



Spectroscopic characterization of Ni/Al₂O₃ catalytic materials for the steam reforming of renewables

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ABSTRACT

Ni/alumina catalytic materials (with 0, 5, 16, 39, 125 and ∞ % wt_{Ni}/W_{support}, using a 5% silica-containing alumina with 170 m²/g surface area) have been characterized by XRD, IR, MicroRaman, UV–vis–NIR techniques. Three types of nickel oxide species have been identified: i) isolated Ni²⁺ species dispersed and strongly interacting with the support surface, predominant when the NiO coverage is well below that of the ‘theoretical monolayer’. ii) Ni oxide-like particles having a vibrational environment similar to that of NiO nanoparticles, but with different Raman and UV spectra, predominant near or well above the ‘theoretical monolayer’. iii) normal NiO particles at even higher Ni oxide contents, characterized by (2M) magnonic and several phononic peaks in the Raman spectrum and normal position for the optical gap (absorption edge at ca. 300 nm). IR spectra of adsorbed CO recorded after reduction in hydrogen suggest that species i) predominantly gives rise to isolated Ni⁰ atoms, producing Ni⁰ polycarbonyls, while species ii) gives rise by reduction to Ni metal particles, over which unusually CO adsorbs producing only terminal species, without any formation of bridging CO species. This may be due to an unusual structure or morphology of these particles. The catalysts have been tested in the steam reforming of ethanol–phenol mixture as well as of pure ethanol. XRD, UV–vis–NIR and Raman studies show that the spent catalysts are largely reduced to metal with the appearance of hexagonal nickel, although unreduced or easily oxidizable centers are also detected.

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1. Introduction

Ni-alumina based catalysts are used industrially for several applications. In particular, Ni on alumina is used in many hydrogenation processes. As for example, Johnson Matthey offers Ni/Al₂O₃ catalysts for both stages of pyrolysis gasoline hydrogenation [1] both operated in the liquid phase at 40–100 °C (first stage) and at 280–330 °C (second stage) at some tens of bar of pressure [2]. Naphtha dearomatization and benzene hydrogenation to cyclohexane can be performed with the NiSAT[®] catalysts offered by Süd Chemie [3] in the liquid phase, or with the BenSat process from Axens operating in catalytic distillation conditions on a Ni catalyst [4]. Ni/Al₂O₃ are also used for the CO_x methanation reaction

operated in the gas phase either to purify hydrogen from CO_x or to produce Substitute Natural Gas e.g. from syngas generated by biomass gasification [5,6]: catalysts of this type are provided, among others, by Johnson Matthey, Süd Chemie and Topsøe. All these processes are performed, according to thermodynamics, at relatively low temperatures (usually <673 K) and under some tens of bar of hydrogen, either in the liquid or in the gas phase.

Ni deposited on aluminate carriers are also largely used for steam reforming processes. These processes are essentially endothermic and are consequently performed at higher temperatures (673–1173 K) and moderate to low pressures. They are used industrially since decades for producing hydrogen by steam reforming of hydrocarbons both in large scale production plants [7] and for fuel cell applications [8], and are under study for other hydrogen production processes such as methane dry reforming [9], bioethanol steam reforming [10] and the steam reforming of tars to purify biomass-derived syngases [11,12]. They may also be of interest as functional layers over the anodes of methane fuelled Solid Oxide Fuel Cells [13]. In these cases, due to the higher reaction temperature, more thermally stable “support” phases than pure alumina

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Table 1
properties of the catalysts.

Notation	NiO loading (% wt ^a)	Ni loading (%wt ^b)	Surface area (m ² /g)	NiO crystal size (nm)
NiO (Siralox 5/170)	0	0	172	–
Ni5	6	5	155	n.d.
Ni16	20	16	137	~10
Ni39	50	39	107	~25
Ni125	160	125	76	~36
NiO	∞	∞	4	~40

^a $100 \times W_{\text{NiO}}/W_{\text{support}}$.^b $100 \times W_{\text{Ni}}/W_{\text{support}}$.

are needed. For this reasons, silica, a stabilizing agent against phase transition of alumina, can be a component, while alkali and alkali earth cations (usually K, Mg or Ca) are usually present, producing aluminate spinels and beta-aluminas refractory supports. Such cations can also moderate surface acidity of the support, useful to limit growth of carbonaceous materials, but also somehow modify the character of Ni centers.

