

Characterization of hydrotalcite materials for CO₂ selective membranes

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1 Introduction

The present concern about climate change has urged researchers and engineers all over the world to go and look for ways of reducing greenhouse gas emissions. Large-scale CO₂ emissions occur at power plants burning fossil fuels or e.g. the production of hydrogen from carbonaceous feed. In these cases pre- or post-combustion CO₂ capture techniques followed by CO₂ storage seems a promising route for reducing emissions. Prerequisite in these processes is the effective separation of CO₂ from mixed gaseous process streams. The purpose of this work is to develop CO₂ membranes to allow for the combination of natural gas reforming with separation of H₂ and CO₂ in separation enhanced reactors, i.e. membrane reactors, for carbon-free hydrogen production or electricity generation.

This paper describes the materials' properties of hydrotalcites, a promising class of compounds for CO₂ membranes. They have already proven their applicability as CO₂ sorbent in sorption enhanced reaction processes [1]. It is of fundamental importance to know the structural stability of this compound in the operational window of a chosen membrane reactor prior to any membrane fabrication. To this end, *in-situ* XRPD and DRIFTS as well as TGA-MS and SEM-EDX measurements have been performed on commercial (Pural) and hydrothermally synthesized homemade samples.

2 Experimental

2.1 Materials and methods

Hydrotalcites are clay-like materials with the general formula $M_6^{2+} M_2^{3+} (OH)_6 CO_3 \cdot 4H_2O$. The composition with Mg-Al is believed to be the most stable one with respect to temperature [2]. Important parameters are compositional range (Mg/Al), crystallinity, stability and decomposition temperature.

In order to determine these properties, commercial Pural MG30, 50, 61 and 70 (Mg/Al = 0,30; 0,50; etc.) and self-hydrothermally synthesized materials have been investigated.

The Pural materials have been used as received and the homemade materials with Mg/Al ratios of 1:1, 1:3 and 9:1 have been hydrothermally prepared in an autoclave (Büchiglasuster limbo 400) at 180°C for 2h and under 13 atm [3].

XRPD patterns of commercial and homemade compositions were recorded on a XRD apparatus (Bruker axis D8 filtered Cu-K α -radiation) at room temperature in order to investigate the crystallinity and the compositional range (Mg/Al) for hydrotalcites. *In-situ* XRPD patterns were recorded on MG50 from room temperature to 450°C under N₂ in a humidified atmosphere RH= 3,5% with and without CO₂ to identify the decomposition temperatures and the influence of CO₂.

DRIFT (Diffuse Reflectance Infrared Fourier Transformed) spectra have been recorded using a Harrick Praying Mantis with a high/low pressure reaction chamber on

MG50 from room temperature to 450°C under N₂ in humidified atmosphere RH= 3,5% with and without CO₂. These experiments were also meant to learn about decomposition conditions and temperature.

TGA (851° Mettler Toledo TSO800GC1 Gas control) attached with a mass spectrometer (MS, Pfeiffer Vacuum) was used to link weight loss of MG50 to decomposed species and to find the decomposition reactions.

SEM imaging (JEOL JSM -6330F) was to look at the microstructural aspect of all the samples and EDX analysis (Thermonoran Vantage 2.4.2 system) was used to reveal the composition of the different compounds formed in the Mg90 hydrothermal synthesis.

2.2 Results

The XRPD patterns of commercial and homemade compositions show that there are no big differences between the patterns apart from the crystallinity, which is much higher for the homemade materials than for the commercial ones. The line broadening is due to amorphicity rather than to particle size effects. Furthermore both homemade and commercial materials contain impurities (figure 1 and 2). The more Aluminium has been used the more Al-impurities are present and *vice-versa* with Mg content. The minimum amount of impurities exists for

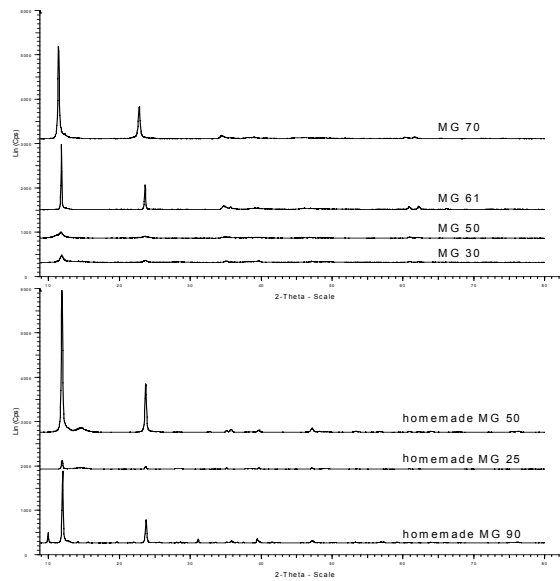


Figure 1: XRPD patterns of Pural (up) and homemade materials (underside)

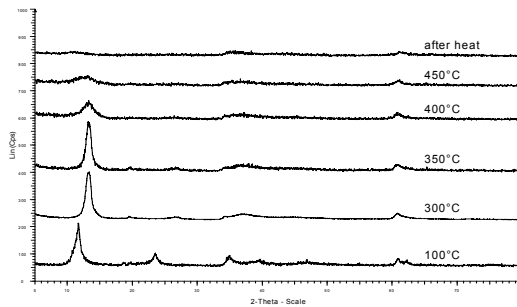


Figure 2: in-situ XRPD patterns of MG50 as a function of temperature

Mg/Al \approx 0,65. In-situ XRPD as a function of temperature show that at 450°C the hydrotalcite structure is fully gone and that it is not recovered after cooling down in a humidified N₂ flow. This is contrary to findings by others [4,5] that a so-called structural memory effect exists on rehydration in humid air.

