

Are Li/MgO and Gd-Li/MgO suitable Catalysts for Methane Coupling?

Sebastian Arndt^{1*}, Ulla Simon¹, Stephan Heitz¹, Torsten Otremba¹, Almuth Berthold¹, Yilmaz Aksu¹, Klaus Peter Dinse², Matthias Driess¹, Helmut Schubert¹, Reinhard Schomäcker¹

¹Technical University Berlin, Berlin, 10623, Germany

²Free University Berlin, Berlin, 14195, Germany

*arndt@chem.tu-berlin.de

Introduction

The known resources of natural gas are large. Therefore, the direct conversion of the main component CH₄ is of strong economical interest [1]. A possible process is the oxidative coupling of methane (OCM), but up to now, this process has not been put into practice, due to a lack of active and selective catalysts. Li/MgO is discussed as a potential catalyst for a commercial application, however, the experimental basis for this conclusion is weak and there are too many unknown facts about this material.

Experimental

Li/MgO has been prepared with different loadings of Li via decomposition of single source precursors, wet impregnation, precipitation and mixed milling. Moreover, Gd-Li/MgO was prepared via a precipitation method, as doped Li/MgO is supposed to have improved properties as compared to undoped Li/MgO.

The catalytic activity for the OCM was determined with a packed-bed reactor for long times on stream to investigate the stability. A detailed structural analysis (XRD, BET, AAS, solid state NMR, partially EPR, TEM and SEM) was performed for selected materials to investigate the changes of the catalyst during the course of the reaction.

Results/Discussion

The initial activity of all prepared Li/MgO samples varies strongly. After 40 hours time on stream, none of the catalysts has reached a steady state, however, the variations were strongly reduced for all materials, indicating that in steady state the activity is approximately the same for all samples, irrespective the preparation procedure. The initial (after 0.3 h) and residual (after 40h) activity is shown in Figure 1, pointing out the diminished variations in the

performance of the catalyst. This intrinsic instability of Li/MgO excludes it from any technical application as OCM catalyst.

A detailed structural analysis revealed that that Li contents higher than 0.03 wt% are not stable and the loss of Li occurs heaviest within the first three hours time on stream. The studied structural changes (Li-content, crystal structure, particle size) did not correlate with the decrease of activity, indicating that the deactivation of Li/MgO follows a rather complex mechanism.

Doping with Gd, did lead to an improved catalyst, regarding the performance. However, also Gd-Li/MgO deactivates and suffers from a loss of Li, despite the fact, that the Gd is integrated into the MgO lattice, as it could be shown with EPR spectroscopy. That indicates, that doping of Li/MgO with transition metal oxides or rare earth oxides, also does not improve the properties sufficiently in order to enable a technical application.

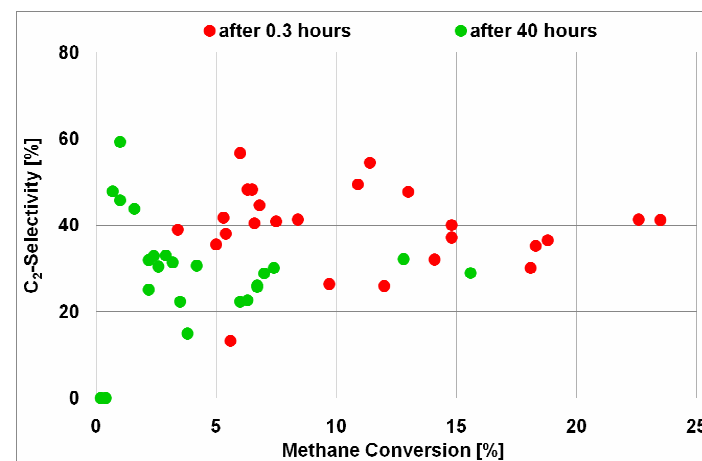


Figure 1. Initial and residual activity of materials from different preparation procedures.

References.

1. J.H. Lunsford, Catal. Today, 63, 165 (2000).