



## On the detectability limits of nickel species on NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic materials



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### ABSTRACT

NiO/Al<sub>2</sub>O<sub>3</sub> mechanical mixtures and impregnated catalytic materials have been prepared and analysed by XRD, DR-UV-vis-NIR, skeletal FT-IR, XPS, FE-SEM techniques. The presence of the carcinogenic and easily reducible NiO phase (bunsenite) is detected by XRD, DR-vis and DR-NIR with a sensitivity limit well lower than 1000 ppm, which is the lower limit by law to classify a NiO-containing waste, such as spent catalysts, as dangerous. This species is also observed by XPS and FE-SEM with a similar sensitivity limit. Hardly reducible surface dispersed Ni<sup>2+</sup> species are also observed by DR-vis with a sensitivity limit lower than 1000 ppm. A surface spinel-like phase, with a composition Ni<sub>x</sub>Al<sub>2</sub>O<sub>3+x</sub>, with  $x \leq 0.25$  is formed at higher loadings, and is distinguished from the highly dispersed Ni<sup>2+</sup> species using IR and XRD. This defective surface spinel like species can be distinguished from stoichiometric bulk NiAl<sub>2</sub>O<sub>4</sub> by applying DR-NIR spectroscopy. The stoichiometric bulk nickel aluminate phase NiAl<sub>2</sub>O<sub>4</sub> (which is also classified as carcinogenic) does not form from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or  $\delta$ -Al<sub>2</sub>O<sub>3</sub> and nickel species at temperatures up to 1073 K.

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### 1. Introduction

NiO/Al<sub>2</sub>O<sub>3</sub> materials are mostly synthesized industrially as precursors of Ni/Al<sub>2</sub>O<sub>3</sub> based supported metal catalysts for hydrogenation of aromatics, acetylenics and dienes and for methanation [1]. They are also of interest for low-temperature steam reforming of organic compounds such as propane [2], ethanol [3,4], biomass tar [5,6], bio-oils [4,7] and for pre-reforming of natural gas [8]. These catalysts are prepared either by impregnation of preformed alumina or by co-precipitation. In real hydrogenation catalysts the amount of nickel in the catalyst is relatively high, of the order of 20–50 wt.% depending on the surface area: easily reducible NiO is observed on the catalyst precursors, which are pre-reduced producing Ni metal nanocrystals weakly interacting with the alumina support, to which catalytic activity is attributed.

Unreduced NiO/Al<sub>2</sub>O<sub>3</sub> materials have also interesting catalytic activity in several reactions of industrial interest [9–15]. In some of these cases, such as for paraffin oxidative dehydrogenation [16,17], the loaded amount of nickel is or may be moderate (e.g. 10 wt%)

and catalytic activity is also found in the absence of detected NiO. In fact, at moderate Ni loadings, hardly reducible bulk or surface spinel-like species are mainly formed by the strong interaction of Ni<sup>2+</sup> with alumina [18]. Reduction of this species gives rise to isolated or slightly clustered Ni metal atoms [19] which are less active but more selective in the methanation of CO<sub>2</sub> with respect to extended Ni metal particles [20], and poorly active in steam reforming of ethanol [18]. Ni<sup>2+</sup> is also a promoter for alumina-supported MoS<sub>2</sub> and WS<sub>2</sub> catalysts for hydrotreating of hydrocarbon flows: in this case the amount of promoter is of the order of 1–2 wt% and it should mostly interact with the supported sulphide phase [21]. A strong interaction of nickel with alumina is to be avoided in this case. Nickel 5 wt% is also reported to act as an activity promoter of Co/Al<sub>2</sub>O<sub>3</sub> catalysts for low-temperature Fischer Tropsch reaction: in this case the impregnation of Ni on alumina must be performed before impregnation of cobalt, while addition of Ni after Co-impregnation is detrimental [22]. This suggests that a strong interaction of Ni with alumina is needed for promotion. NiO/Al<sub>2</sub>O<sub>3</sub> materials are also of interest as adsorbents for water purification from organics [23] and for the preparation of pigments [24], and in relation to the characterization of multilayer scales at the surface of Ni-Al based alloys [25,26].

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**Table 1**  
Main properties of the investigated samples.

Notation	Composition <sup>a</sup>	Preparation	x in Ni <sub>x</sub> Al <sub>2</sub> O <sub>3+x</sub>	BET [m <sup>2</sup> /g <sub>CAT</sub> ]
A700	γ-Al <sub>2</sub> O <sub>3</sub>	Puralox SBA200	0	198
A800	δ-Al <sub>2</sub> O <sub>3</sub>	A700 calcined at 1073 K	0	107
0.1NiOA(MM)	1000 ppm NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Mechanical Mixing	0.0014	197
0.1NiOA(I)	1000 ppm NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation	0.0014	197
1NiOA(MM)	1% NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Mechanical Mixing	0.014	192
6NiOA(1700)	6% NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation calc 700	0.08	165
6NiOA(1800)	6% NiO/δ-Al <sub>2</sub> O <sub>3</sub>	Impregnation calc 800 <sup>b</sup>	0.08	104
20NiOA(I)	20% NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation	0.27	157
50NiOA(I)	50% NiO/γ-Al <sub>2</sub> O <sub>3</sub>	Impregnation	0.67	120
NiAl <sub>2</sub> O <sub>4</sub>	NiAl <sub>2</sub> O <sub>4</sub>	Coprecipitation	1.00	–
NiO	NiO	Calcination of the nitrate at 973 K	–	4

<sup>a</sup> 100\*Wt<sub>NiO</sub>/Wt<sub>Al<sub>2</sub>O<sub>3</sub></sub>.

