Influence of the support on the catalytic behaviour of Ni catalysts for the dry reforming reaction and the tri-reforming process

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ABSTRACT

The influence of different support materials (alumina, ceria, β-silicon carbide and yttria-stabilized zirconia) on the catalytic behaviour of Ni catalysts for the dry reforming reaction and the tri-reforming process has been studied. The influence on the catalytic performance of the composition of the atmosphere surrounding the Ni/YSZ catalyst during the calcination step was also analysed. Temperature-programmed reduction experiments showed remarkable differences in the reduction profile and the degree of reduction of the catalysts as a function of both the support used and the calcination conditions. Ni/YSZ-O_2, the catalyst calcined under an oxygen-poor atmosphere, presented a higher reducibility as a consequence of the higher number of oxygen vacancies in the surface of the support. The Ni/Al_2O_3 catalyst gave the lowest CH_4 and CO_2 reaction rates as a consequence of its low reducibility due to the formation of Ni aluminate. The Ni/CeO_2 catalyst showed the lowest H_2/CO molar ratio for the tri-reforming process. This result can be explained on considering the higher basicity of this catalyst, as shown by CO_2-TPD experiments. The CeO_2 and β-SiC catalysts had the best characteristics as catalytic supports for the tri-reforming process.
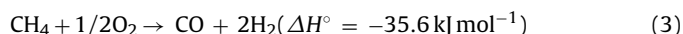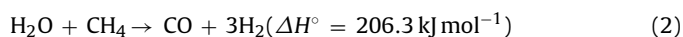
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1. Introduction

The production of synthesis gas is of great interest as a first step in the manufacture of liquid fuels through the Fischer–Tropsch synthesis as well as for other interesting chemical compounds like methanol or dimethyl ether. One of the main characteristics that determines the possible applications of synthesis gas is the H_2/CO molar ratio. For most applications this parameter is too high when the synthesis gas is obtained by steam reforming. Hence, it is of interest to study alternative reforming processes that can yield the desired H_2/CO molar ratio. Dry reforming of methane (Eq. (1)) has been reported in numerous papers [1–3] as a way to obtain synthesis gas using methane and carbon dioxide:

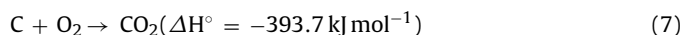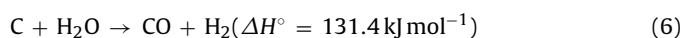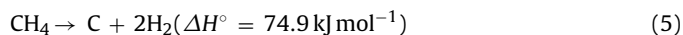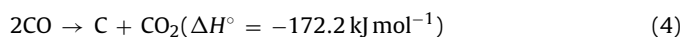$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 (\Delta H^\circ = 247.3\,kJ\,mol^{-1}) \tag{1}$$
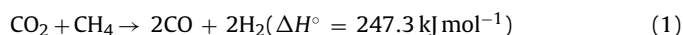
As a result of the stoichiometry of this reaction, the synthesis gas obtained is richer in CO and this makes the gas more suitable for different applications. However, rapid deactivation is commonly observed and the process has a high energy consumption.

Tri-reforming of methane is a synergistic combination of dry reforming (Eq. (1)), steam reforming (Eq. (2)) and partial oxidation (Eq. (3)) of methane:

$$H_2O + CH_4 \rightarrow CO + 3H_2 (\Delta H^\circ = 206.3\,kJ\,mol^{-1}) \tag{2}$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 (\Delta H^\circ = -35.6\,kJ\,mol^{-1}) \tag{3}$$

