

Methane conversion to synthesis gas by CO₂ reforming over bimetallic Ni- Pt and Ni-Pd catalysts

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1. Introduction

The catalytic reforming of CH₄ with CO₂, rather than steam, for the production of synthesis gas has attracted a considerable interest in the past 20 years for both environmental and commercial reasons. In fact it reduces CO₂ and CH₄ emissions and it yields, in the product gas, a low H₂/CO ratio, which is suitable as feed for Fischer-Tropsch plants and for the synthesis of acetic acid, dimethyl ether and oxoalcohols [1]. Moreover there is an additional advantage in those cases in which the reactants are simultaneously available at low cost. The major problem preventing commercialization of the dry reforming is finding a suitable catalyst that will not deactivate under the conditions needed for this reaction.

It has been shown [2] that Pt-based catalysts have high activity in the dry reforming reaction and are less sensitive to carbon deposition compared to Ni-based catalysts, but the latter is the metal most widely studied because of its high activity and low price, pointing to possible industrial application. The idea of this work is to promote Ni by a small amount of platinum or palladium in order to improve the stability of the catalytic system.

2. Experimental

Zirconia support was prepared by precipitation from ZrOCl₂ at constant pH [3], while Al₂O₃ (Alu D – Akzo) was used as received. Supports were impregnated by incipient wetness with Ni(NO₃)₂·6H₂O or H₂PtCl₆ or H₂PdCl₄ aqueous solutions to give a nominal 5% wt Ni or 0.5% wt Pt (or Pd) loaded catalyst. Bimetallic 5% wt Ni-0.5% wt Pt (or Pd) were prepared either by coimpregnation or by successive impregnation. After drying at 383K, samples were calcined at 773K in flowing air, and then characterized by H₂-TPR, chemisorption, XRD and HRTEM measurements.

All reactions were tested in the temperature range 373K-1073K at 10K/min, the effluent gases being analyzed by mass spectrometry and TCD. Reforming reaction was carried out with a total flow of 40 mL/min STP of 5%CH₄ and 5%CO₂ diluted in helium. After reaching the final temperature, these reactions were conducted for 16 hours of time on stream at 1073K. Coking reaction, either via CH₄ or CO temperature-programmed decomposition, were carried out with 5% CH₄/He or 5%CO/He flow. After reforming and coking reactions, samples were cooled to ambient temperature and O₂-TPO experiments were carried out in the same equipment.

3. and 4. Results and discussion

Mono and bimetallic samples were supported on both alumina and zirconia, which are the most used and suitable supports for these catalysts. We have verified that the catalytic performance for the dry reforming is strongly influenced by the support: all catalysts supported on zirconia are more active, in terms of initial activity, than alumina-supported samples. This is evident in the nickel based catalysts, since for example Ni/ZrO₂ starts to

produce H₂ at 590K, about 340K earlier than Ni/Al₂O₃ (930K). An example of temperature-programmed reforming reaction is reported in Figure 1. All catalysts present constant activity for 16 hours of time on stream at 1073K. As shown by CO₂ evolution during TPO, noble metal (Pt or Pd) supported on zirconia do not form coke after 16 hours of CH₄/CO₂ reforming reaction at 1073K, while Ni samples produce a lot of coke. For example the TPO profile of the 5%Ni/ZrO₂ sample presents two different peaks and a band (at 600 K, 760 K and 810-900 K respectively), suggesting the presence of three different carbon species (Fig.2).

In order to study carbon deposition, which originates mainly from two reactions, i.e., methane decomposition (CH₄→C+2H₂) and carbon monoxide disproportionation (2CO→C+CO₂), all catalysts have been tested in both temperature-programmed decompositions. Monometallic Pt based catalysts don't show coke formation neither via CH₄ nor via CO decomposition while on Ni-based samples both these reactions occur. Quantitative data have indicated that CH₄ decomposition is the main source of carbon.

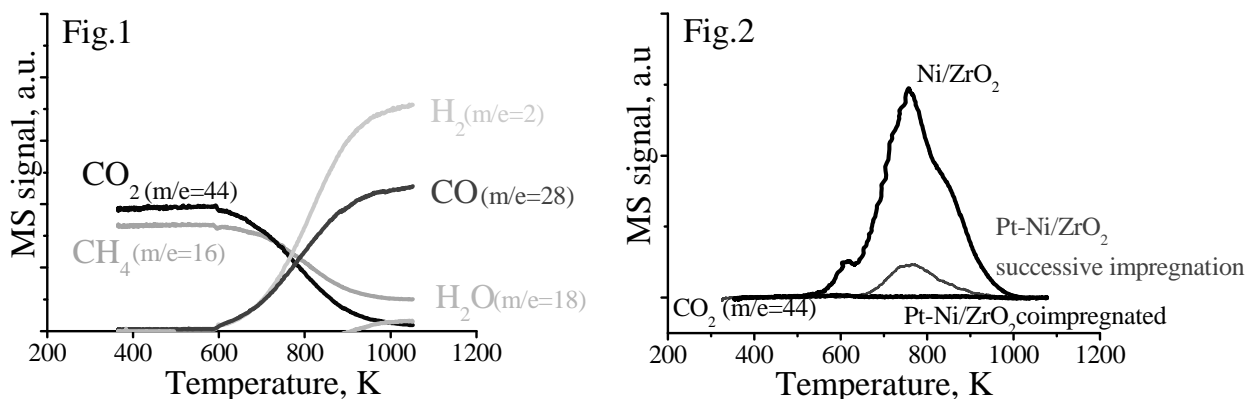


Fig. 1: MS profiles of effluent gas in CO₂ reforming for 5%Ni/ZrO₂(CH₄/CO₂ =1:1; 40 cc/min)-Fig. 2: MS profiles of effluent gas in TPO analyses after 16 hours of time on stream at 1073K.

The addition of platinum or palladium to monometallic Ni-based samples prevents coke formation during 16 hours of time on stream (CO₂ + CH₄) at 1073 K, as reported in the example of Figure 2. The effect of the addition of the noble metal to Ni in enhancing the catalytic performances is sensitive to the preparation method: the best catalytic results were obtained using the coimpregnated samples. The origin of these differences will be discussed together with temperature-programmed decompositions tests and HRTEM measurements. These results clearly show that the presence of the noble metal (Pt or Pd) hinders the accumulation of coke on the catalyst surface.

5. Conclusion

The addition of a noble metal (Pt or Pd) to monometallic Ni-based samples prevents coke formation, improving the stability of the catalytic system.

6. References

- [1] M. Bradford, M. Vannice, Catal. Rev. Sci. Eng., 41 (1999) 1.
- [2] J.H. Bitter, K. Seshan, J. A. Lercher, J. Catal., 183 (1999) 336.
- [3] M. Signoretto, S. Melada, F. Pinna, S. Polizzi, G. Cerrato, C. Morterra, Micr. Mes. Mater. 81 (2005) 19.