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## MgO as Model Catalyst in Oxidative Coupling of Methane

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### Motivation

Oxidative coupling of methane (OCM) to produce ethylene and ethane has been studied over a number of chemically and structurally different mixed metal oxides. One prominent example is Li-doped MgO, where lithium has been proven to act mainly as structural promoter that changes the morphology of the primary MgO particles depending on the initial lithium content<sup>1</sup>, which is in agreement with the attribution of OCM activity to high index planes, like the (110) or (111) plane of MgO.<sup>2</sup>

### Approach

To improve the fundamental understanding and to elucidate relations between surface defects such as low coordinated O<sup>2-</sup> ions or metal ions on the MgO surface and the catalytic properties in OCM, ultra-pure MgO has been chosen as a model system. The aim of the present work is to study the morphological sensitivity of the OCM reaction over MgO catalysts prepared by different methods. The microstructure of the catalysts before and after OCM was analyzed by electron microscopy. The concentration of low coordinated ions present on steps, edges, corners and kinks was determined by photoluminescence and IR spectroscopy.

### Results and discussion

Five different preparation methods were applied to synthesize MgO with varying morphology ranging from large cubic to defect-rich nano-particles. HRTEM clearly shows the presence of edges, steps, and corners in different concentration on the fresh catalysts with a specific surface areas ranging from 10 to 180 m<sup>2</sup>/g and a mean crystallite size determined by XRD ranging from 10 to 65 nm.

The calculated deactivation rates correlate with the stability toward sintering of the primary MgO particles in presence of steam at high temperature. All used catalysts are composed of large particles of similar size (surface area of ca. 10 m<sup>2</sup>/g and mean crystallite size of ca. 70 nm), but the morphology ranges from truncated cubic particles to almost completely round particles exposing higher mean index planes like (111) and (110). Morphological modifications during the OCM reaction are in

agreement with a Wulff profile suggested in an etching study of MgO in wet atmosphere.<sup>3</sup>

With increasing time on stream, the concentration of low coordinated ions on the catalyst surface decreases as observed by CO adsorption studied with infrared spectroscopy and by photoluminescence (PL) spectroscopy. Two-dimensional PL scanning was used to determine the  $\lambda_{\text{exc}}\text{-}\lambda_{\text{em}}$  wavelength couples characteristic for different species. This procedure reveals new bands not yet reported in the literature.<sup>4</sup> The assignment of these bands is discussed comprising knowledge attained by TEM and IR spectroscopy. Adsorption of methane causes the formation of hydroxyl bands around  $3750\text{ cm}^{-1}$  indicating that hydrogen abstraction occurs on MgO even in absence of UV-Vis irradiation and at low temperature.

Fresh catalysts achieve 100 % oxygen conversion and a  $\text{C}_{2+}$  yield of 12 %. The  $\text{CO}_2/\text{CO}$  and  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$  ratios correspond to 3 and 2, respectively. Kinetic studies were performed under steady state operation (after ca. 200 h TOS), where the activation energy for methane conversion was found to vary from 100 to 155 kJ/mol. The  $\text{C}_{2+}$  selectivity increases with increasing  $\text{CH}_4$  conversion, indicating an influence of the actual oxygen partial pressure and the gas phase chemistry on the OCM reactivity. The reaction order differs between 0.7 and 1 for oxygen and between 0 and 0.4 for methane indicating that the abstraction of a hydrogen atom from methane to form a methyl radical may not be the rate determining step in the OCM reaction over MgO.

## Conclusion

The OCM reaction on pure MgO is structure sensitive. Low coordinated ions are present on the fresh catalyst in relative high concentration. These sites are able to activate methane at low temperature yielding high methane and oxygen conversion and good  $\text{C}_{2+}$  selectivity at the beginning of the reaction, while at prolonged reaction times, gas phase contributions become more significant. Strategies for stabilization of the active sites on the surface of the MgO nanoparticles will be discussed.

## References

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