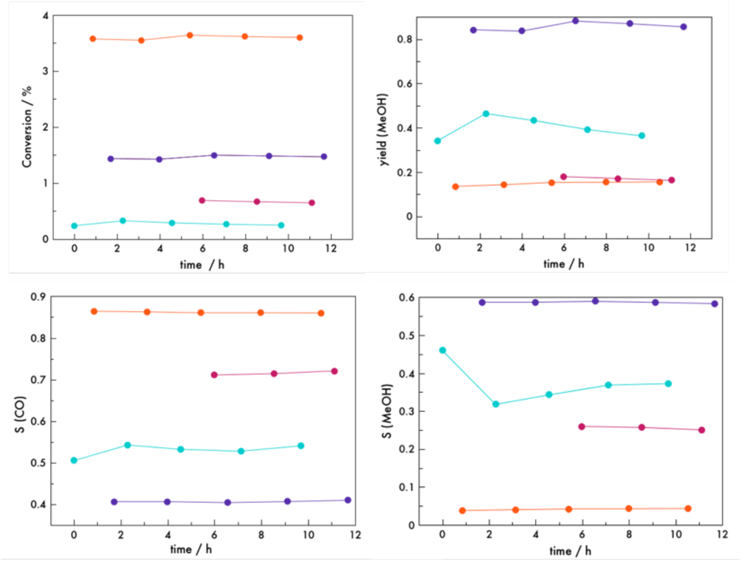
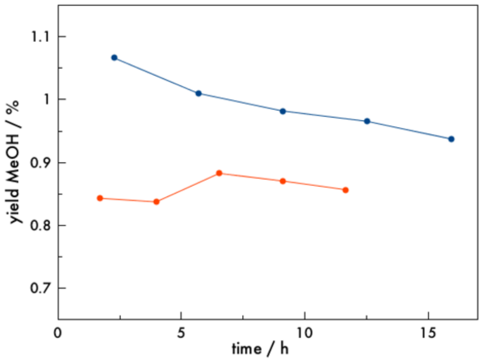


Figure 1. Conversion and selectivities to different products on $In_2O_3@ZrO_2$ ***(purple)***, $In_2O_3@V_2O_5$ ***(orange)***, $In_2O_3@CeO_2$ ***(green)***, $In_2O_3@Nb_2O_5$ ***(red)***.

Two different zirconia supported catalysts were prepared, one by incipient wetness impregnation, and the second by dry ball milling approach. The ball milled sample showed higher methanol yield, which can be explained by creating better dispersion of the active phase on the external surface, which appeared as a result of the milling procedure.

Figure 2. Methanol yield in carbon dioxide hydrogenation reaction using $In_2O_3@ZrO_2$ catalyst prepared by incipient wetness



impregnation (*red*) and dry ball milling (*blue*)

4. Conclusions

The chosen support has a dramatic effect on the performance of In_2O_3 in carbon dioxide hydrogenation. Both conversion and selectivity can be tuned by changing the carrier. CeO_2, ZrO_2 and Nb_2O_5 showed higher methanol selectivity than the commercial Cu-ZnO-Al_2O_3 catalyst. The method of preparation of the supported indium oxide also determines the catalyst's performance. Thus, In_2O_3 supported on zirconia via incipient wetness impregnation method showed lower yield of methanol than In_2O_3 prepared by dry ball milling.

References

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