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CO_2 Cycloaddition with Propylene Oxide using Bifunctional Halometallate Catalysts TBA[MCl_4]

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The transformation of carbon dioxide (CO_2) into value-added organic compounds is a very important research topic in green and sustainable chemistry because this greenhouse gas is an abundant, non-toxic, non-flammable, and renewable C1 feedstock. Among the various CO_2 fixation reactions, the carboxylative cycloaddition of CO_2 with epoxides stands out, as it allows the production of synthetically and biologically important five-membered cyclic carbonates from simple and accessible starting materials in a single step with 100% atom economy.[1]

In this work, we present the results regarding the synthesis, characterization, and study of catalytic properties for the cycloaddition of CO_2 with propylene oxide using bifunctional catalysts of the type TBA[MCl_4] (where TBA = tetrabutylammonium; M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) for the formation of propylene carbonate. The catalysts were obtained by direct addition synthesis between tetrabutylammonium chloride and a metal chloride salt in stoichiometric amounts in an ethanol solution,[2] and the formation of the [MCl_4]$^-$ anions was confirmed by high-resolution mass spectrometry.

Catalyst	Conversion (%)[a]	TON[b]	TOF[c]
$CoCl_2$x $6H_2O$*	39	1984	661
$[TBA]_2(MnCl_4)$	46	2282	761
$[TBA](FeCl_4)$	18	884	294
$[TBA]_2(CoCl_4)$	72	3875	1291
$[TBA]_2(NiCl_4)$	36	1838	612
$[TBA]_2(CuCl_4)$	0	0	0
$[TBA]_2(ZnCl_4)$	37	1858	619

Reaction conditions: 50 mmol PO, Catalyst (0.08 mol%), temperature (100 °C), $P_{[CO2]}$ = 10 bar, time (3 hours). [a]Conversion was estimated from the ^1H NMR spectrum of the reaction mixture. [b]TON = turnover number (moles of epoxide consumed)/(moles of catalyst). [c]TOF = turnover frequency TON . h^{-1}, *Cocatalyst (0,16 mol%).

With the exception of tetrabutylammonium tetrachlorocuprate(II), which did not lead to carbonate formation, all other catalysts resulted in the formation of propylene carbonate with 100% selectivity. Notably, tetrabutylammonium tetrachlorocobaltate(II) stood out as a catalyst, achieving 72% conversion in just three hours of reaction, especially when compared to the binary system containing $CoCl_2$ and TBACl, which only achieved 39% conversion. The bifunctional catalysts of the type TBA[MCl_4] proved to be promising in the synthesis of organic carbonates, notable for their simplicity and low cost of production.

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References

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