



Oxidative coupling of methane over magnesium oxide

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Since the beginning of the oxidative coupling of methane (OCM) story, Lunsford et al.,¹ has put Li-doped MgO (Li/MgO) forward as a suitable and effective catalyst for OCM reaction. However, Li/MgO is suffering from lithium loss at the reaction temperature (about 800 °C).² [Li⁺O⁻] species have been supposed to be the active sites responsible for the conversion of methane in OCM reaction over Li/MgO,³ but there is no clear experimental proof of the presence of these sites under OCM relevant conditions. Finally Li/MgO catalysts contain always transition metal ion impurities like Mn²⁺, Mn⁴⁺, Fe³⁺, and Cr³⁺.⁴ Therefore, the role of [Li⁺O⁻] could be disputable.

On an other side, MgO is also able to catalyze OCM reaction with a comparable C₂₊ yield and even a better space time yield than Li/MgO.⁵ However, MgO as catalyst for OCM reaction was not yet studied systematically, but its catalytic results were only taken as reference for MgO-based catalysts. Beside, it was proven that low coordinated ions (LC) Mg²⁺_{LC}O²⁻_{LC}, present on edges, corners, steps and kinks of MgO surfaces are involved in the heterolytic dissociation of CH₄ into CH₃⁻ and H⁺ at room temperature.⁶ Beside, these LC ions can be thermal or photo activated, and they then give rise to an O⁻ center, which can homolytically dissociate methane into CH₃[·] radicals.^{6, 7}

For this reasons, we have studied the properties of MgO as catalyst for the OCM reaction. The aim of our work is to synthesize MgO free from impurities with different surface area and shape of the primary catalyst particles and then to establish a correlation between the concentration of LC ions on MgO and its catalytic activity in the OCM reaction.

MgO with polyhedral nano-sized primary particles have been prepared by sol-gel synthesis according to Klabunde et al.⁸ Starting from the Mg(OH)₂ gel, three different aerogels have been prepared by heating the gel in an autoclave at 265 °C and 70 bar, spray-drying and vacuum treatment at 50 °C. The obtained aerogels have been calcined in air at different temperatures between 700 °C and 800 °C. The microstructure

of the catalysts has been studied by electron microscopy. LC surface sites have been analyzed by photoluminescence, UV-Vis, and IR spectroscopy of adsorbed CO probe molecules. The surface properties of the fresh and used catalysts will be discussed in terms of the behavior of the catalysts in the OCM reaction.

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