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Investigation of a Ni-based steam reforming catalyst developed for the coating of microstructures

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Abstract

A catalyst based on alumina-supported nickel was synthesized in powder and film form. The alumina support was prepared by a suspension (slurry) coating technique. Afterwards, nickel was added by impregnation, using $Ni(NO_3)_2 \cdot 6H_2O$ as precursor. Adherent, porous, thick (25 µm) alumina films were successfully deposited on microstructures. Initial activity tests regarding the steam reforming of iso-octane at a S/C ratio of 2.34 were performed with the catalyst in powder form in a fixed bed reactor. The chosen reaction conditions were intended to attain full hydrocarbon conversion, in order to represent as close as possible the probable operating conditions in a microreactor for on-board hydrogen production.

Keywords: Slurries; Microstructure; Catalyst support; Films; Hydrogen

1. Introduction

Perspectives for individual transportation indicate the emerging of more rigorous emission regulations for new generations of vehicles and the need to meet stringent efficiency standards. Electric propulsion powered by PEM fuel cell-based technology using on-board generation of hydrogen from fuel presents a realistic medium-term option to tackle both of these upcoming restrictions. However, developing an on-board fuel processor represents a major challenge, considering constrains in volume, weight, start-up and response time of an on-board installed chemical converter with complex heat management and auto-startup capability. Some of these can be addressed by the development of an effective microstructured reactor design, but just as important is identifying highly effective catalyst materials with long lifetime. More specifically, placing the catalyst requires a development of temperature stable well adhering layers with high intrinsic activity. Several catalytic coating techniques are currently employed: sol–gel deposition (Haas-Santo et al., 2001; Chen et al., 2005; Truyen et al., 2006), electrochemical processes (Stefanov et al., 2004), chemical vapor deposition (CVD) (Janicke et al., 2000), the Langmuir–Blodgett (LB) film method (Lojewska et al., 2006), etc. However, the most frequently used coating technique remains the slurry (or suspension) coating (Rouge et al., 2001; Valentini et al., 2001; Agrafiotis and Tsetsekou, 2000; Degenstein et al., 2006; Jiang et al., 2005; Conant et al., 2006).

This study outlines the development of porous, adherent and uniform alumina layers inside the microchannels of stainless steel platelets. Subsequently, catalytic tests were carried out for the iso-octane steam reforming reaction on this Ni/Al_2O_3 catalyst in powder form to prove the activity of the related material.

2. Experimental

2.1. Catalysts preparation

The 15% Ni/Al_2O_3 catalyst is synthesized in powder and film form. The alumina preparation is reported in a former paper (Stefanescu et al., 2006), as well as the method of coating application. Briefly, the slurry employs an organic binder, gamma alumina with a grain size of 2–3 µm and boehmite. The slurry was then either dried and transformed into powder or

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deposited on microstructured stainless steel platelets having the following dimensions: 99.5 mm × 28 mm × 2 mm, each platelet having 40 microchannels: 50 mm length × 400 μm width × 300 μm depth. In both cases, nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$, was used in the impregnation step in an aqueous solution as nickel precursor.

2.2. Catalyst characterization techniques

The specific surface area of the samples was calculated from the N_2 adsorption by using the BET equation. Prior to surface area determination, the powders were outgased at 350 °C for 4 h.

The pore size distribution of each sample was determined by the BJH method from desorption isotherm measurements using an Micromeritics ASAP 2010M apparatus.

The crystalline structure of catalyst phases was examined by X-ray diffraction using a Bruker (Siemens) D5005 apparatus (Cu Kα radiation, 0.154 nm).

The morphology of samples was investigated with scanning electron microscopy (SEM) on a Hitachi S800 instrument. The samples were covered with a thin film of Au–Pd before analysis in order to avoid charge accumulation and to improve image contrast.

