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Particle size effect in the low temperature reforming of methane by carbon dioxide on silica-supported Ni nanoparticles

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ABSTRACT

The influence of nickel particle size in the range of 1.6–7.3 nm on catalyst performance in low temperature CO_2 reforming of methane reaction has been investigated using well-defined catalysts based on a neutral silica support. XAS and XPS studies indicated a reduction degree greater than 90%. The intrinsic Ni/SiO_2 performances were found to be independent of nickel particle size in dry reforming at 773 K using a CH_4/CO_2 ratio of 1.3 at 1 atm, both at an early stage and in steady state conditions. The H_2/CO ratio was also found to be structure in sensitive but is controlled by thermodynamics through the faster reverse water gas shift reaction.

1. Introduction

There has been growing interest in natural gas reforming reactions in the past decade due to the significant increase in petrol demand and price. Even though steam reforming is majorly used in industry for syngas because of its high H_2/CO ratio, CO_2 reforming (dry reforming – DR) is of increasing interest due to the uprising worldwide concern towards global warming and the installation of carbon tax. This endothermic reaction, typically used to tune H_2/CO ratio for off-stream requirements, such as Fischer–Tropsch process. Furthermore, with regards to upcoming energy challenges, DR would be of great interest for the conversion of renewable energies, that is solar energy, into chemicals as energy carriers, as developed for the Adam-Eva process [1–6].

All group VIII metals show activity for steam and dry reforming [7]. Despite the general higher performances of Rh or Ru, Ni is preferred for catalyst preparation for economic reasons. As supports, MgO and γ-Al_2O_3 are typically used for their stability under reaction conditions, that is, high temperatures (>1123 K) and the presence of steam [8,9].

Many attempts have been made to improve Ni-based reforming catalysts. Besides the support, which is preferably basic [10,11], another important parameter is the particle size. For instance, a decrease in particle size of noble metals and nickel has been reported to increase the activity of reforming catalysts at 773–873 K [12–14] and to limit the formation of coke [15–18]. In addition, a recent study of Rh nanoparticles supported, among others, on silica indicated a particle size effect in steam reforming of methane at 500 °C; the intrinsic activity increasing linearly with the metal dispersion [14]. However, in the case of nickel, the study of particle size effects (PSE) on catalyst activity has been performed mostly with aluminium- and magnesium-based supports [13], which are known to favour CO_2 adsorption[19] and to form stable mixed oxides [20], making it difficult to clearly distinguish particle size and support effects [21].

Here, we investigate intrinsic nickel particle size effects in DR, using silica-supported catalysts. Silica was used because it displays a rather neutral acidity/basicity (Lewis and Brønsted) limiting its ability to activate CO_2, and because it allows a high degree of metal reduction[22,23] and low oxygen donation to the metal [24].

Thus, we prepared silica-supported Ni nanoparticles of various sizes, characterized them by TEM, H_2 chemisorption, XPS and X-ray absorption spectroscopy (XAS), in particular to confirm particle

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size and nickel reduction state, and we evaluated their catalytic performances in dry reforming at 773 K in tubular, fixed-bed reactors.

2. Experimental section

2.1. General procedure

Nickel nitrate (98.5%), acetate (99%) and acetylacetonate (95%) were purchased from Sigma–Aldrich. Dry ethanol (99.9%) and dry tetrahydrofuran (99.9%) were used as received, and demineralized water was purified using a Purilab instrument (>10 MΩ cm). Impregnations were carried out using a Schlenk line with Ar (grade 4.5) and 10^{-3} mbar. CO_2 and CH_4 used in catalytic measurements were of 4.5 and 3.5 grade, respectively, while nitrogen was grade 5.0.

2.2. Support material

Silica Aerosil-200 purchased from Evonik was used as a support in all experiments described below: it was first compacted with distilled water, dried, cribbed and further dried at 423 K overnight under vacuum prior to further use.

2.3. Catalyst preparation

2.3.1. Preparation of silica-supported Ni nanoparticles. Representative procedure

An aqueous solution of nickel nitrate (3.6 mL, 0.142 mol L^{-1}) was added dropwise to 3 g of SiO_2 under meticulous mechanical stirring, the volume used corresponding to 95% of the support pore volume. The solid was then dried at 363 K for 12 h using a heating ramp of 1 K min^{-1} and an 80 mL min^{-1} flow of dry air, prior to storage. This solid was then reduced *in situ* prior to all characterization or catalytic tests under H_2 at 773 K for 8 h using a 1 K min^{-1} temperature ramp and a space flow velocity equal or greater than 150 mL min^{-1} g^{-1}.

