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The effect of the addition of Y_2O_3 to Ni/α-Al_2O_3 catalysts on the autothermal reforming of methane

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ABSTRACT

The addition of Y_2O_3 to Ni/α-Al_2O_3 catalysts was investigated by BET surface area measurements, hydrogen chemisorption, X-ray diffraction, UV–vis diffuse reflectance spectroscopy, X-ray fluorescence, temperature programmed reduction, temperature programmed oxidation and cyclohexane dehydrogenation. Autothermal reforming experiments were performed in order to evaluate the methane conversion and proceeded through an indirect mechanism consisting of total combustion of methane followed by CO_2 and steam reforming generating the synthesis gas. The $Y_2O_3 \cdot Al_2O_3$ supported catalysts presented better activity and stability in autothermal reforming reaction. Temperature programmed oxidation analysis demonstrated that the addition of Y_2O_3 resulted in a change of the type or the location of coke formed during reaction. None of the prepared catalyst presented deactivation by sintering under the tested conditions. The improved stability of supported catalysts $Y_2O_3 \cdot Al_2O_3$ was the result of minimizing the formation of coke on the surface of nickel particles.

1. Introduction

Autothermal reforming of methane is considered the best choice for producing synthesis gas for large scale GTL (gas-to-liquids) plants [1–3]. In this process, partial oxidation of methane and steam reforming of methane are combined in the same reactor. There is an optimization of energy consumption since partial oxidation occurs in a burner after mixing of the feedstock and provides energy for the downstream endothermic reforming reactions [4,5]. The economics of this process is favored by an improved design of reactor, burner and heat exchangers. Besides, the H_2/CO ratio can be adjusted varying the $CH_4/O_2/H_2O$ composition in the feedstock, resulting in a H_2/CO ratio close to 2, the desired composition of synthesis gas for Fischer–Tropsch synthesis. Additionally, in order to avoid the need for CO_2 recycling low H_2O/CH_4 ratios must be used [1,2].

The autothermal reforming of methane can be catalyzed by several transition metals, with Pt, Rh and Ru being the most catalytic active. However, Ni has been used due to its low cost and availability [6]. However, carbon deposition due to the severe operational conditions of the reactor also affects the catalytic behavior. In order to extend the lifetime and stability of nickel catalysts, promoters are added, which act as support or active phase modifiers, decreasing the carbon deposition and consequently improving the stability of the catalysts [7,8].

Y_2O_3 has been used as a support for metal catalysts used in methane conversion [8] and improved results have been obtained in terms of stability of the catalysts. In this paper, the addition of Y_2O_3 to Ni/α-Al_2O_3 catalyst was investigated by BET surface area determination, hydrogen chemisorption, X-ray diffraction (XRD), UV–vis diffuse reflectance spectroscopy (DRS), temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and cyclohexane dehydrogenation. Autothermal reforming experiments under low H_2O/CH_4 ratios were performed in order to evaluate the methane conversion and the stability of the catalysts.

2. Experimental

2.1. Catalyst preparation

All nickel catalysts were prepared by incipient wetness impregnation of a $Ni(NO_3)_2 \cdot 6H_2O$ solution with successive impregnation and intermediate drying. After impregnation, the samples were dried at 120 °C for 12 h and calcined (10 °C/min) in a muffle at 650 °C for 6 h (10 °C/min). α-Al_2O_3 (ALCOA 1.5 m^2/g) was used as support after calcination at 800 °C for 6 h. Y_2O_3 support was prepared by calcination of $Y(NO_3)_3 \cdot 6H_2O$ at 800 °C for 1 h. $Y_2O_3 \cdot$α-Al_2O_3 supports, with different yttria contents, were prepared by impregnation of α-Al_2O_3 with an $Y(NO_3)_3 \cdot 6H_2O$ solution, following by drying at 120 °C and calcination at 800 °C for 6 h.

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2.2. BET surface area

Surface area measurements were performed in a Micromeritics ASAP 2010 device. About 1.5 g of each sample was introduced in a quartz cell and attached to the adsorption apparatus. The sample was dried under vacuum at 220 °C for 10 h. The BET surface area was obtained by N_2 adsorption at 77 K.

2.3. X-ray diffraction (XRD)

X-ray diffraction measurements were carried out using a Rigaku (Miniflex) diffractometer with a Cu Kα radiation. The XRD data of calcined samples were collected at 0.04°/step with integration times of 1 s/step and a 2θ range of 2–90°.

2.4. UV–vis diffuse reflectance spectroscopy (DRS)

The samples were characterized at room temperature using a Cary 500 (Varian) spectrophotometer equipment. In order to separate the contribution of the support, the reflectance $R(\alpha)$ of the sample was made proportional to the reflectance of Al_2O_3, and the "Kubelka–Munk" function $F(R)$ was calculated.

2.5. Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) experiments were performed in a quartz micro-reactor coupled to a quadrupole mass spectrometer (Balzers, Omnistar). The samples (150 mg) were dehydrated at 150 °C for 30 min in a He flow prior to reduction. After cooling to room temperature, a mixture of 5%H_2 in Ar flowed through the sample at 30 mL/min, and the temperature was raised at a heating rate of 10 °C/min up to 1000 °C.

