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FT-IR characterization of supported Ni-catalysts: Influence of different supports on the metal phase properties

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ABSTRACT

Supported Ni catalysts (2 wt.% Ni) were investigated by FT-IR and UV–vis-NIR spectroscopy, using CO_2, CH_3CN and CO as probe molecules. The supports studied range from acidic (SiO_2), *via* amphoteric (Al_2O_3, Mg(Al)O) to basic oxides (MgO, CaO).

CO_2 adsorption experiments allowed to obtain the following qualitative scale for the basic strength of O^{2-} sites and $M^{n+}O^{2-}$ pairs: Ni/CaO > Ni/MgO ≥ Ni/Mg(Al)O ≫ Ni/Al_2O_3. On Ni/SiO_2 these sites are absent.

CH_3CN adsorption allowed to reveal acidic and strong basic Lewis sites with the following results: Ni/SiO_2 does not contain basic or acidic Lewis sites. Ni/Al_2O_3 contains acidic Lewis sites but no strong basic Lewis sites. The ratio between the strong basic and the acidic Lewis sites decreases in the order: Ni/MgO > Ni/CaO > Ni/Mg(Al)O. The strength of Lewis acid sites decreases in the order Ni/Al_2O_3 ≫ Ni/Mg(Al)O > Ni/MgO > Ni/CaO.

Interaction of CO at room temperature results into formation of $Ni(CO)_4$ and/or $Ni(CO)_{y<4}$ sub-carbonyls. In the case of Ni/SiO_2 and Ni/Al_2O_3, the sub-carbonyls are weakly interacting with the support. For the other supports, $Ni(CO)_4$ and $Ni(CO)_{y<4}$ sub-carbonyls are stabilized on the metal oxide and give rise to mono- and poly-nuclear complexes (containing 2 or 3 Ni atoms). On Ni/Mg(Al)O, even larger Ni clusters seem to be formed. The support capability of stabilizing mono- and poly-nuclear complexes can be ranked as follows: $SiO_2 \ll Al_2O_3$ < Mg(Al)O < CaO < MgO. A reactivity scale of the Ni^0 particles with CO is also proposed: Ni/SiO_2 ≪ Ni/Al_2O_3 < Ni/Mg(Al)O ≈ Ni/CaO < Ni/MgO.

1. Introduction

Supported Ni catalysts are currently the preferred choice as catalysts for the reforming of light alkanes (C_1–C_3) to synthesis gas (CO and H_2); the major process for converting natural gas into fuels and petrochemicals. This choice is primarily based on the low cost and easy availability of Ni metal. The main disadvantage of the Ni supported catalysts, compared to noble metal catalysts, is a lower stability with respect to carbon deposition (see [1] and refs therein). Many attempts have been made to improve the stability of Ni-based reforming catalysts, and using a basic support has been among the most successful ones [2–6]. It has been debated whether the effect is due to oxygen transfer from the basic oxide to the metal [7–10], to electronic effects [11], or to a higher dispersion of the metal [12]. Recently [13], Ni-based catalysts supported over a variety of oxide materials, ranging from acidic (SiO_2), *via* amphoteric (Al_2O_3, Mg(Al)O) to basic oxides (MgO, CaO), have been tested by some of us for the dry reforming of propane to synthesis gas.

It was demonstrated the major importance of a high Ni dispersion on the intrinsic activity. However, the possibility to achieve a highly dispersed Ni phases was observed to be strictly dependent on the nature of the support material, and particularly on its acid–base character. Thus, it appears of primordial importance a deep characterization of the acid–base and surface properties of the supports, the metal–support interactions and of their effect on the morphology and reactivity of the metal Ni phase.

