**Hydrogenation of CO2 to methanol in zeolite membrane reactors**

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**Highlights**

* Among the tested membranes, zeolite A is the most promising for the purpose.
* The combined traditional + membrane reactor outperforms thermodynamic methanol yields.
* Catalysts less selective to reverse WGS reaction than CuO/ZnO/Al2O3 are more suitable.

**1. Introduction**

This work focuses on the hydrogenation of CO2 to methanol by means of reaction (1), as a way of energy storage that could be applied, for example, to deal with occasional energy overproductions from renewable sources.

CO2 + 3 H2CH3OH + H2O (1)

Zeolite membrane reactors were proposed [1] to allow lower operating pressure and higher yield in the process. H2O removal from the reaction environment would ideally increase yields over the equilibrium ones achievable in a conventional reactor.

In this work, we study the separation performance of several zeolite membranes under different operating conditions. Then, the most suitable zeolite is tested for methanol production in membrane reactor using a conventional CuO/ZnO/Al2O3 catalyst.

**2. Methods**

Permeation behaviour of zeolite-A and mordenite membranes (prepared at *Yamaguchi University* [2]), as well as of a commercial zeolite-T membrane (provided by *Mitsui Engineering*) were tested by feeding a mixture containing CO2, H2, N2 and H2O, and using Ar as sweeping gas.

Reaction tests were carried out in both, a traditional fixed bed reactor (FBR) and a combination of it with a zeolite membrane reactor (FBR+ZMR) by feeding a H2/CO2 mixture in a 3/1 molar ratio. Temperatures were varied in the range 160-260oC. The non-condensable gases from the reaction were analyzed on-line by gas chromatography and the liquids were analyzed by FTIR.

A CuO/ZnO/Al2O3 catalyst was loaded in both FBR and ZMR reactors. It was prepared by co-precipitation of the corresponding salts at constant pH, following literature procedures [3].

**3. Results and discussion**

The separation factor (SF) H2O/CO2 obtained with mordenite membranes was quite low (Figure 1), which seems to do with the formation of cracks. Zeolite T provided good SF at 170oC, but it dropped when was heated up to 240oC. Moreover, measurements at 170oC after heating the membrane at 230oC showed a permanent loss of selectivity which implies that such high temperatures damaged the membrane. Zeolite A provided good separation factors (e.g., SF H2O/CO2 higher than 100) although they decreased at high temperatures (240oC and above).



**Figure 1.** Separation factors for the three tested **Figure 2.** Yield to methanol with the traditional FBR

 zeolite membranes and with the combination FBR+ZMR

An example of comparison of performance using conventional FBR and the configuration FBR+ZMR is shown in Figure 2. The FBR+ZMR combination, using zeolite A as membrane material, outperforms the FBR one in terms of methanol yield. So, yields even over the ones for thermodynamic equilibrium were reached with such a FBR+ZMR configuration.

However, at 240oC reverse WGS reaction is favored by the removal of water through the membrane and thus the selectivity to methanol is lower with the FBR+ZMR configuration at this temperature, increasing the formation of CO. This strongly suggests that a catalyst with more selectivity to methanol at low pressure than the standard CuO/ZnO/Al2O3 should be developed, in order to fully profit from the advantage provided by the removal of water through the zeolite membrane.

**4. Conclusions**

The obtained results open the door for further research, since they show that the zeolite-A membrane reactor can provide higher yields to methanol than the conventional one, allowing operation at lower pressure than the current industrial processes. Further optimization of the full system is necessary to be competitive with the current technology.

**References**

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