Catalysis Science & Technology

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Rudolf, B. Dragoi, A. Ungureanu, A. Chirieac, S. Royer, A. Nastro and E. Dumitriu, *Catal. Sci. Technol.*, 2013, DOI: 10.1039/C3CY00611E.

Catalysis Science & Technology



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

RSCPublishing

www.rsc.org/catalysis

Cite this: DOI: 10.1039/coxx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

NiAl and CoAl Materials Derived from Takovite-like LDHs and Related Structures as Efficient Chemoselective Hydrogenation Catalysts

Constantin Rudolf,^a Brindusa Dragoi,^{*a} Adrian Ungureanu,^a Alexandru Chirieac,^a Sébastien Royer,^b Alfonso Nastro, ^c and Emil Dumitriu^a

s Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

The catalytic performance of metallic catalysts derived from layered double hydroxides (LDHs) precursors with nickel or cobalt incorporated in the brucite-like layers besides aluminium (*i.e.*, NiAl takovite-like materials and related CoAl) was investigated for the first time in the chemoselective

- ¹⁰ hydrogenation of cinnamaldehyde. The precursors in the as-synthesized and calcined forms were thoroughly analysed by ICP, XRD, nitrogen physisorption, DR UV-vis spectroscopy, TPR and in-situ XRD after temperature-programmed reduction. According to the XRD results, both as-synthesized samples contained purely LDH phases with degrees of crystallization depending on the nature of incorporated metal cations (*i.e.*, the CoAl sample presents larger crystallites than NiAl takovite-like
- ¹⁵ sample). For the calcined NiAl and CoAl samples, well-crystallized oxide phases of NiO and Co_3O_4 , respectively, besides amorphous alumina and corresponding spinels were evidenced by XRD. The TPR and in situ XRD results for the calcined samples indicated strong metal-alumina interactions, which resulted in depressed sintering of evolved metal nanoparticles in the high-temperature range of 600-800 °C, in well agreement with TEM analysis. Materials derived from the studied HDL systems are found to
- ²⁰ be efficient catalysts for the hydrogenation of cinnamaldehyde, showing enhanced control over the activity or selectivity, depending on the nature of active metals and the thermal regime of the catalyst activation.

Introduction

Published on 10 October 2013. Downloaded by Yale University Library on 10/10/2013 18:05:07.

The hydrogenation of cinnamaldehyde (CNA) is one of the most ²⁵ studied catalytic reductive processes. Though CNA molecule has high degree of unsaturation (*i.e.*, aromatic ring, C=O and C=C double bonds), its partial hydrogenation preferentially occurs in the side aliphatic chain forming hydrocinnamaldehyde (HCNA) and cinnamyl alcohol (CNOL), respectively [1; 2; 3]. Both

- ³⁰ hydrogenated products are of industrial interest and therefore there is challenging to develop high performance catalysts which are selective either to HCNA or CNOL. HCNA is used as inhibitor of the potato tubers sprouting [4] or for the preparation of pharmaceutical products such as HIV protease inhibitors [5],
- ³⁵ while CNOL is largely used in perfumery and flavour industries [3]. For instance, it is frequently used in blossom compositions such as lilac, jasmine and lily of the valley, hyacinth and gardenia, to impart balsamic and oriental notes to the fragrances. It could be noted that hydrocinnamyl alcohol (HCNOL), the
- ⁴⁰ product of total hydrogenation, has practical applications, as well. Therefore, it is a component in perfumes [**6**], while in adequate chemicals mixture has bactericidal properties [**7**].

The most part of the catalysts used for the hydrogenation of CNA to HCNA and CNOL are based on noble metals such as Rh ⁴⁵ [8-9], Pd [10-12], Pt [13, 14], Au [15-17], Ru [18], *etc.* In the

presence of such catalysts high selectivities towards HCNA or CNOL were obtained (e.g., 100 % unsaturated aldehyde at 79 % conversion of CNA on Rh(III)-hexamolybdate/ γ -Al₂O₃ [9]; ~ 88 % HCNA at total conversion of CNA on Pd/polyketone [8]; 50 % ⁵⁰ unsaturated alcohol at 50 % conversion of CNA on Pt supported on carbon aerogel [11]; 48 % unsaturated alcohol at 60 % conversion of CNA on Ru/carbon nanofiber [18], but the catalytic phases based on noble metals are very expensive and in limited amounts as offer.

