Methane conversion to synthesis gas by CO\textsubscript{2} reforming over bimetallic Ni- Pt and Ni-Pd catalysts

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1. Introduction

The catalytic reforming of CH\textsubscript{4} with CO\textsubscript{2}, 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 CO\textsubscript{2} and CH\textsubscript{4} emissions and it yields, in the product gas, a low H\textsubscript{2}/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 ZrOCl\textsubscript{2} at constant pH [3], while Al\textsubscript{2}O\textsubscript{3} (Alu D – Akzo) was used as received. Supports were impregnated by incipient wetness with Ni(NO\textsubscript{3})\textsubscript{2}6H\textsubscript{2}O or H\textsubscript{2}PtCl\textsubscript{6} or H\textsubscript{2}PdCl\textsubscript{4} 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 H\textsubscript{2}-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%CH\textsubscript{4} and 5%CO\textsubscript{2} 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 CH\textsubscript{4} or CO temperature-programmed decomposition, were carried out with 5% CH\textsubscript{4}/He or 5%CO/He flow. After reforming and coking reactions, samples were cooled to ambient temperature and O\textsubscript{2}-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/ZrO\textsubscript{2} starts to
produce $\text{H}_2$ at 590 K, about 340 K earlier than Ni/Al$_2$O$_3$ (930 K). 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 1073 K. As shown by CO$_2$ evolution during TPO, noble metal (Pt or Pd) supported on zirconia do not form coke after 16 hours of CH$_4$/CO$_2$ reforming reaction at 1073 K, while Ni samples produce a lot of coke. For example the TPO profile of the 5%Ni/ZrO$_2$ 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 ($\text{CH}_4 \rightarrow \text{C}+2\text{H}_2$) and carbon monoxide disproportionation ($2\text{CO} \rightarrow \text{C}+\text{CO}_2$), all catalysts have been tested in both temperature-programmed decompositions. Monometallic Pt based catalysts don’t show coke formation neither via CH$_4$ nor via CO decomposition while on Ni-based samples both these reactions occur. Quantitative data have indicated that CH$_4$ decomposition is the main source of carbon.

The addition of platinum or palladium to monometallic Ni-based samples prevents coke formation during 16 hours of time on stream ($\text{CO}_2+\text{CH}_4$) 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