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METHANE DRY REFORMING IN CATALYTIC MEMBRANE REACTORS

Introduction

CH_4 is an important resource for both energy generation and chemical production, but it is also a relevant greenhouse gas. On the other side, the main attention concerning the environmental impacts on global warming is devoted to CO_2 emissions and a strong motivation to use CO_2 for chemical transformations is raising. Moreover in recent years considerable attention has been paid to the possibility to exploit biogas which contains relevant amounts of both CH_4 and CO_2.

In this context the Methane Dry Reforming (MDR) reaction is gaining a growing interest since syngas (H_2 +CO) at a ratio close to the unit can be produced.

MDR is generally carried out on both noble metals and Ni(Co) based catalysts [1]. One of the main drawbacks of the MDR process is related to catalyst deactivation due to carbon deposition on the active sites. Nanotubes often are formed altering the catalyst structure and blocking the catalytic sites.

Membrane Reactors are currently studied since they can offer a better integration of reactivity and separation in a single unit, significantly improving the process yields. On the other side, Catalytic Membrane Reactors (CMR) have been proposed as an alternative to classical fixed bed reactors in various situations since they can work with segregated reactants or improve the contact between the reactants on the active sites.

In this work, the influence of porosity of CMR on conversion and selectivity (H_2/CO ratio) and carbon formation was studied for the MDR reaction using either Ni or Rh based catalytic membranes.

Experimental

Commercial tubular ceramic membranes with an asymmetric structure constituted of a macroporous alumina support supporting an inner layer with smaller pore size were used for the catalyst deposition. The catalytic membranes were synthesized via two different methods: ion exchange (Rh catalyst) and homogeneous precipitation through urea decomposition (Ni catalyst). Different catalytic membranes having decreasing pore size of the inner layer were prepared (Fig. 1). The catalytic membranes were characterized by FE-SEM/EDX, gas permeability, N_2 physisorption at 77K.

Both the flow-through and the monolith-like CMR configurations were studied in order to verify the variation on performance with the flow regime and mass-transfer related parameters. As comparison a fixed bed reactor was studied and on both the reactors the carbon deposition was investigated.

Results and discussion

EDX analysis during the FE-SEM observations of the membrane cross-sections revealed that the catalyst loading was higher in the inner porous layer when smaller the pore size was. Almost all Ni was located in the inner layer for the 5 nm alumina membrane, while for the 70nm membrane a Ni concentration of about 4% was found in the inner layer and 1% in the rest of the macroporous support. The total Ni catalyst loading was very similar among all the membranes. The layered structure of each membrane allowed to explain the results of the gas permeability tests.

For all the catalytic test the equilibrium conversion was calculated for comparison with the experimental data (Fig. 2). At high residence times the experimental conversion overlapped the equilibrium one, while increasing the space velocity a lower conversion was found and then the activation energy was estimated. By applying the Weisz Modulus it was found that the CMR exploited a pure kinetic regime [2].

On the basis of material balances during the reaction runs, the formation of carbon due to CO disproportionation and to the reverse water gas shift reactions was evaluated. The post-reaction characterizations on the catalytic membranes showed that while in the macroporosity some carbon deposition occurred, for the 5 nm pore size membrane the small pore size hindered the carbon nanotube growth, therefore protecting the Ni active sites.

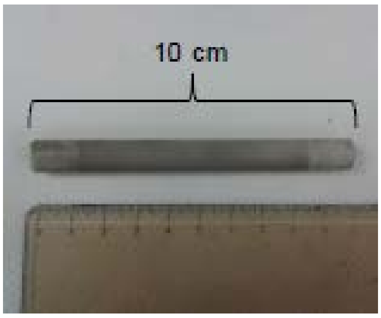

Fig. 1. 20 nm pore size catalytic membrane

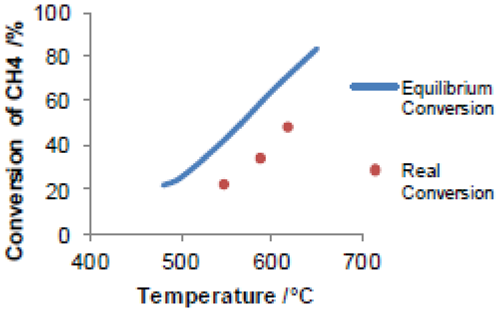

Fig. 2. Conversion vs temperature for the 70nm CMR in the flow-through configuration, N_2:CO_2:CH_4 = 2:2:1

Conclusions

MDR was carried in the CMR with high effectiveness. Permeation tests along with the calculated mass transfer-related parameters from experimental data allowed to conclude that the reaction is not diffusion-limited in the CMR. It was shown that deactivation by coke-blocking did not occur when the majority of the catalyst was located within a thin mesoporous layer suggesting a mechanical limitation to the carbon structure growth.

Acknowledgment

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References

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