The use of mono- and bimetallic catalysts based on non-noble 55 metals such as Cu, Ni and Co for selective hydrogenation reactions, including the hydrogenation of α,β -unsaturated aldehydes such as cinnamaldehyde, was also reported in several papers, either in liquid or gas phase [19-25]. Such materials 60 presented interesting catalytic performances which depend on a wide variety of factors such as the nature of active sites, interaction with the support, reaction and catalyst activation conditions, nature of the second metal and so on. For instance, a CNOL selectivity of ~ 45 % was reported on Cu-Co/SiO₂ 65 bimetallic catalyst [20]. It was shown that the rate of CNOL formation is essentially increased on spinel Cu-Ni(Co)-Zn-Al catalysts compared to Cu/SiO2 or binary Cu-Al samples due to the formation of surface $Cu^{o}-M^{2+}$ dual sites ($M^{2+} = Co$, Ni, Zn). Ni⁰/TiO₂ also manifested high activity in the hydrogenation of 70 CNA with very high selectivity to HCNA (98 % at CNA conversion of 66.2 % in iso-propanol and under 2 MPa hydrogen pressure [22] while Ni⁰/MCM-41 converted 94.6 % CNA with a selectivity to HCNA of 44.2 % [25].

In this contribution we report an original process to obtain 5 highly active and chemoselective catalysts based on non-noble metals, those process is easy to perform and not expensive. Usually, the mixed oxides of reducible cations obtained via layered double hydroxides (LDHs) are effective catalytic precursors because the LDHs are obtained as well-organized and 10 compositional versatile crystalline materials. Indeed, interesting catalytic performances were previously reported in the hydrogenation of CNA over materials derived from assynthesized hydrotalcite-like materials with Ni, Cu or Co incorporated in MgAl or ZnAl matrixes (e.g., 60 % HCNA at 15 total conversion of CNA on MgCuAl or 90 % CNOL at 9 % conversion of CNA on ZnNiCoAl (Ni:Co = 8 : 2)) [26]. However, it was demonstrated that the acid-basic sites associated with the magnesium or zinc cations promote the secondary reactions of aldol condensation of aldehydes, which negatively

- ²⁰ influences the yield to the hydrogenation products [27]. To circumvent these drawbacks, in the present investigation we report for the first time the use of Mg(Zn)-free Ni- and Co-based catalysts derived from binary takovite (NiAl) and related CoAllayered double hydroxides (M/Al ratio of 2/1) in the ²⁵ chemoselective hydrogenation of cinnamaldehyde. As it is known, takovite-based catalysts are able to activate various reactions such as methanation of CO, Fischer-Tropsch reactions and steam reforming of methane [28]. Interestingly, the first patent about the application of layered double hydroxides for the ³⁰ catalytic hydrogenations mainly claimed the use of reduced oxide derived from takovite and related hydrotalcite-like structures [29]. In addition, these bicomponent catalysts allow the
- preparation of a large amount of metals highly dispersed on alumina, which is difficult to achieve for metal supported ³⁵ catalysts obtained by conventional impregnation. Materials derived from takovite and related materials are found to be efficient hydrogenation catalysts, showing enhanced control over the activity or selectivity, depending on the nature of active metals and the thermal regime of the catalyst activation.

40 Experimental

Catalyst preparation

All chemicals were used as received: aluminium nitrate (Al(NO₃)₃·9H₂O, 98%, Sigma-Aldrich), nickel nitrate ⁴⁵ (Ni(NO₃)₂·6H₂O, 98%, Sigma-Aldrich) and cobalt nitrate (Co(NO₃)₂·6H₂O, 98%, Sigma-Aldrich) as metal precursors, sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃ 99.8%, Merck) as precipitating agents. For catalytic runs, the chemicals were also used as purchased: trans-cinnamaldehyde ⁵⁰ (C₆H₅CH=CHCHO, 98%, Merck) as reagent and propylene carbonate (C₄H₆O₃, 99%, Sigma-Aldrich) as solvent.

