Mesocellular silica foam-based Ni catalysts for dry reforming of CH$_4$ (by CO$_2$)

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ABSTRACT

Nickel-containing mesocellular silica foam (MCF) catalysts were prepared for dry reforming of methane (DRM). Different methods were used for the synthesis of the MCFs supports in order to enhance their surface areas and pore volumes. The incorporation of nickel was done by three different methods: incipient wetness impregnation, two-solvents post-synthesis method and direct one-pot synthesis introduction. All prepared materials were calcined then characterized by N$_2$ sorption, X-Ray Diffraction (XRD), Transmission Electronic Microscopy (TEM), Temperature Programmed Reduction (TPR) and X-Ray Fluorescence (XRF). Their catalytic performances were tested in DRM between 200 and 770 °C, then for 4 h (stability test) at 650 °C, using a Gas Hourly Space Velocity (GHSV) of 36 L g^{-1} h^{-1} and an equimolar ratio of reactants. Promising results were obtained by using direct synthesis method (DS) in which small Ni particles in strong interaction with the support were formed.

1. Introduction

Since two decades, ordered mesoporous materials (OMMs) templated by surfactant micelles have attracted great interest because of their predictive synthesis approach and their various potential applications [1–6]. From the beginning, the subject of pore size tailoring captured special attention. On SBA-15, in particular, studies have shown that the pore diameter can be tailored from about 5 to 30 nm using block copolymers of different molecular weights and tri-methylbenzene (TMB) as a swelling agent [7]. However, it was soon realized that the addition of too large amounts of TMB to the synthesis mixture leads not only to pore size enlargement, but also to a transition from the 2-D hexagonal structure (SBA-15) to a 3-D structure due to the formation of mesocellular foams (MCF) [8,9].

Mesocellular silica foam (MCF) is among the promising materials to address the challenges associated with small pores. This sponge-like material has a three-dimensional structure with large uniform spherical cells (15–50 nm) that are accessible via large windows (5–20 nm). It thus provides an open structure that favors mass transfer [10]. MCFs have been tested for drug release [11], as enzyme carriers [12], as packing material for high-speed size-exclusion chromatography [13], and as catalytic supports for different reactions [14–16]. Especially,

they have been used to disperse rhodium in catalysts that were found active and stable for dry reforming of CH$_4$ by CO$_2$ [17], attesting of the potential interest of this type of supports for this reaction.

Nowadays, the reaction of dry reforming of methane with CO$_2$ is considered with great attention because it allows converting two greenhouse gases (CH$_4$ and CO$_2$) into syngas with consequent strong environmental benefit. CO$_2$ reforming of CH$_4$ has the strong advantage of producing a clean syngas (CO and H$_2$) mixture in an equimolar ratio, suitable for the Fischer-Tropsch synthesis (FTS) [18–20] that is an important process for the production of liquid hydrocarbons.

In the process of methane dry reforming, the main reaction (CH$_4$ + CO$_2$ → 2 H$_2$ + 2 CO) occurs in the gas phase, in addition to secondary reactions like the reverse water gas shift (RWGS, CO$_2$ + H$_2$ → CO + H$_2$O), methane decomposition (CH$_4$ → 2 H$_2$ + C) and CO disproportionation known as Boudouard reaction (2 CO → CO$_2$ + C). The last two reactions produce carbon that can contribute to catalyst deactivation by forming carbonaceous deposits on the inner and/or outer catalytic surfaces [21]. Besides, Boudouard reaction occurs at low temperatures while the main DRM reaction and methane decomposition require high temperatures. Therefore, a major problem in the dry methane reforming process is the lack of effective catalysts that can (i) operate efficiently and (ii) maintain good stability and selectivity under

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the required severe high temperature reaction conditions [17]. Supported noble metals, such as Rh, Ru and Ir, are known as highly active, selective and stable phases for DRM [22,23], substantially preventing coke formation. Nowadays, the substitution of noble metals by more available and less expensive active phases is an important economic issue. Nickel is, to this respect, the transition metal having shown the most promising activity in DRM, but having lower stability than noble metals due mainly to Ni sintering and to carbon deposition over the Ni active sites and around the grains of the catalysts, causing deactivation during DRM [24,25].

Hence, it seemed interesting in this work to check, for the first time, the suitability of the MCFs siliceous support for preparing Ni-based catalysts to be used in DRM. In addition to allowing high dispersion and stabilization of the Ni nanoparticles (NPs) on the silica walls, the specific textural features of MCFs, characterized by a 3D porosity with large pore diameters and opened windows, could enhance the homogeneity of Ni incorporation and increase the accessibility of the reactants to the active sites. Two different types of MCF silica supports with slightly different textural properties were synthesized. Nickel (5 wt %) was introduced into these supports using three different methods; incipient wetness impregnation, two-solvents impregnation or direct one-pot synthesis. The structure and porosity of the samples as well as the nickel dispersion at various steps of preparation and use were analyzed. The influence of the large pores of MCFs on metal deposition and on the activity, stability and selectivity of the prepared catalysts in dry reforming of methane were studied. The catalytic performances were also compared to thermodynamic curves given by the HSC Chemistry Software under similar reaction conditions.

2. Experimental

2.1. Catalysts preparation

The mesocellular silica foam synthesis was performed according to the method described by Widyaningrum et al. [16]. First, 4 g of the triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P123) were dissolved at 40 °C in a mixture of HCl (20 mL, 37%) and distilled water (120 mL). Then, 4 g of TMB were added dropwise to the mixture under strong stirring in order to get a microemulsion. Two hours later, tetraethylorthosilicate (TEOS, 9 mL) was added and the resulting suspension was stirred at th e same temperature for 20 h. After hydrothermal treatment for 24 h at 100 °C, the suspension was filtered and the recovered solid was washed, dried and calcined under air flow at 550 °C for 5 h (heating rate 1 °C/min). This calcined sample is called **MCF**. The exact same procedure, except for adding 48 mg of NH₄F just before the hydrothermal treatment, was followed to prepare sample **MCF(N)**.

