Influence of Al$_2$O$_3$ on the performance of CeO$_2$ used as catalyst in the direct carboxylation of methanol to dimethylcarbonate: elucidation of the reaction mechanism

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The direct carboxylation of alcohols to dialkylcarbonates (Eq. 1) is a topic of great interest due to the role played by the latter in the chemical and energy industry.

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2\text{ROH} + \text{CO}_2 \rightarrow (\text{RO})_2\text{CO} + \text{H}_2\text{O} \tag{1}
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Heterogeneous catalysts such as CeO$_2$, \textsuperscript{[1]} ZrO$_2$ \textsuperscript{[2]} or TiO$_2$ \textsuperscript{[3]} have been used but they suffer of a serious drawback represented by their de-activation due to a redox process occurring on the surface of the catalyst. Modification of ceria by loading alumina strongly reduces the oxidation of methanol and the consequent reduction of Ce(IV) to Ce(III) with increase of both the life of the catalysts and their selectivity. The combination of surface techniques (XPS and BET) with structural techniques (XRD) has allowed a good characterization of the working catalysts. Spectroscopic analyses (DRIFT and multinuclear solid state and solution NMR) have permitted the monitoring of the species formed on the surface of the catalyst and released from it. The formation of DMC takes place in successive steps such as (i) interaction of methanol with the catalyst surface with the formation of the surface-bound $^{-}\text{OCH}_3$; (ii) building on the catalyst surface of the hemicarbonate moiety [$^{-}\text{OCH}_3$–$^\text{OC(O)OCH}_3$]; and (iii) reaction of the latter with the gas-phase methanol to afford the organic carbonate. \textsuperscript{[4]}

References


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