2.3.2. Screening of the preparation parameters

In addition to water, dry ethanol and dry tetrahydrofuran were used as solvents for the impregnation. The volumes used for the impregnation were 1.47 mL $g_{SiO_2}^{-1}$ and 1.45 mL $g_{SiO_2}^{-1}$, respectively. In the case of organic solvents, the impregnated powder was dried for 48 h in a vessel semi-opened to air before further drying in a dry air flow at 363 K for 12 h. Nickel acetate and nickel acetylacetonate were also used as the nickel precursor. Finally, the drying step was independently modified to tune the particle size by drying the impregnated samples at 393 K for 12 h in an air-circulating oven using a 2 K min^{-1} temperature ramp.

2.3.3. Catalyst terminology

A catalyst prepared using nickel nitrate and water with a targeted nickel loading of 1 wt.% is referred to as Ni_1/SiO_2-(H_2O,NO_3). Ethanol, tetrahydrofuran, nickel acetate and nickel acetylacetonate are referred to as EtOH, THF, CH_3CO_2 and acac, respectively. The catalyst Ni_5/SiO_2-(EtOH,NO_3) was dried using an air-circulating oven.

2.4. Catalyst characterization

2.4.1. Physisorption of N_2

Nitrogen adsorption–desorption at 77 K was measured on an ASAP2020 from Micromeritics. Before the measurement, the samples were outgassed under vacuum (10^{-3} mbar) at 623 K for 2 h. Total surface area was calculated using the BET method [25]. The t-plot method was used to discriminate between micro- and meso/macro-porosity [26].

2.4.2. Chemisorption of H_2

Chemisorption experiments were performed on a BELSORB-max from BEL JAPAN. Around 200 mg of catalyst was reduced *in situ* under a 30 mL min^{-1} flow of pure H_2 at 773 K for 8 h using a ramp of 1 K min^{-1}. The sample was then degassed at 623 K for 3 h under vacuum (10^{-6} mbar). The chemisorption measurements were performed at 298 K, the pressures at equilibrium being recorded when the pressure variation was below 0.02% per minute. Nickel particle size estimations are based on a truncated octahedron geometry, assuming complete reduction, semi spherical particles and a H/Ni adsorption stoichiometry factor of 1 [27]. The experimental points were fitted with a Langmuir adsorption equation (cf. below), and the amount of surface nickel was calculated from the quantity adsorbed at saturation (Q_{max} in the model). The dispersion refers here to the molar ratio between surface metal and bulk metal, the latter being calculated from the nickel salt impregnation.

$$\theta = \frac{Q_{ads}}{Q_{max}} = \frac{\sqrt{KP}}{1+\sqrt{KP}}$$

2.4.3. Chemisorption of CO_2

The study was carried out on a BELSORB-max from BEL JAPAN. The support (ca. 1 g) was degassed at 500 °C under dynamic vacuum (10^{-6} mbar). The adsorption measurements were performed at 500 °C, the pressures at equilibrium being recorded when the pressure variation was below 0.3% per minute. In order to take into account temperature gradients inside the analysis cells, an empty cell was systematically used as a volume standard.

2.4.4. Transmission Electron Microscopy

TEM images were carried out on a Philips CM120 operated at 120 kV or on a Jeol 2100F operated at 200 kV. All samples were reduced under a flow of pure H_2 at 773 K for 8 h using a ramp of 1 K min^{-1} and were then transferred under argon in a vial into which air slowly diffuses through a needle at ambient temperature (referred to here as passivation). All samples were dispersed in pentane using ultrasound prior to the grid preparation. The particle size distributions were obtained from a minimum of 350 particles. An estimation of the reduced particle size from the studied NiO_x samples was performed using the bulk nickel oxide (II) and reduced nickel densities for particle diameters smaller than 3 nm. In the case of bigger particles, taking into account the nickel surface passivation by its oxide, a NiO layer of ca. 1 nm depth was considered [28]. The standard deviation (SD – variation from the average) is also given and converted to $Ni^{(0)}$.

2.4.5. XRD

The *in situ* X-ray powder diffraction data were collected on a Panalytical X'Pert Pro MPD diffractometer equipped with a diffracted beam graphite monochromator (λCu Kα = 0.154184 nm) and a X'Celerator real-time multiple strip (RTMS) detector using the Bragg–Brentano flat plate geometry.

2.4.6. XPS

The XPS experiments were performed using a Kratos Axis Ultra DLD (Delay Line Detector), and the data were acquired using the monochromated Al K-alpha radiation source. The survey scans were obtained at a pass energy (PE) of 160 eV and the region scans at a PE of 40 eV. The samples were charge neutralized during the acquisition. All the data were referenced using the Si 2p peak position at 103.5 eV.

2.4.7. EXAFS

Transmission data were obtained at the Ni–K edge at HASYLAB (DESY) on DORIS III beam-line X1 (RÖMO II). The data reduction