Two samples of layered double hydroxides, CoAl and NiAl with a molar ratio 2:1, were prepared by co-precipitation at low supra-saturation method. An aqueous solution containing the ⁵⁵ corresponding metal sources and a solution containing Na₂CO₃ (0.8 M solution) and NaOH (1.6 M solution) were simultaneously added at a flow rate of 0.7 ml⁻min⁻¹ under vigorous stirring and

constant temperature (30 °C) and pH (9.0).

The precipitates were recovered by filtration and then washed ⁶⁰ with deionized water to remove Na⁺ ions. After washing, the resulting solid was dried at 40 °C up to constant weight. Before use, the samples were calcined at 450 °C for 5 h under static air (heating ramp of 1.5 °C min^{-1}) and then reduced for 10 h at 500 °C under H₂ flow (1 L h⁻¹), with a heating ramp of 1.5 °C min^{-1} . ⁶⁵ CoAl sample was also reduced at 700 °C.

Catalyst characterization

Chemical composition (Co, Ni and Al) of the samples was performed on a Perkin sequential scanning inductively coupled plasma optical emission spectrometer (Optima 2000 DV). Before 70 analysis, a known amount of sample was digested in a diluted HCl solution and then heated under microwave until complete dissolution. XRD measurements were performed on a Bruker AXS D8 apparatus with monochromatic CuK α radiation (λ = 0.15406 nm wavelength) at room temperature. The patterns were ⁷⁵ recorded from 5 to 70 ° 2θ , with a step of 0.02 °. The crystallite sizes were calculated using the Scherrer equation: $d_{hkl} = \lambda/\beta \cos\theta$, where λ = incident ray wavelength (0.15406 nm); β = peak width at half height (rad) after Warren's correction for instrumental broadening; and θ = Bragg angle. Nitrogen physisorption was 80 carried out at -196 °C on an Autosorb MP-1 instrument from Quantachrome. Surface areas and pore volumes were calculated from the corresponding isotherms using conventional algorithms.

Diffuse reflectance UV–visible (DR UV–vis) spectra were recorded on a Shimadzu UV-2450 spectrometer equipped with an sintegrating sphere unit (ISR-2200). The spectra were collected in the range between 190 – 800 nm by using BaSO₄ as the reflectance standard. *In situ powder XRD patterns* were recorded

on a Bruker D8 ADVANCE X-ray diffractometer equipped with a VANTEC-1 detector, using a CuK α radiation ($\lambda = 1.54184$ Å) 90 as X-ray source. The powder samples were placed on a kanthal followert (EaCAL) equity. The data mere callected in the 20 mere

filament (FeCrAl) cavity. The data were collected in the 2θ range from 10 to 80° with a step of 0.05° (step time of 2s). Phase identification was made by comparison with ICDD database. The diffractograms were recorded after *in situ* reduction from 30 to

⁹⁵ 800 °C under a flow of 3 vol.% H₂ in He (30 mL min⁻¹). The data were collected 3 times at each temperature. *TEM* images were obtained using a on a JEOL 2100 instrument (operated at 200 kV with a LaB₆ source and equipped with a Gatan Ultra scan camera). *Temperature programmed reduction* experiments were

performed on an Autochem chemisorption analyser from Micromeritics, equipped with a TCD and MS (Omnistar, Pfeiffer) detectors. About 100 mg of as-synthesized LDH were inserted in a U-shape microreactor. Before each TPR run, the catalyst was activated at 120 °C for 4 h under a flow of simulated air (30 mL ¹⁰⁵ ·min⁻¹). After cooling to 50 °C, the H₂ containing flow was attributed (20 mL mist¹ - 2 mil¹⁰). (4)

stabilized (30 mL min⁻¹, 3 vol.% H_2 in Ar) and the TPR was performed from 50 to 800 °C with a temperature ramp of 2 °C min⁻¹.

