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MgO catalysts for the OCM reaction: Synthesis, structure defects and reactivity

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Introduction

Lunsford et al. have studied lithium doped magnesium oxide (Li/MgO) since 1985 as a suitable and effective catalyst for the OCM reaction. In Li/MgO, [Li⁺O⁻] species have been supposed to be the active sites responsible for the conversion of methane.¹

However, Zavyalova et al.² suggest recently that the Li content in the Li/MgO precursors induce a change in shape after calcination from cubic via truncated octahedral to platelet morphologies with high-index faces exposed, accompanied by an almost complete loss of Li. This conclusion is consistent with the work of Hargreaves et al.³. They have found that the most selective MgO is characterized by a greater proportion of higher index mean crystal planes, e. g. {111} surfaces.

The aim of our work is to synthesize MgO with varying abundance of coordinatively unsaturated sites on the surface and to analyze relations between surface defects and the catalytic activity of MgO in the OCM reaction.

Experimental

MgO with different primary particle morphology has been prepared according to 5 different preparation methods: precipitation of Mg(NO₃)₂ with NaOH (P-MgO) and Na₂CO₃ (B-MgO), sol-gel synthesis (SG-MgO), hydrothermal post treatment of MgO in a microwave autoclave (HT-MgO) and smoke MgO (S-MgO). These materials were compared with ultra pure MgO (99.998% m. b.) purchased from Alfa Aesar (C-MgO). The precursors were calcinated at 850 °C for 3 hours, heating rate 5 °C/min, in a flow of 20 % O₂/80 % Ar. Coordination and concentration of low coordinated ions have been analyzed by TEM, photoluminescence, UV-Vis and IR spectroscopy of adsorbed CO. The catalytic activity of the catalysts in the OCM reaction has been tested at 750 °C and a contact time of 0.05 g.s/ml in a plug flow reactor set up equipped with GC analytics applying a feed composition (CH₄/O₂/N₂) of 4/1/4.

Table 1: Correlation between selectivity and catalysts structure.

Sample	cube length (nm)	relative surface defect	X _{CH₄} (%)	S _{C₂} (%)
S-MgO	100	-	0.6	70.7
P-MgO	100	+	0.7	53.3
B-MgO	50-25	-	1.4	54.8
HT-MgO	25	+	1.5	38.6

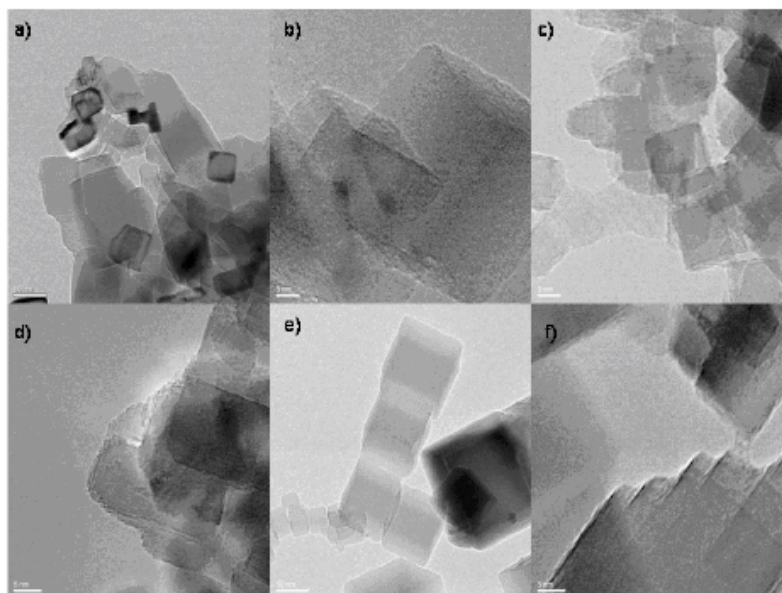


Figure 1: TEM of (a) P-MgO, (b) B-MgO, (c) SG-MgO (d) HT-MgO, (e) S-MgO and (f) C-MgO.

Results and discussion

The TEM pictures of the catalysts prepared by different synthesis methods show different morphology from perfect cubic for S-MgO to highly defected structures for HT-MgO or SG-MgO (see Fig. 1). The size of the particles is varying from ca. 100 nm to ca. 10 nm. The first catalytic results show that for the same methane conversion in steady state (S-MgO/P-MgO and B-MgO/HT-MgO) the C₂ selectivity is better for catalysts that exhibit the lowest amount of steps and kinks observed by TEM (see Tab. 1 and Fig.1).

Analysis of the used catalysts is in progress in order to verify whether the precursor structure is preserved during OCM reaction.

References:

1. Driscoll, D. J. et al., *JACS* **1985**, 107, (1), 58-63.
2. Zavyalova, U. et al., *ChemCatChem* **2010**, submitted.
3. Hargreaves, J. S. et al., *Journal of Catalysis* **1992**, 135, (2), 576-595.