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Behaviour of nickel–alumina spinel (NiAl_2O_4) catalysts for isooctane steam reforming

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ABSTRACT

The suitability of NiAl_2O_4 -based catalysts for steam reforming of isooctane, which is used here as a surrogate for gasoline, was examined at moderate temperatures (600–700 °C) during a relatively prolonged time on stream (about 30 h). A series of catalysts with a varying nickel loading in the 10–33 wt.% range were prepared by co-precipitation. This synthesis route was shown to be adequate to produce nickel/alumina catalysts with a small Ni particle size (8–10 nm). The catalytic behaviour and the extent of the observed loss of conversion were mainly controlled by the available metallic surface area. Coke formation in the form of both amorphous and graphitic filamentous carbon was identified as the main reason for deactivation. Thus, the best catalytic results corresponded to a 17 wt.% Ni loading since it showed the lowest specific carbon deposition per surface area of metallic sites. At elevated reforming temperatures (650 and 700 °C) noticeably higher conversion values were obtained and the stability was enhanced, which suggested that coking did not induce a marked effect on the catalytic behaviour.

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Introduction

Catalytic steam reforming of gasoline, compared to partial oxidation and oxidative steam reforming, has the advantage of producing larger hydrogen yield which may be used in stationary and mobile fuel cells applications [1]. Noble metals catalysts offer high activity and low carbon deposition [2], but their implementation may be cost-prohibitive. Ni-based catalysts are interesting alternatives due to their competitive costs although they are susceptible to deactivation essentially due to

active phase sintering, carbon deposition and sulphur poisoning [3]. For this reason, design of new formulations capable of developing suitable metal/support interactions, with the aim of improving the activity and stability, is essential.

It is widely accepted that over Ni/alumina catalysts the reforming reactions are sensitive to the structure of the Ni initial precursors. In this sense, nickel aluminate (NiAl_2O_4) has been proposed as a catalytic precursor that, after its reduction, leads to metallic nickel with strong Ni/ Al_2O_3 interactions [4,5]. Moreover, in our previous studies we showed that the NiAl_2O_4 preparation method influenced the distribution of the metallic

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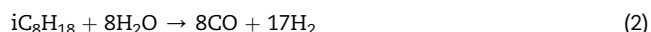
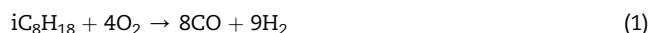
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Ni species and the resultant activity and stability in various methane reforming processes [6,7]. Nevertheless, little is known about the performance of these nickel catalysts in the reforming of heavy hydrocarbons, especially in the case of gasoline [8,9].

Most of the studies related to catalyst screening for the reforming of gasoline select isooctane as a model component. There are two main types of reaction to yield hydrogen from isooctane, namely partial oxidation (Reaction 1) and steam reforming (Reaction 2). Also the combined process known as oxidative steam reforming can be used. Steam reforming, although it is an endothermic process and requires an extra input of energy for vaporisation of water, is usually preferred due to its larger H₂ yield.



The main objective of this work is therefore to analyse the efficiency of NiAl₂O₄ loaded alumina systems prepared by co-precipitation in isooctane (typical molecule found in gasoline) steam reforming. A special attention was paid, by varying the Ni loading, to determining correlations among catalytic behaviour, physico-chemical properties and resistance to deactivation. Results for a bulk NiAl₂O₄ were used as a reference for comparison. Further, spent catalysts were characterised in order to define the main deactivating phenomena.