The simultaneous combination of these three reactions could avoid some of the problems associated with the single reactions. For example, the quantity of coke deposited (Eqs. (4) and (5)) is lower than that for the dry reforming process due to the reaction of coke with water and oxygen (Eqs. (6) and (7)). Furthermore, the process has lower energy consumption than dry or steam reforming due to the occurrence of partial oxidation and, in addition, it may be possible to modify the H_2/CO molar ratio by changing the feed composition:

$$2CO \rightarrow C + CO_2 (\Delta H^\circ = -172.2\,kJ\,mol^{-1}) \tag{4}$$

$$CH_4 \rightarrow C + 2H_2 (\Delta H^\circ = 74.9\,kJ\,mol^{-1}) \tag{5}$$

$$C + H_2O \rightarrow CO + H_2 (\Delta H^\circ = 131.4\,kJ\,mol^{-1}) \tag{6}$$

$$C + O_2 \rightarrow CO_2 (\Delta H^\circ = -393.7\,kJ\,mol^{-1}) \tag{7}$$

In the work described here, the dry reforming and tri-reforming processes were studied using nickel as the active metal and four

different supports, namely γ-alumina (γ-Al$_2$O$_3$), yttria-stabilized zirconia (YSZ), silicon carbide (SiC) and ceria (CeO$_2$). Nickel has been selected by several authors [1,4,5] as the active phase for reforming reactions due to its high activity, interesting redox properties and relatively low cost. Nickel has also been identified as the best option for tri-reforming [6]. However, the catalytic activity of Ni-based catalysts is markedly influenced by the nature of the support [7], which affects the reducibility and metal dispersion. Alumina-based materials are frequently selected as supports for reforming catalysts due to their mechanical and thermal resistance under the required reaction conditions [8,9]. ZrO$_2$ and systems based on ZrO$_2$-like YSZ have been investigated as supports for Ni catalysts in methane reforming reactions and these materials show high thermal stability and a high ionic conductivity due to the presence of defects in the crystal surface, where molecular oxygen can be easily activated, thus increasing its reactivity [2]. CeO$_2$ has been highlighted by several authors as a promising promoter and/or support for Ni catalysts [10,11]. One of the most interesting properties of this material is its capacity to store and/or release reversibly high quantities of O$_2$ [12]. Silicon carbide has attracted interest as a result of the development of its porous form (β-SiC) [13]. SiC exhibits a high thermal conductivity and mechanical strength, a low specific weight and chemical inertness. These properties are required for good catalyst supports, especially for highly endothermic and/or exothermic reactions [14] where precise control of the temperature within the catalyst bed is extremely important.

In our previous work [15] we studied the influence of the Ni precursor on Ni/CeO$_2$ and Ni/β-SiC catalysts for the tri-reforming process. The results of this work showed that metal particle size and metal-support interactions could be key factors that influence the catalytic behaviour. In this sense, the work described here was carried out in order to compare the catalytic behaviour of Ni-based catalysts supported on different conventional and non-conventional materials for the dry reforming and tri-reforming processes for methane.

2. Experimental

2.1. Catalyst preparation

Five supported nickel catalysts were prepared from four different supports. The supports used were γ-alumina (MERCK), yttria-stabilized zirconia with a Y$_2$O$_3$/ZrO$_2$ molar ratio of 0.08 (IONOTEC), β-silicon carbide (SICAT CATALYST) and CeO$_2$, which was obtained by calcination of cerium ammonium nitrate (NH$_4$)$_2$Ce(NO$_3$)$_6$ (SIGMA ALDRICH) in air at 1173 K for 2 h. The catalysts were prepared by the wet impregnation method using nickel nitrate Ni(NO$_3$)$_2$·6H$_2$O (PANREAC) as the metal precursor. After impregnation, the catalysts were dried in air overnight at 393 K and calcined in air at 1173 K for 2 h. An additional catalyst was prepared with YSZ as the support, using different calcination conditions. In this case, the calcination step was carried out in the reactor with a flow of 0.6% oxygen in nitrogen and a total flow of 30 N ml min^{-1}. This catalyst is denoted as Ni/YSZ-O$_2$.