Hydrogenation of trans-cinnamaldehyde

¹¹⁰ The catalytic runs were carried out in a round-bottom three-neck glass reactor equipped with a bubbler, magnetic stirrer and a reflux condenser. The reaction was performed at atmospheric pressure under the following conditions: 0.265 g of catalyst, 1.0 ml of trans-cinnamaldehyde, 25.0 ml of propylene carbonate as

solvent, hydrogen flow of 1.0 L h⁻¹, reaction temperature of 150 °C, and agitation speed of 900 rpm. Samples of reaction mixture were periodically withdrawn and analyzed with a gaschromatograph (HP 5890 equipped with a DB-5 capillary column $_5$ (25 m \times 0.20 mm \times 0.33 μ m) and FID detector). The identification of the products from the reaction mixture was accomplished from the retention time of the pure compounds and verified by GC-MS (Agilent 6890N system equipped with an Agilent 5973 MSD detector and a 30-m DB-5-ms column). The 10 quantitative analyses were performed by taking into consideration the FID response factor for each compound. The total conversion of cinnamaldehyde and the selectivity towards different hydrogenation products were calculated as previously reported [30]. For the recyclability tests, the catalysts were recovered by 15 centrifugation from the end reaction mixture, washed with fresh propylene carbonate and ethanol, and then dried under vacuum before the reactivation.

Results and discussion

Catalysts characterization



²⁰ The chemical compositions of LDH precursors were evaluated by ICP and are presented in Table 1.

Fig. 1 Powder X-ray diffraction for the as-synthesized LDHs.

- As noted, the Co/Al and Ni/Al ratios in the final solids are slightly different from those of the synthesis mixture (2.18 and 2.05 for Co/Al and Ni/Al, respectively *vs* 2.0). These small variations of the final M²⁺/Al ratios are usual and are due to the preferential precipitation of one cation to another [**31**]. According ³⁰ to these values, the complete incorporation of aluminium at pH =
- 9 did not occur during the synthesis, especially for the Co/Al sample.

The crystalline structure of LDH precursors was investigated by powder X-ray diffraction. As shown in Fig. 1, the diffraction 35 patterns for the as-synthesized LDH samples display the characteristic diffraction peaks of crystalline hydrotalcite-like LDHs, which are indexed in a hexagonal lattice with R-3m rhombohedral symmetry [1]. It should be noted that for CoAl sample the diffraction peaks are sharper and narrower suggesting 40 improved crystallinity (larger particle size) than for NiAl sample. On the basis of the difractogramms, the structural parameters (*i.e.*, basal distances $-d_{003}$, a and c parameters and the crystallite sizes) were calculated and are provided in Table 1. As it can be observed, d_{003} displays values of 7.82 and 7.75 Å for CoAl and 45 NiAl, respectively, which are higher than that of the MgAl hydrotalcite (7.65 Å) [32]. However, it should be taken into account that the thickness of the brucite layer of hydrotalcite is 4.8 Å [32], the amount of water (data not shown here) is almost the same for both samples while the counteranion is carbonate in 50 both cases. Hence, the increase of the d_{003} value for NiAl and CoAl can be explained by the increase in the thickness of brucitelike sheets due to the substitution of AI^{3+} by Ni^{2+} and Co^{2+} [**31**]. These structural results confirm the incorporation of the metallic

cations into the brucite-like layers of the samples. 55 **Table 1** Physical properties of the as-synthesized LDHs

| Sample | M/Al ^a (molar ra Synthesis | tio) ICP | Ionic radius for M ²⁺ (pm) ^b | $d_{003}^{ m c}$ (Å) | a ^d (Å) | c ^e (Å) | D ₍₀₀₃₎ ^f (nm) | D ₍₁₁₀₎ ^g (nm) |
|--------|---|-------------|---|-------------------------|-----------------------|-----------------------|---|---|
| CoAl | 2 | 2.18 | 74.5 | 7.82 | 3.06 | 23.46 | 17.41 | 32.64 |
| NiAl | 2 | 2.05 | 69.0 | 7.75 | 2.96 | 23.25 | 4.33 | 9.73 |

^aM = Co, Ni; ^b[**33**]; $d_{002} = \lambda/2sin\theta$; ^da = $2d_{110}$; ^ec = $3d_{003}$; ^fD₍₀₀₃₎ = crystallite size in *c* direction; ^gD₍₁₁₀₎ = crystallite size in *a* direction.