Experimental

Catalysts preparation

Three alumina-supported NiAl₂O₄ catalysts were prepared by co-precipitation. The process was conducted by the drop-by-drop addition under constant stirring of a 0.6 M solution of NH₄OH into an aqueous solution of a mixture of Ni(CH₃-COO)₂·4H₂O and Al(NO₃)₃·9H₂O (1:2 Ni/Al molar ratio) and powered γ-Al₂O₃ alumina (133 m² g⁻¹, 0.3–0.5 mm, SA 6173, Saint-Gobain). The temperature was kept at 25 °C during the precipitation and the pH was fixed at 8. Afterwards the precipitates were aged for 30 min before being filtered and washed with hot deionised water. The use of nickel acetate instead of nickel nitrate can give additional advantages in terms of dispersion and crystallite size of the resultant catalyst [10]. On the other hand, it should be noted that there were no changes in the transition alumina structure after calcination at 850 °C for 8 h in comparison with the as-received sample.

The catalysts were labelled as CP/A(10), CP/A(17) and CP/A(24) and the corresponding nickel loadings were 10, 17 and 24 wt.%, respectively. Also a NiAl₂O₄ bulk catalyst (CP(33) sample with a 33 wt.% Ni loading) was prepared following the same route without using the commercial alumina as a support. All the samples were dried at 110 °C overnight and then calcined at 850 °C in static air for 4 h at a heating rate of 10 °C min⁻¹. As a reference reforming catalyst a commercial Rh/A sample was used (1%Rh/Al₂O₃, 132 m² g⁻¹, Alfa Aesar).

Catalyst characterisation

The catalysts were characterised by N₂ physisorption at –196 °C, wavelength dispersive X-ray fluorescence (WDXRF), X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature programmed reduction with hydrogen (H₂-TPR) and temperature programmed desorption of NH₃ (NH₃-TPD). The spent samples were characterised by XRD, TEM, thermogravimetry coupled to mass spectrometry (TGA-MS) and Raman spectroscopy. The experimental details of each analytical technique are described elsewhere [7,11].

Catalytic tests

The catalytic tests for steam reforming of isooctane were performed, on 125 mg of catalyst, in a flow reactor operating at atmospheric pressure. The reaction mixture was composed of 1.95 vol% iC₈H₁₈ and H₂O (H₂O/C = 3) diluted in N₂ with a total flow rate of 800 cm³ min⁻¹ (7500 cm³ iC₈H₁₈ g⁻¹ h⁻¹, 1.95% iC₈H₁₈/46.8%H₂O/N₂). Prior to the reaction, the nickel catalysts were activated by reduction with 5%H₂/N₂ at 850 °C for 2 h whereas the rhodium catalyst was reduced at 700 °C. The experiments were carried out at constant temperature (in the 600–700 °C range) for about 30 h. Feed and effluent streams were analysed online by a MicroGC (Agilent 3000) equipped with a TCD detector. On the basis of the molar flow at the inlet and outlet of the reactor, conversion and yields to the main reforming products were calculated according to the following equations:

$$X(iC_8H_{18}), \% = \frac{F(CO_{out}) + F(CO_2_{out}) + F(CH_4_{out})}{8 \cdot F(iC_8H_{18}_{in})} \cdot 100 \quad (3)$$

$$Y(H_2) = \frac{F(H_2_{out})}{9 \cdot F(iC_8H_{18}_{in})} \quad (4)$$

$$Y(CO) = \frac{F(CO_{out})}{8 \cdot F(iC_8H_{18}_{in})} \quad (5)$$

$$Y(CO_2) = \frac{F(CO_2_{out})}{8 \cdot F(iC_8H_{18}_{in})} \quad (6)$$

$$Y(CH_4) = \frac{F(CH_4_{out})}{8 \cdot F(iC_8H_{18}_{in})} \quad (7)$$

This way of calculating the conversion of the reforming reaction reflects the activity of the investigated catalysts in the conversion of the feed into the main reforming products (CO, CO₂ and CH₄). On the other hand, the thermodynamic data were calculated via the HSC Chemistry software package by the GIBBS program using the so-called Gibbs Energy Minimization Method.

Results and discussion

Characterisation of the fresh samples

Table 1 summarises the characterisation results of the reduced nickel aluminate catalysts. XRD and H₂-TPR analyses pointed out the efficiency of the synthesis route based on co-

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