2.6. Hydrogen chemisorption

Hydrogen chemisorption was performed by a volumetric method in a Micromeritcs ASAP 2010C device. The sample (500 mg) pretreatment consisted of drying at 150 °C for 30 min under a 30 mL/min He flow, followed by reduction under 30 mL/min of H_2 at 800 °C. The samples were outgassed under vacuum of 500 °C. All the chemisorption measurements were performed at 35 °C. Both total and reversible H_2 isotherms were measured. H/Ni ratios were calculated using the irreversible H_2 uptake.

2.7. Cyclohexane dehydrogenation

Cyclohexane conversion was used as a structure-insensitive reaction to evaluate the number of exposed Ni atoms of the samples. This reaction was performed at atmospheric pressure in a flow quartz reactor (13 mm i.d.). The samples (100 mg) were previously dried at 150 °C for 30 min under He flow (30 mL/min) and reduced at 800 °C under H_2 flow (30 mL/min). The reactant mixture was obtained by bubbling hydrogen through a saturator containing cyclohexane at 12 °C (H_2/C_6H_{12} = 13.6). The temperature was varied between 250 and 320 °C. The effluent gas phase was analyzed by an on-line gas chromatograph (HP-5890) equipped with a flame ionization detector and an HP Innowax capillary column. Under these conditions, there was no significant deactivation of the catalysts and there were no diffusional or thermodynamic limitations.

2.8. Autothermal reforming of methane

Autothermal reforming of methane was performed in a continuous quartz reactor (13 mm i.d.) at atmospheric pressure. The samples were previously dried at 150 °C for 30 min under He flow (30 mL/min) and reduced at 800 °C under H_2 flow (30 mL/min) for 2 h. The reaction was carried out at 800 °C. A reactant mixture containing (67 mL/min), O_2 (33 mL/min) and H_2O (12.6 mL/min) was used. The H_2O content of the feed stream was obtained by flowing the CH_4 and O_2 reactant mixture through a saturator containing H_2O at 49 °C. CH_4:O_2 ratio of 2:1 and a flow rate of 100 mL/min were used. In order to avoid temperature gradients, the catalyst samples (10 mg) were diluted with inert SiC (90 mg). The exit gases were analyzed using a gas chromatograph VARIAN CP3800 equipped with a thermal conductivity detector (TCD) and a Supelco Carboxen 1010 tplot column.

2.9. Temperature programmed oxidation (TPO)

TPO experiments were performed in a multipurpose unit coupled to a Balzers Omnistar quadrupole mass spectrometer. The samples, used previously in the autothermal reforming reaction, were dried at 150 °C for 30 min, under He flow (30 mL/min) and cooled to room temperature, followed by an increase of temperature under O_2/He (30 mL/min) flow in a rate of 10 °C/min to 800 °C.

2.10. Catalyst ageing experiments

The samples (100 mg) were previously dried at 150 °C for 30 min, under He flow (30 mL/min) and reduced at 800 °C under H_2 flow (30 mL/min). The catalysts were aged at 800 °C during 24 h over all catalysts under a gas mixture containing He (30 mL/min) and H_2O (3.8 mL/min) obtained using a saturator at 49 °C. The samples were transferred to the cyclohexane conversion reaction system in order to evaluate the number of surface metallic sites after the ageing processes. The samples were dried at 150 °C for 30 min under He flow (30 mL/min) and reduced at 500 °C under H_2 flow (30 mL/min), before the activity was tested under the same conditions already described for the conversion of cyclohexane.

3. Results and discussion

3.1. BET surface area

The surface areas of the prepared catalysts are shown in Table 1. The 8%Ni/α-Al_2O_3 catalyst showed a surface area equal to 3.7 m^2/g, consistent with the fact that α-Al_2O_3 was used as support [9,10]. The Ni/Y_2O_3 catalyst showed a BET surface area of 18.6 m^2/g which is higher than the typical value of 10 m^2/g reported in the literature for Y_2O_3 supported catalysts [11–14], probably due to the differences in the preparation method used for Y_2O_3. The $Y_2O_3 \cdot Al_2O_3$ supported catalysts showed an increase in the surface area with the increase of Y_2O_3 content.

3.2. X-ray diffraction (XRD)

Fig. 1 presents the diffractograms of α-Al_2O_3, Y_2O_3 and $Y_2O_3 \cdot Al_2O_3$ and of the respective nickel supported catalysts. The vertical dotted lines indicate NiO diffraction peak positions. In the case of the 8%Ni/α-Al_2O_3 the diffraction pattern included NiO lines

Table 1
BET surface area of Ni/α-Al_2O_3, Ni/$Y_2O_3 \cdot Al_2O_3$ and Ni/Y_2O_3 catalysts.

Catalyst	BET surface area (m^2/g)
8%Ni/α-Al_2O_3	3.7
8%Ni/Y_2O_3	18.6
8%Ni/2%$Y_2O_3 \cdot Al_2O_3$	5.8
8%Ni/2.5%$Y_2O_3 \cdot Al_2O_3$	6.4
8%Ni/5%$Y_2O_3 \cdot Al_2O_3$	8.2