<sup>b</sup> the support was previously calcined at 1073 K, too.

The interaction of Nickel species with alumina is also relevant in relation to the activity of γ-Al<sub>2</sub>O<sub>3</sub> as an adsorbent to remove Ni<sup>2+</sup> and other heavy metals from water [27] and as Ni trap to limit the formation of metallic nickel in FCC catalysts [28]. Due to the classification as carcinogenic compounds of both NiO and NiAl<sub>2</sub>O<sub>4</sub>, the determination of their presence in amounts of the order of 1000 ppm wt, or their absence or lower loading in spent FCC catalysts is needed to classify them as dangerous/non dangerous wastes [29]. A similar question occurs with the possible toxicity of nickel containing pigments [30] and the qualification of nickel species emission inventory for oil-fired boilers [31].

In this study we addressed the problem of the detection limits of the toxic NiO and NiAl<sub>2</sub>O<sub>4</sub> phases in NiO/Al<sub>2</sub>O<sub>3</sub> materials. The aim is to provide information on the ways to determine the classification (dangerous/non dangerous) of Ni-containing materials and to define the presence of the differently active species.

## 2. Experimental

### 2.1. Materials preparation

Data on the catalysts used are summarized in Table 1. The samples composition can be expressed as Ni<sub>x</sub>Al<sub>2</sub>O<sub>3+x</sub> where x=0 for alumina and x=1 for nickel aluminate spinel. Puralox Sba 200 (“pure” Al<sub>2</sub>O<sub>3</sub>), produced by Sasol, was used as received (A700) or “stabilized” by calcination at 1073 K for 5 h (A800) as catalyst support. NiO, prepared by thermal decomposition of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O at 973 K, was carefully mechanically mixed in prefixed amounts with alumina to produce “mechanical mixtures”. Several portions of these mixtures were analysed to check reliability of the measures and sampling reproducibility. The preparation of impregnated samples was performed through wet impregnation of an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. A step of drying at 363 K for 5 h was then performed and the samples were finally calcined at 973 K or 1073 K.

### 2.2. Materials characterization

Surface area measurements were done with the single point method by adsorption of nitrogen at the liquid nitrogen temperature (assuming 16.2 Å<sup>2</sup> the area of a N<sub>2</sub> molecule) in a volumetric line, after outgassing at 473 K for 30 min in vacuum.

X-Ray diffraction patterns were recorded using Cu Kα radiation (λ = 0.15406 nm). XRD analysis of the samples were obtained using a vertical powder diffractometer X'Pert. The patterns were collected in the 25–100° 2θ range with a step of 0.02° and a counting time for each step in-between 9 and 20 s depending on the Ni loading. Powder patterns were indexed by comparing experimental results to the data reported in the Pearson's Crystal Data [32] and JCPDS-ICDD databases [33].

Skeletal IR spectra were recorded using KBr pressed disks (weight 0.808 g) and a Nicolet Nexus instrument (OMNIC software, DTGS detector, 100 scans). All the spectra are reported in common scale. UV–vis-NIR spectra were collected on pure powder with a JASCO V570 instrument.

XPS measurements were performed using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg Kα radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra were recorded in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI-ACCESS ESCA-V6.0F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian-Lorentzian curves in order to determine the binding energy of the different element core levels more accurately.

A Scanning Electron Microscope (SEM) Zeiss SUPRA 40 VP microscope, equipped with a field emission gun was used to investigate sample morphology. This instrument is equipped with a high sensitivity “InLens” secondary electron detector and with a EDX microanalysis OXFORD “INCA Energie 450 × 3”. Samples were suspended in ethanol under ultrasonic vibrations to decrease particle aggregation. A drop of the resultant mixture was deposited on a Lacey Carbon copper grid and the dried sample was then imaged.

## 3. Results

### 3.1. X-ray diffraction study

In Fig. 1 the XRD patterns of the samples under study are reported. The pattern of the A700 sample is consistent with that of cubic γ-Al<sub>2</sub>O<sub>3</sub>, JCPDS Table 75-0921. After calcination at 1073 K (A800), the XRD pattern is slightly different: the more evident complexity in the 2θ range 30°–40° and the partial resolution of two components in the peaks near 2θ ~46° and ~67° (4,0,0 and 4,4,0 spinel peaks, respectively) can be taken as an evidence of a tetragonally distorted defective spinel alumina similar to δ-Al<sub>2</sub>O<sub>3</sub>, JCPDS card 088-1609 [34], or γ'-Al<sub>2</sub>O<sub>3</sub> [35].

The addition by impregnation of 0.1 wt% (i.e 1000 ppm, 0.1NiOA(I)) and of 6 wt% NiO at the surface of both starting aluminas (samples 6NiOA(1700) and 6NiOA(1800)) does modify significantly the XRD pattern neither of A700 (γ-Al<sub>2</sub>O<sub>3</sub>) nor of A800 (δ-Al<sub>2</sub>O<sub>3</sub>). No additional peaks can be observed. At higher Ni loadings, (20 wt% and 50 wt% NiO on A700, samples 20NiOA(I) and 50NiOA(I)), the XRD pattern of γ-Al<sub>2</sub>O<sub>3</sub> undergoes some modifications. The two most intense 4,4,0 and 4,0,0 spinel peaks shift very slightly to lower angles together with the growth in intensity of the reflection 5,1,1 and, in particular, of the 3,1,1 spinel peaks, showing the progressive formation of a XRD pattern similar to that of NiAl<sub>2</sub>O<sub>4</sub> spinel phase [36,37]. Additionally the 2,0,0, and 2,2,0 XRD peaks of the NiO (bun-

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