

Study on the deactivation of Ni/Al₂O₃ based catalysts in methane dry reforming

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1. Introduction

Syngas and hydrogen are mainly produced by steam reforming of natural gas (NG). Although the proved reserves of NG are still relevant, a great attention is now focussed on the exploitation of biogas not only for energy generation but also for chemicals production. Biogas composition depends on the source but in general contains more than 50% of methane and usually more than 30 % of carbon dioxide.

The Methane Dry Reforming (MDR) reaction is gaining a growing interest since syngas (H₂+CO) at a ratio close to the unit can be produced starting from a biogas. MDR is usually carried out both on noble metals and Ni (Co) based catalysts [1]. One of the main drawbacks of the MDR process with Ni based catalysts is related to deactivation due to carbon deposition. While metal dispersion was identified as one of the main factors affecting the carbon formation, the support plays a key role in the mechanism of deactivation. The presence of promoters can help to reduce the catalyst fouling due to carbon deposition. Another important effect on the formation of carbon can be related to the support pore size and its distribution. In particular it seems that a smaller pore size might limit carbon formation due to a confinement effect.

Catalytic membrane reactors (CMRs) can be considered as a particular category of structured reactors where the pore size and the catalyst distribution can be easily adapted to meet some reaction requirements. The main feature of the catalytic membrane reactor is related to the possibility of exploiting i) porous layers with tailored pore size, ii) tailored catalyst distributions and iii) different reactant feeding configurations. Recently, the CMR performance in the MDR process was investigated using W based catalyst and a flow-through configuration in order to improve the contact between reactants and catalytic sites by exploiting a Knudsen diffusion regime and an higher activity was observed [2].

In this work, the deactivation of Ni based catalysts was investigated with the aim of better understanding some of the factors related to carbon formation by using both laboratory fixed bed reactors (FBRs) and CMRs. The flow-through configuration of the CMR was studied in addition to the monolith-like configuration by using catalytic layers with different average pore sizes in order to both verify the variation on performance with the mass transport regimes and to investigate the tendency to carbon formation.

2. Methods

The MDR process was studied with Ni/Al₂O₃ catalysts in a fixed bed reactors (FBR) and catalytic membrane reactors. In FBRs were tested both a commercial (HTC 400 Ni 1,2 RP, Johnson Matthey) and lab-made catalysts obtained by either impregnation methods or via the homogeneous precipitation (HP) method with urea. The catalytic membranes were prepared by using porous asymmetric tubular supports with differen

nominal pore size of the inner layer (5nm, 20nm, 70nm). In some catalysts Ceria as a promoter was introduced in the support porosity by wet impregnation. The powder catalysts and catalytic membranes were characterized by using FT-IR, physisorption at 77K, field emission scanning electron microscopy (FE-SEM). Gas permeability characterizations were carried on the catalytic membranes. The morphology of the deposited carbon after the catalytic runs was investigated by FE-SEM. The MDR catalytic tests were carried in a pilot plant in the range 380°C-500°C by feeding mixtures composed of CH₄, CO₂ and N₂ and the products were analysed by gas chromatography. In addition tests on the CH₄ decomposition as well as on the Boudouard reaction were carried out to investigate some carbon formation conditions. Chemical equilibrium compositions were calculated considering the carbon formation reactions.

3. Results and discussion

The commercial Ni catalyst had a trilobe shape, a size of about 1x6 mm with, a metal loading of about 16% and a specific surface area (BET) of 160 m²/g. Most of the pore fall in the range between 3 and 30 nm (Figure 1). For the lab made catalyst the average alumina pore size was 5 nm. After reaction all the Ni based catalyst were covered by a layer of carbon (Figure 2). Carbon formation usually proceeded through the growth of carbon nanotubes with the nickel particles staying on the top of the growing tip. The activation energies around 39kJ/mol suggested an effect of the intraparticle diffusion on the overall reaction rate for the lab-made Ni catalysts. The activation energy found in the CMRs in the flow-through mode were noticeably higher suggesting both an improved contact of the reactants on the catalytic sites and the minimization of the intraparticle mass transfer resistances.

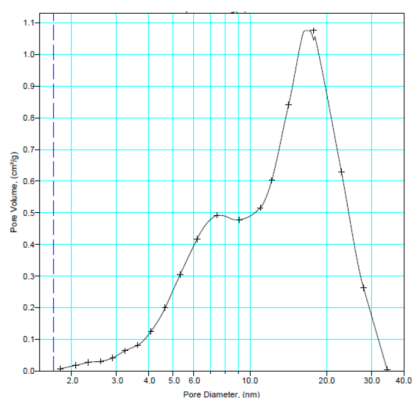


Figure 1. Pore size distribution by the BJH method for the commercial Ni/Al₂O₃ catalyst.

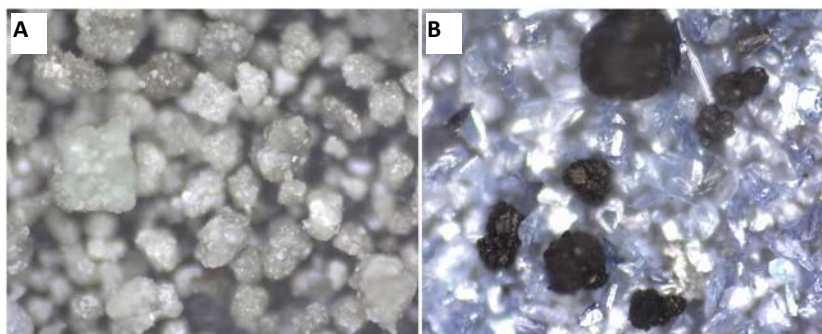


Figure 2. Optical microscopy of a Ni/Al₂O₃ lab-made catalyst before and after the MDR reaction.

4. Conclusions

Ni based catalysts were affected by the formation of carbon as observed from both the increase of the pressure drop along the fixed bed and the analysis of the post-reaction catalysts. The presence of Ceria only partially reduced the carbon formation. It was observed an activation energy that was pore size dependent indicating the limiting effects of intraparticle diffusion. On the other side a smaller pore size associated with smaller Ni clusters seemed to suppress the carbon formation. According to the obtained results, the MDR reaction was efficiently carried out in the CMR. It was shown that deactivation by coke-blocking of the active sites did not occur when the majority of the catalyst was located within a thin mesoporous layer (nominal pore size of about 5nm). It seems that in the small pore size the carbon nanotubes or whiskers could not grow and since the thickness of the catalytic layer in the membrane was very low (about 2 μm for the 5 nm catalytic membrane) the intraparticle mass transfer resistance was not affecting the overall reaction rate. In the CMRs with pore size progressively larger, nanotubes were free to grow and were expectedly identified.

References

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