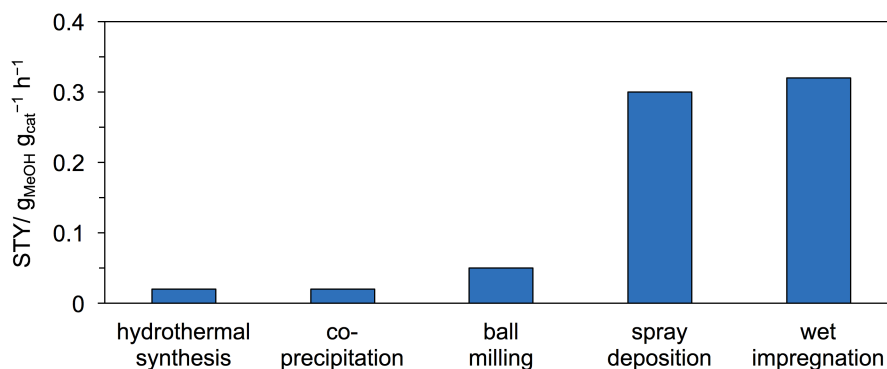


## Impact of degree of interaction and particle size on the efficiency of $\text{In}_2\text{O}_3$ -based catalysts for $\text{CO}_2$ hydrogenation to methanol

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In order to reduce anthropogenic  $\text{CO}_2$  emissions, the identification of routes in which carbon dioxide can be utilized as a chemical feedstock is a highly sought goal in the scientific community. One attractive approach comprises its hydrogenation to methanol, which serves as a fuel and a starting material for the manufacture of a multitude of chemicals. So far, only one commercial process for  $\text{CO}_2$ -based methanol production has been developed (Carbon Recycling International, 5 million liters in 2015),<sup>1</sup> since most of the heterogeneous catalysts investigated suffer from limited selectivity, mainly due to the competitive reverse water gas shift reaction, and/or short lifetime. Recently, we have introduced indium oxide (9 wt.%) supported on zirconia as a highly selective and extraordinarily stable material for this transformation.<sup>2</sup> In that study, we gathered evidence that the electronic interaction between the carrier and the active phase as well as the reaction conditions play a crucial role in the formation of selective active sites, *i.e.*, surface oxygen vacancies. Here, we aim at achieving a deeper understanding of this catalyst to improve its methanol space time yield. In order to vary the distribution and degree of contact between  $\text{In}_2\text{O}_3$  and  $\text{ZrO}_2$ , we applied various preparation methods, *i.e.*, wet impregnation, spray deposition, ball milling, hydrothermal synthesis, and co-precipitation. Preliminary tests under industrially-relevant temperature and pressure conditions showed that the first two protocols produce superior catalysts (**Figure 1**). Since XRD indicated that the particle size of  $\text{In}_2\text{O}_3$  is smaller in these solids, we are currently producing additional materials with variable In content to tune the dimensions of the  $\text{In}_2\text{O}_3$  crystallites. Characterization through a battery of state-of-the-art techniques will be coupled to the catalytic assessment to establish structure-performance relations and attain even more efficient materials.



**Figure 1** Space time yield (STY) of methanol in the direct hydrogenation of  $\text{CO}_2$  over  $\text{In}_2\text{O}_3$ - $\text{ZrO}_2$  catalysts prepared by different synthesis methods.

[1] <http://carbonrecycling.is/george-olah/2016/2/14/worlds-largest-co2-methanol-plant>

[2] O. Martín, A. J. Martín, C. Mondelli, S. Mitchell, T. F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferré, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2016**, 55, 6261.