2.2. Catalyst characterization

Ni metal loading was determined by atomic absorption (AA) spectrophotometry using a SPECTRA 220FS analyser. Samples (ca. 0.5 g) were treated with 2 ml of HCl, 3 ml of HF and 2 ml of H$_2$O$_2$ followed by microwave digestion (523 K). Surface area/porosity measurements were conducted using a QUADRASORB 3SI sorptometer with N$_2$ as the sorbate at 77 K. The samples were outgassed at 523 K under vacuum (5 × 10^{-3} Torr) for 12 h prior to analysis. Specific surface area was determined by the multipoint BET

method. Specific total pore volume was evaluated from N$_2$ uptake at a relative pressure of P/P_o = 0.99. Temperature-programmed reduction (TPR) experiments were conducted in a commercial Micromeritics AutoChem 2950 HP unit with TCD detection. Samples (ca. 0.15 g) were loaded into a U-shaped tube and ramped from room temperature to 1173 K (10 K min^{-1}) with a reducing gas mixture of 17.5% v/v H$_2$/Ar (60 N ml min^{-1}). Raman spectroscopy was carried out on a Bruker Senterra Raman Microscope at an excitation wavelength of 532 nm. Temperature-programmed desorption (TPD) experiments were conducted in a commercial Micromeritics AutoChem 2950 HP unit with TCD detection. The sample (0.15 g) was loaded into a quartz tube, reduced and pretreated in He. After cooling, 30 N ml min^{-1} of CO$_2$ (99.99% purity, Praxair certified) was passed through the sample for 30 min at a constant temperature of 323 K. Finally, the gaseous and weakly adsorbed carbon dioxide was removed by a steady flow of He for a further 30 min. The sample was then heated in 50 N ml min^{-1} of He at a heating rate of 10 K min^{-1} up to 1173 K. Static chemisorption experiments on the reduced samples were carried out at 308 K in the pressure range of 100–450 Torr in a Micromeritics ASAP 2010 unit equipped with a chemisorption controller using H$_2$ as the titrant. The samples were then evacuated and cooled down. Two parallel isotherms were obtained; the first one is a measure of both the physisorbed and chemisorbed H$_2$, whereas the second concerns the physisorbed H$_2$ only. Assuming a 2:1 stoichiometry for H:Ni, the difference between the two isotherms was used to obtain the Ni dispersion. XRD analyses were carried out on a Philips X'Pert instrument using nickel-filtered Cu-$K\alpha$ radiation. The samples were scanned at a rate of 0.02 step^{-1} over the range 5° ≤ 2θ ≤ 90° (scan time = 2 s step^{-1}). Transmission electron microscopy (TEM) analyses were carried out on a JEOL JEM-4000EX unit with an accelerating voltage of 400 kV. Samples were prepared by ultrasonic dispersion in acetone with a drop of the resulting suspension evaporated onto a holey carbon-supported grid. Mean nickel particle size, evaluated as the surface-area weighted diameter ($\bar{d}_s$), was calculated according to:

$$\bar{d}_s = \frac{\sum_i n_i d_i^3}{n_i d_i^2} \qquad (8)$$

where n_i represents the number of particles with diameter d_i ($\sum_i n_i \geq 400$).

2.3. Catalyst activity measurements

The catalytic activity measurements were carried out in a tubular quartz reactor. The reactor was 45 cm long and had a diameter of 1 cm. The catalyst was placed on a fritted quartz plate located at the end of the reactor. The temperature of the catalyst was measured with a K-type thermocouple (Thermocoax) placed inside the inner quartz tube. The entire reactor was placed in a furnace (Lenton) equipped with a temperature control system. Reaction gases were Praxair certified standards of CH$_4$ (99.95% purity), CO$_2$ (99.95% purity), O$_2$ (99.99% purity) and N$_2$ (99.999% purity), with the latter used as the carrier gas. The gas flow was controlled by a set of calibrated mass flowmeters (Brooks 5850 E and 5850 S). The water content in the reaction mixture for the tri-reforming experiments was controlled using the vapour pressure of H$_2$O at the saturator temperature (24 °C). All lines located downstream from the saturator were heated to a temperature above 373 K to prevent condensation. The saturation of the feed stream by water at the working temperature was verified by a blank experiment in which the amount of water trapped by a condenser was measured for a certain time and then compared with the theoretical value. Prior to the reaction, catalysts were reduced in a flow of pure H$_2$ at a rate of 100 N ml min^{-1} at 673 K (Ni/CeO$_2$, Ni/YSZ and Ni/YSZ-O$_2$) or 973 K (Ni/Al$_2$O$_3$ and Ni/SiC). The feed composition (by volume %)