Fig. 2 DR UV-Vis spectra for the as-synthesized LDHs

60 Information on the oxidation state as well as the coordination

of the cations into the brucite-like sheets was provided by DR UV-vis spectrometry. The recorded spectra are displayed in Fig. 2. Because Al³⁺ has *d*0 configuration, it does not show absorption bands in the UV-vis spectra. Therefore, the spectra show the ⁵ bands mainly associated to the d – d transitions of Ni²⁺ (*d*8) and Co²⁺ (*d*7) cations. As illustrated in Fig. 2, a characteristic band around 205 and 250 nm for NiAl and CoAl, respectively due to the O²⁻ \rightarrow Mⁿ⁺ charge transfer transitions was identified in each corresponding spectrum [**34-37**].

The incorporation of cobalt in CoAl sample resulted in the formation of a three component absorption band positioned at ~ 450, 490 and 520 nm which was ascribed to Co^{2+} in octahedral coordination [**38**]. Additionally, an absorption band centered at ~

600 nm is observed and it may be attributed to d–d transitions in 15 low spin of octahedrally coordinated Co^{3+} cations [**39**]. Nevertheless, this band is much less intense in comparison to the band at ~ 520 nm, indicating that a minor amount of cobalt exists as Co^{3+} .

For NiAl sample, two double important bands are observed. ²⁰ The first one is located at ~ 375 and 420 nm and the second one at ~ 630 and 730 nm. Two spin-allowed transitions ${}^{3}A_{2g}(F) \rightarrow$ ${}^{3}T_{1g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$ were assigned to the bands at 375 and 730 nm, respectively, while the bands at 420 and 630 nm were assigned to spin forbidden transitions ${}^{3}A_{2g}(F) \rightarrow {}^{1}E_{g}(D)$ and ${}^{25}{}^{3}A_{2g}(F) \rightarrow {}^{1}T_{2g}(D)$ [**28**]. Both bands correspond to Ni²⁺ in octahedral coordination.



Fig. 3 N₂ adsorption-desorption isotherms for the as-synthesized (A) and calcined-mixed oxides (B) samples

 Table 2 Textural properties of as-synthesized and calcined LDHs

| Sample | ${\displaystyle \mathop{S_{BET}}\limits_{(m^2.g^{-1})}}$ | V_{pore} (cm ³ .g ⁻¹) |
|----------------------|--|---|
| CoAl | 68 | 0.44 |
| NiAl | 69 | 0.49 |
| CoAl-MO ^a | 219 | 0.93 |
| NiAl-MO ^a | 229 | 1.27 |

³⁰ ^a MO - mixed oxides

Published on 10 October 2013. Downloaded by Yale University Library on 10/10/2013 18:05:07

The textural properties of the samples were evaluated from the nitrogen adsorption-desorption isotherms (Fig. 3A). The isotherms are of type IIb [**45**, **46**] and originate from the ³⁵ adsorption of nitrogen in the void spaces between the plate-like particles. The shape of the hysteresis loops (type H3) indicates a large distribution of the slit-shaped mesopores for both samples. The textural properties, *i.e.* the specific surface areas and pore volumes are summarized in Table 2. The obtained values are in ⁴⁰ agreement with those already reported for these kinds of materials [**31**, **32**]. As expected, the calcination of these solids at 450 °C gave rise to changes in the texture of solids. Indeed, for

the calcined CoAl (denoted as CoAl-MO) and NiAl (denoted as

CoAl-MO) samples the isotherms illustrated in Fig. 3B are of 45 type IV with larger hysteresis loops, especially for NiAl sample. This indicates improved mesoporosity, which is a positive feature for catalysis as the diffusional limitations are restricted. As a result, the surface areas of MO-materials are almost three times the surface areas calculated for the as-synthesized materials. These increases might also indicate that the formation of highly stable spinels was avoided, which typically occurs for LDHs containing transition metals cations in the layer and carbonate as counteranion [**46**].

