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## MgO as Model Catalyst in Oxidative Coupling of Methane

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### Motivation

Li/MgO has been reported to be an efficient catalyst in the oxidative coupling of methane (OCM) to ethane and ethene.<sup>1</sup> Zavyalova et al.<sup>2</sup> have shown that lithium acts as a flux during calcination leading to morphological transformation of the MgO particles depending on the initial Li content. This study is consistent with the attribution of OCM activity to high index planes, like the (110) or (111) plane of MgO.<sup>3</sup>

### Approach

The aim of the present work is to study the sensitivity of the OCM reaction toward the morphology of pure MgO catalysts and to analyze relationships between surface defects and the catalytic activity. The microstructure of the catalysts before and after OCM was studied by electron microscopy. The concentration of low coordinated ions present on steps, edges, corners and kinks was determined by photoluminescence and IR spectroscopy including the adsorption of CO and CH<sub>4</sub> as probe molecules.

### Results and discussion

Various preparation methods, such as sol-gel synthesis, combustion of metallic Mg, hydrothermal post-treatment and microwave hydrothermal treatment of a commercial MgO have been applied resulting in materials with specific surface areas ranging from 17 to 177 m<sup>2</sup>/g and particle sizes (XRD) ranging from 15 to 65 nm. The particle morphology changes from cubic (combustion) to defect-rich nano-particles (sol-gel synthesis). High resolution TEM clearly shows the presence of edges, steps and corners in different concentration.

The catalysts differ in their OCM performance and deactivation rate. The catalysts deactivate over a period of 200 h, after which steady state is achieved. During this deactivation phase, the catalyst particles experience strong morphological changes where all samples have a tendency to sinter into larger and smoother particles with less defects observable on their surface. Catalyst deactivation is concurrent with the contraction of the MgO unit cell and the disappearance of mono-atomic steps on the surface.

Kinetic studies were performed on the five MgO catalysts under steady state operation, where the activation energy was found to vary from 100 to 155 kJ/mol. Surprisingly, the C<sub>2+</sub> selectivity increase with increasing CH<sub>4</sub> conversion, indicating a probable influence of the gas phase on the OCM reactivity.

FTIR experiments shown, that CH<sub>4</sub> interacts on the MgO surface with a Lewis acid-base pair (Mg<sup>2+</sup><sub>LC</sub>O<sup>2-</sup><sub>LC</sub>). In the presence of CO, CH<sub>4</sub> interacts weakly only with basic O<sup>2-</sup><sub>LC</sub> sites. Used catalysts exhibit a larger proportion of sites available for CH<sub>4</sub> adsorption in the presence of CO, as fresh catalyst, probably due to the formation of high index planes on restructured particles (e.g. for commercial MgO catalysts, 5% before reaction and 30 % after reaction). The formation of hydroxyl bands around 3750 cm<sup>-1</sup>, indicate that the hydrogen abstraction occurs on MgO even in absence of UV-Vis irradiation and at low temperature. Adsorption of CO molecules on MgO allows the discrimination of low coordinated magnesium ions present on terraces, edges and corners.

3D photoluminescence spectroscopy of MgO shows new bands not previously reported in the literature.<sup>4</sup> On used catalysts, the band attributed to edges and corners disappear, due to sintering and smoothing of the particles during the deactivations phase, in agreement with FTIR and TEM results.

### Conclusion

The OCM reaction on pure MgO catalyst is structure sensitive. Low coordinated ions present on fresh catalyst at relative high concentration are responsible for the high methane and oxygen conversion and good C<sub>2+</sub> selectivity at the beginning of the reaction. After some time on stream, the nanoparticles become larger and smoother, changing in tandem with the observed reactivity, i.e. the activity drops and the contribution of gas phase reactivity become more significant.

### References

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