CO methanation on Ni/Al₂O₃ catalysts in the presence of hydrocarbons

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Introduction

The decision to terminate in a few years the operation of nuclear power plants in several countries of the EU increased the need for the development of efficient production/conversion systems. The conversion of dry biomass to energy carriers like CH₄ through the CO methanation reaction is one of the desirable routes along this direction [1]. Ni/Al₂O₃ catalyst is considered state-of-the-art for this application. However, it suffers from deactivation due to carbon deposition, caused mainly by hydrocarbons (e.g. C_2H_4 , C_2H_2 , etc.) that are present in the feed. Several ways have been proposed in the literature aiming either to avoid or remove carbonaceous deposits on nickel catalysts [2, 3].

Materials and Methods

A series of M-modified 15 wt% Ni/Al₂O₃ catalysts with various M/(M+Ni) molar ratios were synthesized by impregnating M and Ni on γ -Al₂O₃ [4]. All materials were characterized with response to their textural, structural, crystallographic properties and reducibility using BET, XRD, EXAFS, NMR, STEM, Raman and TPR. The activity for CO methanation was evaluated in a fixed-bed reactor using 25 vol% H₂-5 vol% CO in N₂ (GHSV=118000 mLg-1h⁻¹). The stability tests were conducted in the presence of 2000 ppm C₂H₄, whereas the amount/type of carbon deposits was estimated by TPO.

Results and Discussion

 Ni/Al_2O_3 lost 20% of its initial activity at 320°C in the first 4 hours after addition of C_2H_4 . The stability of Ni/Al_2O_3 was greatly enhanced by the addition of low amount of M (Fig. 1), which did not exhibit any activity loss. TPO of the catalysts after the stability test indicates that the amount and type of carbon deposits change upon addition of M (inset of Fig. 1).

No nickel carbide/amorphous carbon are detected in M-Ni/Al₂O₃ that are characterized by the low temperature TPO signal (ca. 300–400°C). Nickel carbide is considered to form by diffusion of carbon in the Ni lattice and leads to the formation of filamentous carbon, detachment of Ni particle from the support and deactivation. The origin of the enhanced catalytic performance arises likely from the structural modifications observed in the Ni phase upon modification. Electron microscopy reveals that Ni domains exist with lattice distortions/dislocations, whereas the well dispersed nature of M and the intimate contact between M and Ni are evidenced by NMR and Raman spectroscopies. These structural modifications earbon to be unfavorable for the formation of carbidic nickel and/or amorphous carbon.



Fig. 1: Stability test at 320°C in the presence of C₂H₄ and TPO (inset graph)

In summary, by means of a combination of catalytic studies physicochemical and spectroscopic characterization, we show that modification of a Ni/Al_2O_3 results in a material stable and resistant to carbon deposition, for SNG production.

References

- 1. J. Kopyscinski, T.J. Schildhauer, S.M.A. Biollaz, Fuel 89 (2010) 1763-1783.
- 2. A. Fouskas, M. Kollia, A. Kambolis, Ch. Papadopoulou, H. Matralis, Appl. Catal. A, 474 (2014) 125-134.

3. A. Kambolis, H. Matralis, A. Trovarelli, Ch. Papadopoulou, Appl. Catal. A. 377 (2010) 16-26.

4. A. Kampolis, T. Schildhauer, O. Kröcher, Patent application in progress.