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Influence of Pt addition to Ni catalysts on the catalytic performance for long term dry reforming of methane

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ABSTRACT

The influence of Pt addition (in very low concentrations) to a Ni/(10%)/Al_2O_3 catalyst in its catalytic performance during long-term experiments of dry reforming of methane was studied.

The monometallic Pt(0.5%)/Al_2O_3 catalyst displayed a pronounced deactivation during 6500 min reaction time, mainly due to a significant sintering of the metallic phase, whereas the monometallic Ni(10%)/Al_2O_3 catalyst showed a high and stable activity along the reaction time.

Compared with the Ni(10%)/Al_2O_3 catalyst, the bimetallic Ni(10%)Pt(0.5%)/Al_2O_3 sample showed a higher, and stable catalytic activity during the 6500 min reaction time and a markedly lower carbon deposition. TEM images reveal much less carbon formation and filament grow and this leads to expect a higher stability in long term processes. Characterization techniques indicate that nickel and platinum are in close contact during the simultaneous reduction of the two oxide precursors and that geometric effects (dilution and blocking) are mainly responsible for the excellent catalytic behaviour of the bimetallic NiPt catalyst.

1. Introduction

Processes like steam reforming and partial oxidation of methane are commonly used to transform natural gas into synthesis gas or more valuable products. Due to the extended use of synthesis gas as feedstock for several chemical processes, i.e. fuel cells, methanol synthesis and Fischer–Tropsch reaction [1–7], there has been an increasing interest in the production of synthesis gas from natural gas by the CO_2-reforming of methane, also called dry reforming of methane (DRM). Additionally, DRM provides low H_2/CO ratios required for hydroformylation and carbonylation reactions.

In spite of the initial difficulties, the study of the methane reforming with CO_2 has been progressively increased. A very important driving force to develop new technologies and catalysts is derived from the potential application of this process for the preservation of the environment, since CO_2 plays an important role in the greenhouse effect. Furthermore, a comparative study about the production of acetic acid using three processes – that is, the steam reforming, the partial oxidation and the CH_4 reforming with CO_2 – it was concluded that the operative cost of the methane reforming with CO_2 is lower than those of the other two processes [8]. Hence, this process seems to be a promising route from an economic point of view and it also appears an adequate tool for the environmental protection.

The commonly used catalysts for the DRM reaction are Ni-based ones. Unfortunately, under reforming conditions, carbon deposits could block the catalyst pores and encapsulate the active sites, which would lead to the catalyst deactivation [3,9,10]. However, carbon formation can be reduced or suppressed by using adequate promoters and supports. With respect to promoters, Juan-Juan et al. [11] studied the effect of the potassium content in the structure and properties of the Ni active phase and in the activity and selectivity of NiK/Al_2O_3 catalysts for DRM. Besides, it is well known that noble metals inhibit coke formation. Moreover, it has been reported that the addition of noble metals to Ni catalysts can promote the reducibility of Ni, and stabilize its degree of reduction during the catalytic process [12–14]. Chen et al. [12] found that the noble metal addition to Ni improves the catalyst stability and reducibility. Tomishige et al. [14] observed that the catalytic activity for the autothermal reforming of methane was increased when small amounts of Pt were added to Ni/Al_2O_3 catalysts. Pawelec et al. [3] reported, for bimetallic PtNi catalysts supported on ZSM-5, an improvement of the catalytic activity and stability for DRM, which was attributed to an increase of the nickel dispersion caused by the

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