The reducibility and extent of metal-alumina interactions for ⁵⁵ the calcined LDHs precursors were investigated by TPR (Fig. 4). The TPR profile for CoAl-MO sample displays two main maxima of reduction. Based on in-situ XRD results (see below), the first peak, centered at ~ 350 °C, was assigned to the reduction of Co_3O_4 spinel to CoO while the second one, centered at ~ 700 °C, ⁶⁰ was attributed to the reduction of CoO to Co⁰. Nevertheless, the reduction of Co²⁺ in amorphous CoAl₂O₄ cannot be totally ruled out at 700 °C [**40**, **41**], although the characteristic peaks of the spinel were not detected by *in situ* XRD (see below). The TPR profile of NiAl-MO sample shows one minor and broad peak

15

between 200 and 400 °C and a major peak at 400 - 800 °C with maximum at ~ 630 °C and a shoulder at ~ 560 °C. The first peak is attributed to the reduction of Ni²⁺ in a minor NiO phase with no interaction with the support [42]. The reduction temperatures at \sim s 560 °C and ~ 630 °C are assigned to the reduction of Ni^{2+} in NiO

- in strong interaction with alumina and/or NiAl₂O₄ [41, 43, 44], also noticing that the characteristic peaks of the spinel were not detected by in situ XRD (see below). Because the TCD signal baseline is recovered after the reduction of nickel and cobalt $_{10}$ cations, it can be affirmed that (i) there is good accessibility of H₂
- to completely reduce nickel and cobalt cations and (ii) metallic Ni⁰ and Co⁰ are in some extent supported on alumina and accessible to gas phase.



Fig.4 TPR profiles of the calcined LDHs.

In order to elucidate the nature of intermediate crystalline phases formed during the reduction process, the calcined CoAl-MO and NiAl-MO samples were reduced under hydrogen flow at different temperatures in the range of 30 - 800 °C and analyzed 20 in situ by XRD. The recorded diffractograms are displayed in Fig. 5a (for CoAl-MO) and Fig. 5b (for NiAl-MO). The XRD patterns registered at 30 °C for NiAl-MO and CoAl-MO (enlarged in Fig. 5c) show diffraction lines that fit the characteristic patterns for NiO (ICDD 047-1049) [47] and Co₃O₄ (ICDD 42-1467) [43, 48,

 $_{25}$ **49**] phases, respectively. The Co₃O₄ spinel is detected in the XRD patterns of the CoAl-MO up to 300 °C. After reduction at 400 °C, the typical diffraction lines of the Co-spinel disappeared while new diffraction peaks appeared at $2\theta = 36.47, 42.37$ and 61.47° . These peaks are unambiguously assigned to the diffraction from 30 the (111), (200) and (220) planes of CoO crystal lattice (ICDD 48-1719) [50] (Fig. 5d). As observed from Fig. 5A, the intermediate CoO phases are not reducible up to a reduction temperature of 700 °C, providing clear evidence that the peak at 700 °C in the TPR profile for CoAl-MO (Fig. 4) is due to the 35 reduction of CoO to metallic cobalt. Therefore, it is obvious that the calcination of CoAl generated mainly Co₃O₄ whose reduction under H₂ takes place in two steps. However, this high reduction temperature (i.e., 700 °C) suggests a strong interaction between cobalt and alumina. Additionally, XRD showed that the alumina 40 generated by the calcination of the CoAl sample (and NiAl sample) is amorphous [51]. As noted, the crystalline CoAl₂O₄ spinel is still not observed in the diffractograms recorded at 700 °C reinforcing the idea of the amorphous state of alumina in the sample. The strong interaction between cobalt and alumina can 45 also explain the absence of the typical diffraction peaks of the metallic Co⁰ in the diffractograms after further reduction at 800 °C, which indicates that the generated nanoparticles are stable against sintering. For NiAl-MO sample, traces of NiO can be still observed in the XRD patterns after reduction at 600 °C (Fig. 5d), 50 which is in accord with TPR showing that the complete reduction of NiO takes place at ~ 750 °C. After reduction at 500 °C, new small diffraction lines attributed to metallic Ni⁰ phase (ICDD 04-0850) [52] appeared in the diffractograms. Thus, the most intense peak ($2\theta = 44.5^{\circ}$) is attributed to (111) plane of Ni⁰ 55 overlapping with the diffraction peak of the kanthal sample holder. The other two broad peaks observed at $\sim 52~$ and $\sim 76~^\circ$ and associated to the (200) and (220) planes [52], respectively, are well defined but they are too small to accurately calculate the average crystallite size of Ni⁰ nanoparticles. The reduction at 600 60 °C generated new Ni⁰ phases and the diffraction peaks are more intense. The calculated average crystallite size of the resulting Ni⁰ nanoparticles is 3.6 nm according to Scherrer's equation. Further increase in the reduction temperature to 700 and 800 °C results in the formation of slightly larger Ni⁰ nanoparticles with average 65 crystallite sizes are of 5.5 and 5.8 nm, respectively. In similarity with the CoAl sample, the results obtained for NiAl suggest a limited sintering of nickel nanoparticles in the high-temperature range of 600-800 °C because of the strong interaction between nickel and alumina [52].