In the present work, on one hand the acid–base properties of the support materials, as well as the support heterogeneity, have been addressed by means of FT-IR spectroscopy with CO_2 and acetonitrile as probe molecules. IR spectra of adsorbed CO_2 also allow a correlation with TPD data previously reported [13]. In addition, acetonitrile was chosen due to its high selectivity toward strongly basic sites and to its amphoteric character, making this probe fully adapted to investigate nature, strength and amounts of surface Lewis or Brønsted basic and acid sites. On the other hand, the effect of the surface properties of the support on the morphology and

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Table 1
Ni loading, specific surface area, Ni metal reduction degree, minimum, maximum and mean Ni metal particle diameter determined on samples reduced in H_2/N_2 (10/90) mixtures (data from ref. [13]).

	Ni loading (wt.%)	Specific surface area (m^2/g)	Reduction (%)[a]	D_{min} (Å)[a]	D_{max} (Å)[a]	D_M (Å)[a]
Ni/SiO_2	1.9	100	92	52	113	80
Ni/Al_2O_3	1.8	100	60	57	97	75
Ni/Mg(Al)O	1.6	165	22	34	69	55
Ni/MgO	1.9	117	22	38	55	45
Ni/CaO	2.8	16	84	62	114	80

[a] Determined by magnetic measurements on reduced samples; data cross-checked with TEM measurements.

reactivity of Ni metal phase has been addressed mainly by FT-IR spectroscopy using CO as probe, and by UV–vis-NIR spectroscopy.

2. Experimental

2.1. Sample preparation

Ni/SiO_2 was synthesized by calcination of SiO_2-40 (Fluka, grain size 0.2–0.3 mm) at 825 °C for 10 h followed by impregnation with an aqueous solution of nickel nitrate. The product was then dried over night at 100 °C and calcined at 750 °C for 8 h in air.

Ni/Al_2O_3 was prepared by impregnating δ-Al_2O_3 Puralox Scca-90 (Condea) with an aqueous solution of nickel nitrate. The product was then dried over night at 100 °C and calcined for 8 h at 750 °C in air.

Ni/MgO and Ni/CaO were prepared by synthesizing the corresponding double hydroxides, $Mg_{0.98}Ni_{0.02}(OH)_2$ and $Ca_{0.98}Ni_{0.02}(OH)_2$, by co-precipitation at constant pH (12.0 ± 0.1) at 40 ± 2 °C in a specially designed apparatus. During synthesis the two reactant solutions, A (OH^- balanced by K^+; ≈250 ml) and B ($Mg^{2+} + Ni^{2+}$ or $Ca^{2+} + Ni^{2+}$ balanced by $NO_3{}^-$; 80 ml) as well as the product solution C (initially 160 ml deionized water), were kept at constant temperature in a water bath. The whole system was kept under inert conditions by Ar flushing and the pH controlled through a feed-back loop using a pH-meter. The obtained products were washed with diluted NH_4OH solution and dried over night at 90 °C. Phase purity of the samples was confirmed by powder X-ray diffraction (XRD). The double hydroxides were converted into the corresponding oxides in a fluidized bed reactor kept at 650 °C and 750 °C in N_2 atm for 14 h, respectively, then cooled to RT under inert conditions.

The Ni/Mg(Al)O catalyst was prepared by first synthesizing the corresponding hydrotalcite-like material (see ref. [14]) with nominal composition $Mg_{5.88}Ni_{0.12}Al_2(OH)_{16}CO_3 \cdot nH_2O$ and (Mg + Ni)/Al = 3 by co-precipitation at constant pH (11.5 ± 0.1) and temperature (40 ± 2 °C). During synthesis the two reactant solutions, A ($CO_3{}^{2-}$ and OH^- balanced with K^+; ≈730 ml) and B ($Mg^{2+} + Ni^{2+} + Al^{3+}$ balanced with $NO_3{}^-$; 250 ml) as well as the product solution C (initially 500 ml deionized water), were kept at constant temperature and controlled pH. The obtained product was washed and dried over night at 90 °C. Powder X-ray diffraction showed that the obtained hydrotalcite like material was a pure phase.