2.3. Experimental conditions for catalytic tests

Activity tests were performed with the catalyst in powder form using a quartz tube (internal diameter 4 mm and 200 mm length) packed with 50 mg of catalytic powder. Prior to charging in the center of a quartz reactor, the catalyst was sieved to obtain a particle fraction between 200 and 300 μm. Silicon carbide (particles size 150 μm) was admixed for a better heat transfer in a catalyst/silicon carbide weight ratio of $\frac{5}{8}$. Before the activity tests, catalysts were reduced in a flow of 40% H_2 in argon (total flow = 100 sccm). The temperature was raised from 25 to 800 °C at a rate of 5 °C/ min, kept for 4 h at 800 °C and decreased to 600 °C in a flow of argon. The reactant feed stream of: 1.2% C_8H_{18}, 22.5% H_2O, 76.3% Ar (total flow = 211 sccm) was kept constant rising the temperature with 5 °C/ min up to 800 °C and decreasing thereafter back to 600 °C in a stepwise operation performing 1-h dwell steps at 650, 700, 750 and 800 °C.

Precise temperature measurement was accomplished with two K-type thermocouples, placed in the middle of the oven and in the center of the catalytic bed, respectively. The pressure drop over the reactor was recorded using a heated electronic pressure transducer connected to the feed line at reactor entrance.

3. Results and discussions

3.1. Catalyst characterization

X-ray diffraction patterns of samples calcined at 800 °C during 4 h are reported in Fig. 1. It can be observed that a reduction in hydrogen at temperatures as high as 800 °C is necessary in order to form metallic nickel grains on the gamma alumina support. The latter observation is coherent with temperature programmed reduction (Niemantsverdriet, 2000) experiments in hydrogen (data not shown) indicating a significant water release at temperatures slightly below 800 °C.

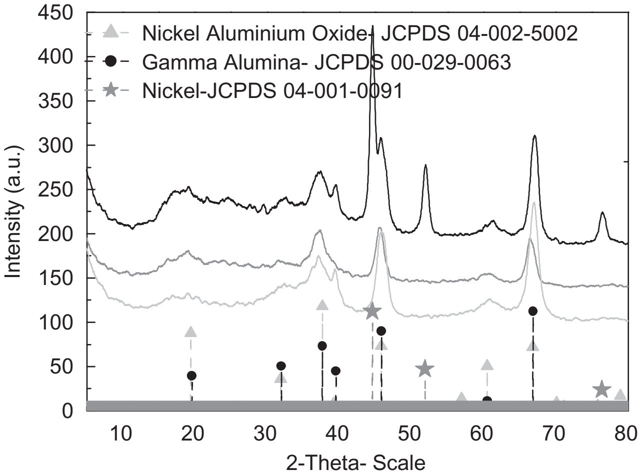

Fig. 1. Powder XRD patterns of alumina (——) and 15% Ni/Al_2O_3 reduced in hydrogen at 500 °C (——) and 800 °C (——).

Table 1
The specific surface area (S_{BET}) and pore volume calculated from nitrogen adsorption–desorption isotherms

	S_{BET} m^2/g	SEF m^2/m^2	Pore volume (cm^3/g)	Average pore diameter d_h (nm)
Al_2O_3	149	≈ 800	0.48	12.8
15% Ni/Al_2O_3	95	–	0.47	19.4

The mean pore diameter d_h is calculated assuming a cylindrical pore geometry taking S_{BET} as the pore surface area, $d_h = 4\,V/S$.

The porosity measured on powders (S_{BET}, pore volume, pore radius) and coated platelets (surface enhancement factor (SEF)) are reported in Table 1. Specific surface areas of alumina as high as 149 m^2/g can be considered as a reasonable result, taking the high calcination temperature into account. Addition of nickel decreases, as expected (Kim et al., 2004; Nandini et al., 2005; Erhan Aksoylu and Ilsen Onsan, 1997), the initial surface area by 36%. It does, however, not affect the pore structure, both samples present a clear hysteresis loop indicating the presence of mesopores (Fig. 2). The pore volume remains the same while the average pore diameter grew by 3 nm agreeing with findings of Nandini et al. (2005).

An important parameter for a coated microstructured platelet is the SEF. It is defined as the ratio between the measured surface area of the coated platelet and the geometrical surface area of the platelet (Haas-Santo et al., 2001; Sandu et al., 2006). The calculated SEF is around 800 m^2/m^2 indicating that the catalyst exposes an 800 times enlarged surface for the steam reforming reaction. Moreover, the layer coverage in the microchannel is uniform, with no cracks in alumina film being