Catalysis Science & Technology

Catalysis Science & Technology Accepted Manuscript



Fig.5 In situ XRD after reduction at different temperatures for the calcined samples: A) CoAl-MO; B) NiAl-MO; C) XRD patterns registered for both samples after thermal treatment at 30 °C; D) XRD patterns registered for both samples after thermal treatment at 600 °C.

5

The morphostructural properties of the NiAl and CoAl catalysts after reduction under hydrogen were investigated by TEM analysis. Representative images are displayed in Fig. 6.



Fig. 6 TEM images for NiAl (a) and CoAl (b) after reduction at 800 °C.

As a first remark, traces of typical morphology with hexagonal plate-shaped particles are observed for NiAl sample, while for CoAl the brucite-like sheets are no longer maintained. This difference suggests higher stability of the brucite-like sheets ¹⁰ when they contain nickel besides aluminium. Likewise, a monodisperse distribution of the metal particles with a size of 5-6 nm is observed for NiAl sample (Fig.6A). For CoAl sample, very small metal particles are observed in Fig. 6B, those sizes are difficult to evaluate. These results are in good agreement with ¹⁵ XRD data which indicated nickel crystallite size of ~ 6 nm for NiAl sample and highly dispersed cobalt metal particles in the

Hydrogenation of the cinnamaldehyde

case of CoAl sample.

The catalytic properties of calcined NiAl and CoAl samples after $_{\rm 20}$ reduction at 500 $^\circ C$ were evaluated for the liquid phase



hydrogenation of cinnamaldehyde (CNA).

Scheme 1 Reaction pathways for hydrogenation of cinnamaldehyde

- It is worth remembering that (i) these two catalysts contain alumina that bring some acidity in the reaction medium and (ii) depending on the nature of the active sites (redox and/or acidbase sites), the reaction scheme of the conversion of cinnamaldehyde can be very complex [**53**]. Despite the presence
- ³⁰ of alumina, the reaction products identified by GC-MS are mainly the result of the hydrogenation reaction. More precisely, in the case of NiAl-MO, condensation products below 2 mol % were identified whereas no traces of condensation or any other additional products were observed in the case of CoAl-MO
- ³⁵ sample. Consequently, the results of the hydrogenation reaction are exclusively discussed herein. The evolution of CNA conversion with the reaction time as well as the selectivities to the hydrogenation products are comparatively shown for both catalysts in Fig. 7.
- 40 As mentioned in the introduction, CNA molecule has two

double bonds in the side chain that makes the hydrogenation reaction to follow two possible ways: (i) the hydrogenation of C=C bond with the formation of hydrocinnamaldehyde (HCNA) and (ii) the hydrogenation of C=O bond when cinnamyl alcohol ⁴⁵ (CNOL) is formed (Scheme 1). The chemoselective hydrogenation towards the unsaturated alcohol is difficult to

achieve since the thermodynamics favors the hydrogenation of the C=C over the C=O by ~35 kJ/mol and for kinetic reasons the reactivity of the C=C group is higher than C=O group in the ⁵⁰ hydrogenation reactions [**54**].

Depending on the catalyst composition, different catalytic behaviors can be noted (Fig. 7). Therefore, NiAl sample exhibited very high catalytic activity while CoAl-MO sample was moderately active. These results clearly show that a reduction 55 temperature of 500 °C was sufficient to generate very active metallic sites in the case of NiAl catalyst (complete conversion of CNA after 90 min of reaction), albeit the TPR results suggested that the nickel cations are not fully reduced to metallic nickel under these conditions. However, since the catalyst used in the 60 catalytic runs were kept much longer under hydrogen at this reduction temperature, the degree of reduction is likely to be more elevated. For CoAl sample, the generated metallic sites converted ~ 50 % of CNA after 300 min of reaction. Moreover, it can be observed that the main product is HCNA on NiAl sample, 65 while CNOL is the main reaction product on CoAl sample (Fig 7). Also, the catalytic curves displayed in Fig. 7 show that in the case of NiAl sample, a selectivity of ~ 95 % HCNA can be achieved. The distribution of products is more equilibrated on

achieved. The distribution of products is more equilibrated on CoAl sample, with the highest selectivity obtained for CNOL at \sim 70 60 % whatever the CNA conversion.