The synthesized samples, Ni/SiO_2, Ni/Al_2O_3, Ni/MgO and Ni/CaO were activated by heating to 650 °C in a fluidized bed reactor for 14 h in an atmosphere of 10% H_2/Ar. The Ni/Mg(Al)O was activated by fluidizing the corresponding hydrotalcite-like material in 10% H_2/N_2 for 14 h at 650 °C. All samples were then cooled to ambient temperature in the same atmosphere and finally passivated by passing 2% O_2/N_2 over the material for 1 h. The Ni loading of each material was determined by ICP-AES analysis. The Ni content and BET areas of the passivated samples are reported in Table 1.

All catalysts studied here originated from the same preparation batch as those studied by magnetic measurements (results reported in Table 1) and catalytic testing in a previous study [13], except for Ni/Mg(Al)O, which originated from a different preparation batch but was prepared exactly as the corresponding material used for catalytic testing (Ni/Mg(Al)O type II).

2.2. Spectroscopic characterization

Absorption/transmission FT-IR spectra were recorded on a Perkin-Elmer FT-IR 2000-X spectrophotometer working in the range 7200–580 cm^{-1} at a resolution of 2 cm^{-1} (equipped with a Hg–Cd–Te cryodetector). For the FT-IR analysis, the passivated samples were compressed into self-supporting wafers (∼20 mg/cm^2). The wafers were mounted in a suitable IR cell which allowed both heating (up to 700 °C) and cooling down to RT *in situ* under vacuum ($\sim 1 \times 10^{-4}$ mbar) or under controlled atmospheres. Before adsorption of probe molecules, the samples were outgassed in vacuum at 650 °C for 60 min to remove hydroxyl groups and carbonate species at the surface, and subsequently reduced in 10% H_2 (Matheson, C.P.) in N_2 (Matheson, C.P.) mixture for 30 min at 600 °C. Finally, the samples were outgassed at the same temperature for 10 min and cooled down to RT. CO or CO_2 (Matheson, C.P.) or CH_3CN (Carlo Erba, RPE) were then admitted at increasing doses and outgassed thereafter at RT. In the figures all FT-IR spectra are reported as difference between spectra recorded after and before interaction with the probe molecule.

UV–vis-NIR diffuse reflectance spectra were measured at RT in the range 56,000–4000 cm^{-1} on a Perkin-Elmer λ 19 spectrophotometer. The powdered sample (1 g) was mounted in a suitable cell which allowed heating (up to 700 °C) *in situ* under vacuum ($\sim 1 \times 10^{-4}$ mbar) or in controlled atmospheres. Before CO adsorption, the powder was outgassed for 2 h at 600 °C, subsequently reduced in 10% H_2/N_2 mixture for 1 h at 600 °C, evacuated at the same temperature for 10 min and finally cooled down to RT. The UV–vis-NIR spectra are reported without manipulation.

3. Results and discussion

3.1. Sample characterization

In a previous study, the Ni reduction degree and metal particle size for the same materials as those studied here were determined by using magnetic measurements, cross-checked with TEM measurements, both for samples simply passivated or thereafter reduced in H_2/N_2 (10/90) mixtures [13]. Results concerning reduced catalysts are summarized in Table 1. It can be noted that Ni/MgO and Ni/Mg(Al)O have a significantly low reduction degree (ca. 22%). This observation is probably related to the presence of large Ni^{2+} amounts into the MgO lattice, due to the similar cationic radius of Ni^{2+} (0.69 Å) compared to Mg^{2+} (0.72 Å) and to the preferred NaCl structure of both NiO and MgO [15]. The reduction degree of Ni/Al_2O_3 (ca. 60%) is intermediate between Ni/MgO, Ni/Mg(Al)O and the other two materials. It is known from literature that poorly reducible NiO–Al_2O_3 phases, such as $NiAl_2O_4$ spinel, may be formed after calcination at elevated temperatures [16], and although such phases were not visible by XRD, their formation cannot be ruled out.