Nickel was incorporated within above supports by two different post-synthesis methods using Ni(NO₃)₂.6H₂O as Ni precursor salt. In all cases, the theoretical Ni loading was 5 wt%. In details, the **Ni₅/MCF-IWI** and **Ni₅/MCF(N)-IWI** materials were prepared by incipient wetness impregnation (IWI). To do so, a given volume (set equal to the silica pore volume as determined by N₂ physisorption) of a nickel-containing aqueous solution (0.25 g Ni(NO₃)₂.6H₂O) was added to 1 g of calcined MCF and MCF(N), respectively. Each resulting sample was dried for 2 h at room temperature, then at 60 °C overnight, and finally calcined at 550 °C for 5 h (heating rate 1 °C/min). The **Ni₅/MCF-TS** and **Ni₅/MCF(N)-TS** samples were prepared by the two-solvents method [26] which consisted in suspending 1 g of calcined support (either MCF or MCF(N)) in 20 mL of cyclohexane, then adding dropwise a volume of water equal to the silica porous volume (as previously determined by N₂ physisorption) and containing the appropriate amount of nickel precursor (0.25 g Ni(NO₃)₂·9H₂O). The recovered solids were dried 3 days at room temperature, then overnight at 60 °C, and they were finally calcined as above.

In addition, two samples were prepared by the direct synthesis (one-pot) method, which consists to introduce the metal during the synthesis of the support [27]. The difference between these two samples was the amount of nickel added in the synthesis gel. For the first one (sample **Ni₀.₉-MCF-DS**), the procedure was as follows: 4 g of P123 were dissolved in a mixture of 120 mL of distilled water and 20 mL of HCl (37 wt %) for 3 h at 40 °C. After adding 4 g of TMB and stirring for 2 h, 1.3 g of Ni(NO₃)₂·9H₂O (corresponding to a theoretical Ni loading of 5 wt%) was introduced in the solution under stirring. Then, 8 mL of TEOS was added. After pH-adjustment to 8 with 30% NH₃ aqueous solution in order to favor metal incorporation, the resulting mixture was aged for 20 h at 40 °C and transferred into a Teflon bottle for hydrothermal treatment at 100 °C for another 24 h. The solid was recovered by filtration, washed, dried then calcined at 550 °C for 5 h (heating rate 1 °C/min). The nickel content in the obtained **Ni₀.₉-MCF-DS** sample was only 0.9 wt%, due to Ni loss in the filtrates. To increase this content and approach those in the impregnated materials, the synthesis procedure was repeated using 3 g of Ni(NO₃)₂·9H₂O and 6.3 mL of TEOS to give sample **Ni₁.₉MCF-DS**.

2.2. Catalyst characterizations

Chemical (Si and Ni) compositions were determined on a XEPOS spectrometer (Spectro Ametek) by X-Ray Fluorescence (XRF). Quantitative data were obtained using the MicroPowder method combining the well-established fundamental parameters approach to XRF spectrometer calibration with automatic correction for matrix effects by using the Compton backscatter information from the sample to calculate the matrix interference.

Textural properties were determined from N₂ adsorption-desorption isotherms recorded on an ASAP 2020 (Micromeritics) apparatus. Prior to measurements, the samples were degassed under vacuum for 2 h at 250 °C. Specific surface areas were obtained using the BET equation. Pore diameters and specific pore volumes were determined using the BJH model.

X-ray Diffraction (XRD) data were recorded on a X'Pert3 Powder diffractometer (PANalytical, Netherlands) using CuKα radiation. The average nickel particle size for each sample was calculated from the Scherrer equation: $D = K\lambda/\beta\cos\theta$, where K is a constant (K = 0.9), $\lambda = 1.5405\,\text{Å}$, β is the full width at half maximum (FWHM) of the diffraction peak and θ is the peak position.

Nickel reducibility in the prepared (calcined) materials was studied by Temperature Programmed Reduction (TPR), carried out on an Autochem 2920 (Micromeritics) apparatus equipped with a TCD detector. The samples (80 mg) were heated on a quartz wool in a U-shaped quartz sample tube from room temperature to 800 °C at a rate of 10 °C min⁻¹ using a gaseous mixture (25 mL min⁻¹) of 5 vol% H₂/Ar. An ice and salt bath was used to remove water formed during reduction before the TCD detector.

Transmission Electronic Microscopy (TEM) analyses were performed on a JEOL-2010 (LaB) microscope operating at 200 kV. Before observation, the sample powder was dispersed in ethanol, the resulting suspension was deposited on a copper grid coated with a porous carbon film and the grid was left in ambient atmosphere for ethanol evaporation.

2.3. Catalytic measurements

The catalysts were tested in a PID ENG & TECH Microactivity Effi Reactor. Powder catalysts were loaded into the reactor (on quartz wool) and reduced *in-situ* at 650 °C for 2 h (rate 10 °C min⁻¹) in a 5% H₂/Ar flow (30 mL min⁻¹) in order to ensure a complete reduction of nickel oxide into metallic nickel. After pretreatment, the temperature was decreased down to 200 °C and the test of dry reforming of methane was started. It was conducted under atmospheric pressure, using a reactant ratio CH₄/CO₂ of 1:1 (diluted at 10% each in Ar) and a total GHSV value of 36 L g⁻¹ h⁻¹ (100 mg of catalyst used for each test).

First, the activity of the catalyst as function of the temperature was