DRIFTS measurements show that the presence of 0,1 atm of CO₂ during the experiments stabilizes the hydrotalcite structure to somewhat higher temperatures in the order of 25°C in conserving more carbonate interlayer (1360cm⁻¹) and giving less magnesium carbonate (1420 cm⁻¹).

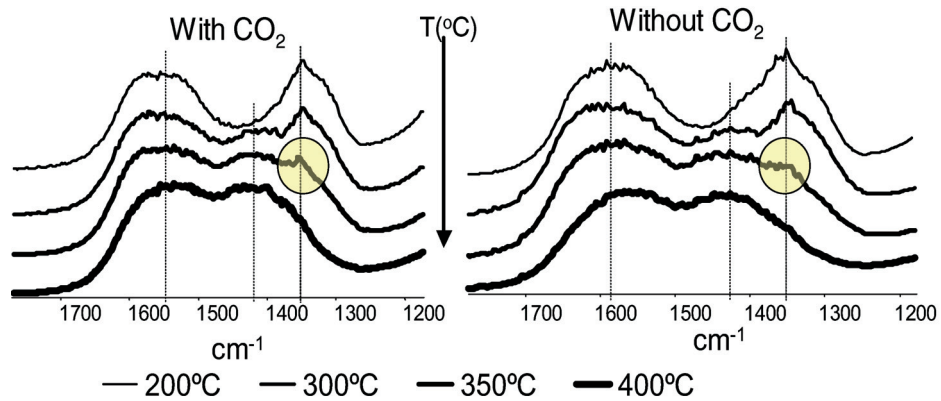


Figure 3: Pural MG50 DRIFT spectra as a function of temperature with and without CO₂

TGA-MS studies on Pural MG50 material confirm that at increasing temperature the hydrotalcite decomposes in four steps and is fully gone above 450°C. Up to 350°C only water, while above this temperature also CO₂ evolves.

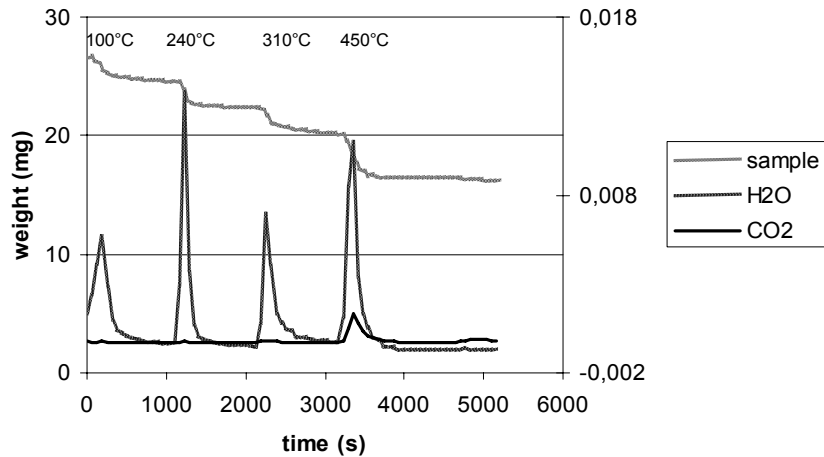


Figure 4: Pural MG50 TGA/MS study

SEM-EDX analysis of a hydrothermally made Mg90 reveals that apart from very Mg-rich phases a hydrotalcite phase is present with about 60% Mg.

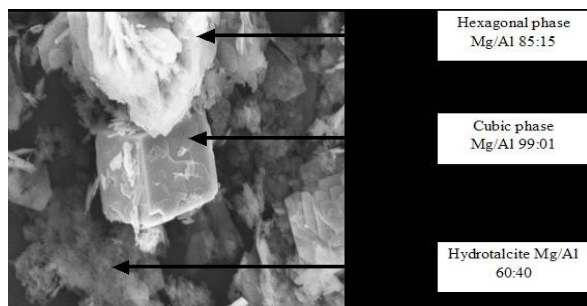


Figure 5: EDX picture of homemade Mg90

3 Discussion and conclusions

Commercial and homemade hydrotalcites seem to exist in a rather narrow phase width, where Mg/Al is about 65%. Large deviations invariably lead to the formation of impurity phases being either Mg or Al rich. Hydrothermal synthesis always gives more crystalline materials than the Pural commercial ones. The often reported 'structural memory effect' could not be reproduced in using a wet atmosphere. This does not mean that the sorption characteristics cannot be recovered. The active species are presumably just the hydroxyl groups and not the structure as such. The operational window for hydrotalcite as a membrane material is limited to 400°C. Since this is the target temperature for our membrane reactor (i.e. water gas shift) process this means that hydrotalcites are a viable option as a membrane material. It is still unknown whether hydrotalcites show bulk diffusion of CO₂, which opens the possibility of using dense membranes with high selectivity.

Acknowledgements

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References

- [1] H.T.J. Reijers, S.E.A. Valster-Schiermeier, P.D. Cobden, R.W. van den Brink. *Ind & Eng Chem Res*, **45**, 2522 (2006)
- [2] M. Tsuji. *Mat.Res.Soc.*, **8**, 1137 (1993)
- [3] M.M. Rao, B.R. Reddy, M. Jayalakshmi, V.S. Jaya, B. Sridhar. *Mat.Res.Bull.*, **40**, 347 (2005)
- [4] K.L. Erickson, T.E. Bostrom, R.L. Frost. *Mat.Let*, **59**, 226 (2005)
- [5] T. Stanimirova, G. Kirov. *Sofia U. Geology Directory 1*, **92**, 121 (2000)