

Catalytic heterogeneous route for the synthesis of dimethyl isosorbide using dimethyl carbonate as methylating agent

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The dimethyl isosorbide (DMI) is obtained by alkylation, and traditionally, alkylating agents such as methyl halides have been used, which present a series of drawbacks, such as toxicity and the high energy consumption associated with the production and the generation of VOCs. Recently the use of dimethyl carbonate (DMC) has been proposed as an alkylating agent. DMC, a genuinely green reagent, is a fascinating substitute of highly toxic phosgene for carboxylation reaction and methyl halides (or dimethyl sulfate) for methylation reaction [1] Generally, DMC can play the role of a methoxycarbonylating agent or a methylating agent with the presence of a nucleophile (Y⁻), intensively relying on the reaction condition simultaneously, e.g., the nature of catalyst and reaction temperature [1,2].

The use of dimethyl carbonate and a strong base excess at 90°C (Fig 1) provides selectivities to 100% DMI after 20 hours [2]. However, this catalytic process requires the neutralization and separation steps associated with most homogeneous catalytic reactions.

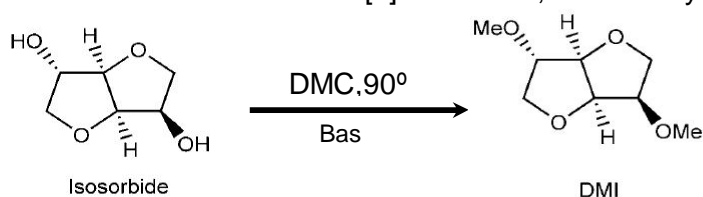


Figure 1. Synthesis of dimethyl isosorbide

The selectivity depends intensively on the properties of catalyst. As reported by Tundo [2], isosorbide could be quantitatively methylated by reacting with DMC in the presence of a strong base, which led mostly to the formation of carboxymethylated products in the presence of a weak base.

In this contribution a heterogeneous catalytic route is envisaged by using as catalyst MgAlO_x mixed oxides derived from hydrotalcite thermally treated (Mg/Al molar ratio of 3). The complete conversion of isosorbide is accomplished within the first hour but the DMI is not observed until 7 hours of reaction and its yield increases up to 100% after 24 hours of time on stream (Figure 2). The reutilization of the catalyst has shown a decline in DMI yield up to 52% after 4 runs even though the isosorbide conversion was of 100%.

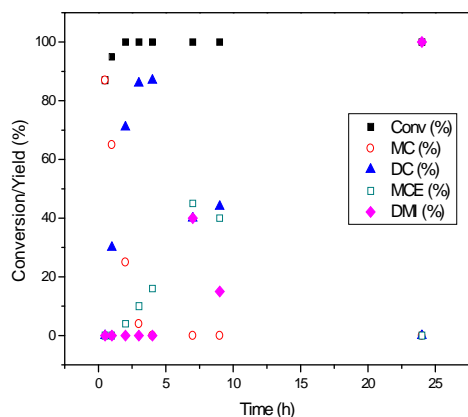


Figure 2. Isosorbide conversion and yield to reaction products. Reaction conditions: [iso] = 0.02 M; mass cat = 150 mg; Volumen reaction = 5 mL; 110°C; 24 h; 300 rpm.

REFERENCES

- [1] P. Tundo, M. Selva, *Acc. Chem. Res.* 35 (2002) 706-716.
- [2] P. Tundo, F. Aricò, G. Gauthier, L. Rossi, A.E. Rosamilla, H.S. Bevinakatti, R.L. Sievert, C.P. Newman, *ChemSusChem* 3 (2010) 566-570