Such Ni-based catalysts are either produced by impregnation of preformed alumina-based carriers with Ni compounds, or by coprecipitation of Ni salts with the components of the “support”, both followed by calcination. Thus, a mixed oxide containing NiO is usually the precursor of the catalyst. It is usually believed that the nature of the obtained oxide precursor is a primary factor in the generation of most properties of the resulting catalyst, which is mostly assumed to be essentially metallic although the possible role of unreduced centers cannot be excluded. On the other hand, oxidized NiO/Al₂O₃ catalysts are also of interest due to their activity in oxidative de-hydrogenation of alkanes [14,15], Selective Catalytic Oxidation of ammonia to nitrogen [16] and ozonation reactions as well as ozone decomposition [17]. The redox properties of materials based on NiO/Al₂O₃ are of interest in relation to their possible use as oxygen carrier materials in Chemical Looping Combustion and Reforming [18].

On the frame of studies on the catalytic steam reforming of biomass tar [19], and on the production of hydrogen from ethanol steam reforming [20], we prepared and tested a series of NiO/alumina catalytic materials. Here we will report and discuss about the properties of these materials, and we will try to relate them to those of the real catalysts and of the spent ones, which will be the object of further investigation.

2. Experimental

2.1. Catalysts preparation

Siralox 5/170 (95% w/w Al₂O₃, 5% w/w SiO₂) from Sasol has been used as the support. The presence of 5% SiO₂ allows to increase the stability of transitional alumina towards phase transition. Ni–alumina catalysts (Table 1) have been prepared by wet impregnation using Ni(NO₃)₂·6H₂O water solution, followed by drying and calcination at 973 K for 5 h.

2.2. Catalysts characterization

X-ray diffraction patterns were carried out by using a vertical powder diffractometer X'Pert with Cu K α radiation ($\lambda = 0.15406$ nm). The patterns were collected in the 20–100° 2 θ range with a step of 0.02° and a counting time for each step of 3 s. Powder patterns were indexed by comparing experimental results to the data reported in the Pearson's Crystal Data database [21].

The specific surface area was calculated applying the multipoint BET method [22] using a modified Sartorius symmetrical microbalance, described elsewhere [23].

DR-UV–vis–NIR spectra have been recorded with a Jasco V570 instrument.

Skeletal IR spectra were recorded using KBr pressed disks (weight 1.01 g) and a Nicolet Nexus instrument.

A Renishaw Raman System 2000 spectrometer with a He–Ne laser (632.8 nm) excitation source and equipped with a Peltier Cooled CCD as detector and a Leica Optical Microscope was used for carrying out the analysis. Spectra were recorded with a 50 \times objective following previously applied parameters as: integration time (10 s), number of acquisitions (1 or 9), Raman shift (from 4000 to 100 cm⁻¹). A filtering system was also applied in order to vary laser power (100%, 50%, 25%, 10%, 1%).

For IR studies of the adsorption of CO, pressed disks of the pure catalysts powders were activated “in situ” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. The catalyst disk was first submitted to a treatment in air for 30 min, followed by evacuation at 773 K before the adsorption experiments. In order to obtain the reduced catalyst, after the mentioned evacuation, it was put into contact with H₂ ~400 Torr at 773 K, for 30 min, and successively outgassed at the same temperature. CO adsorption was performed at 133 K by the introduction of a known dose of the gas (10 Torr) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected using a Nicolet Nexus FT instrument, during evacuation upon warming at increasing temperatures between 133 K and 273 K.

2.3. Catalytic experiments

A tubular silica glass flow reactor, containing a fixed bed with 44.1 mg of catalyst mixed with 440 mg of silica glass particles (60–70 mesh sieved). For experiments simulating biomass tar abatement the reactor was fed with 40 Nml/min (GHSV = 54,000 h⁻¹) of a gaseous mixture 39.3% He, 54.6% water, 4.1% ethanol and 2% phenol mol/mol. For the thermal conversion experiment the bed was constituted by 484.1 mg of silica glass. A phenol–water–ethanol single phase liquid solution was pumped through a HPLC pump (Shimadzu Corp. LC-D10 AD) in an appropriate heating section at 583 K of the feed line to produce a gas whose composition corresponds to 168 g/Nm³ of ethanol + phenol (84.9 g/Nm³ of phenol), and 439 g/Nm³ water vapour in the He inert carrier. For ethanol steam reforming experiments, the reactor was fed with 6 Water/Ethanol molar ratio in He 41.6% carrier with GHSV = 51,700 h⁻¹. The evaluation of activation energies during partial reactants conversion at low temperature 573–773 K allowed us to exclude at least in this temperature region significant diffusion limitations. In order to reveal conditioning effect catalytic experiments were performed both rising and reducing reaction temperature (773 K, 873 K, 973 K, 1023 K and reverse).

Product analysis was performed with a GC/MS (Focus-ISQ Thermoscientific), in order to have a precise identification of the compounds, and with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between the detectors, a nickel

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