Advanced Membrane Reactors: Applicability of Hydrotalcites as CO₂ Selective Membranes

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Introduction
Global warming increased a lot these last decades mostly due to greenhouse gases effect like CO₂. The aim of this work is to selectively separate and capture CO₂ from SR/WGS gas mixtures. Hydrotalcites are known to be good adsorbents for CO₂ and the aim of this presentation is to show whether or not this material is suitable as a CO₂ selective membrane in the presence of hydrogen at around 400°C. The reactions involved are the following:

Steam Reforming: \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \)

Water Gas Shift: \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \)

Stability
- a) When temperature increases the (003) peak is shifted because of interlayer space decrease due to loss of water. Decreasing temperature in the presence of water and CO₂ does restore the structure.
- b) CO₂ flushing stabilizes the structure to a somewhat higher temperature.
- c) Four decomposition steps involving water and the last one also CO₂. Decomposition occurs between 300°C and 400°C.

Synthesis
To increase crystallinity we used hydrothermal synthesis in an autoclave at 180°C under 13 bars. We used this method for all the home-made samples. Starting materials: Al and Mg nitrates.

\[ \text{HTC: } (M^{2+}_nM^{3+}_m)(OH)_{2n/2} \cdot yH_2O \]

CO₂ adsorption and membrane tests
CO₂ adsorption seems to follow two different mechanisms as a function of temperature. The two different steps at low and high temperature might be due to the two active species contained in the sample.

Membrane permeancy tests on 2.5 mm thick discs follow Knudsen diffusion for He and CO₂. This shows that there is no bulk transport through hydrotalcites.

Characterization of HTC powders
Homemade samples are more crystalline than the Pural ones. Deviation from Mg/Al of 2 gives Mg or Al rich by-products.

Conclusions
Hydrotalcite materials only exist in a small Mg/Al ratio window as a pure phase, which is around 2. It is possible to make highly crystalline materials using hydrothermal synthesis. There is no memory effect on decreasing the temperature in a humid gas atmosphere. Hydrotalcite materials are totally decomposed at 400°C and are therefore not feasible as a membrane material in the chosen application. Furthermore they do not show any bulk transport of CO₂.

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