



Activation of Oxygen - Key to the Oxidative Coupling of Methane (OCM) Reaction

Lukas Thum



Since the 1980's, many materials have been investigated as suitable catalysts for the OCM reaction with limited success so far. The major challenge is the direction of the reaction towards the desired higher hydrocarbons ethane and ethane (C_{2+}) while suppressing the thermodynamically favored deep oxidation towards carbon monoxide and carbon dioxide. The yield of 30% C_{2+} apparently represents an insurmountable barrier that has yet to be surpassed.¹ Non-reducible basic oxides such as alkaline earth oxides as well as rare earth oxides have been found as promising catalyst materials. Even though the bond dissociation energy of methane is large with 423 kJ/mol, controlling the activation



of oxygen is much more important to direct the selectivity towards the desired products. In case of basic non-reducible oxides, *e.g.*, CaO, the capability of the material to activate oxygen appears to be directly linked to the OCM reactivity, and it appears that the dissociation of O_2 is most likely the bottleneck of the reaction.² The strong basicity, which is needed for the reaction, is also a major weakness of those materials, forming stable hydroxides and carbonates. The latter are incapable of activating oxygen even at high temperatures². To improve the O_2 activation, electron-rich transition metal centers can be inserted into the alkaline earth host lattice, which provide electrons via tunneling to adsorbed oxygen lowering its dissociation barrier.³ First-row transition metal-doped calcium oxides were synthesized, characterized and tested in the OCM reaction. In a screening Zn, Ni and Mn were found to have a beneficial effect for the selectivity and activity in the OCM reaction, whereas Co and Cr dopants were found to be disadvantageous. The impact of the dopant is most effective in low doping concentrations (< 0.1 at%), showing a minimum in the apparent activation energy. At higher concentrations, clustering appears to reduce the efficiency. An increased line broadening in EPR signals due to dipole-dipole interactions is observed for Mn-doped CaO as well as a diminishment of the surface derived photoluminescence for the higher doped samples, indicating the generation of sites for non-radiative relaxation and therefore a significantly changed electronic surface structure.

¹U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, *ChemCatChem*, **2011**, 3, 1935.

²L. Thum, M. Rudolph, R. Schomäcker, Y. Wang, A. Tarasov, A. Trunschke, R. Schlögl, *The Journal of Physical Chemistry C*, **2019**, 123, 8018.

³N. Nilius, H.-J. Freund, *Accounts of Chemical Research*, **2015**, 48, 1532.