It is well documented that the catalytic performance of a solid in the hydrogenation of CNA is influenced by several factors, between them the particle sizes and the electronic structure of the metallic active sites [1], both being considered to explain the 75 catalytic results reported herein. As it was shown by in-situ XRD, larger Ni⁰ nanoparticles are supposed to form in comparison with Co⁰ nanoparticles at similar reduction temperature. Although the calculation of the particles sizes after reduction at 500 °C was not feasible, the difference in size was suggested by the presence of ⁸⁰ the weak diffraction peaks of Ni⁰ and absence of those for Co⁰. The electronic structure of the metal is taken into consideration because it defines the interaction between the metal surface and the reactant molecule. Previous studies stated that nickel has similar behavior as Pd and Rh meaning that it favors the 85 hydrogenation of C=C bond while cobalt is included in the same group with Pt and Ru having a moderate selectivity to CNOL [55].

From theoretical considerations [56] and studies of the reaction mechanism [53], the formation of CNOL should be ⁹⁰ favored by enhancing the electron density of the metal that will determine the repulsive four electron interaction of the metal with the C=C bond to decrease. The electron density can be correlated with the metal *d*-band width. Indeed, cobalt with larger *d*-band width than nickel (4.0 vs 3.0 eV) [57] is more selective toward ⁹⁵ the unsaturated alcohol. However, this factor cannot be independently discussed because the electron density depends also on the particle size. Thus, the electron density of the *d*-orbitals declines with the decrease of the particle size with direct

consequence on the selectivity to CNOL. Nitta et al. [58] found for supported Co nanoparticles prepared from cobalt chrysotile and cobalt precipitated on silica, that the selectivity to CNOL increases with the particle size, up to \sim 95 mol % for cobalt

s nanoparticle of ~ 24 nm in size. Similar size-dependent effects were observed in the case of platinum supported on carbon and graphite [55].



Fig. 7 CNA conversion *vs* time and selectivity to reactions products for NiAl (A) and CoAl (B) samples (Test conditions: T_{reduction} = 500 °C; T_{reaction} = 150 °C, 0.265 g catalyst; 1 mL of CNA, 25 mL propylene carbonate as solvent, H₂ flow = 1 L h⁻¹, stirring rate = 900 rpm).

For the catalytic results presented herein, the size of the cobalt nanoparticles lower than the detection limit of the XRD (< 3 nm) should be taken into consideration to explain the moderate selectivity to CNOL (~ 60%) and the low selectivity to HCNA (~ 30%). It can be assumed that that the adsorption of both double bonds is allowed on the small particles of cobalt but the adsorption of C=O bond is predominant. Indeed, Fig. 7 right shows that hydrogenations of C=C and C=O bonds are parallel ²⁰ reactions, even when the total hydrogenation to HCNOL becomes obvious (*i.e.*, at *iso*-conversion of ~ 30%).

Published on 10 October 2013. Downloaded by Yale University Library on 10/10/2013 18:05:07

10

On the other side, the adsorption of CNA on NiAl sample predominantly occurs via C=C bond, as also observed for highly dispersed nickel nanoparticles supported on SBA-15 [59]. In that ²⁵ case, the reduction of Ni/SBA-15 at 350 °C generated a catalyst that totally converted CNA in 300 min of reaction with a selectivity to HCNA of 94 mol % on the whole range of conversion. It can be concluded that the very high activity of NiAl sample doubled by the outstanding selectivity to HCNA ³⁰ endorse this sample as a high-performance catalyst in the hydrogenation of C=C double bond of cinnamaldehyde.

Due to the presence of the alumina in the catalyst composition, it is interesting to observe if there is any influence of it on the catalytic behavior of the samples. On the basis of the

³⁵ literature reports, the influence of the alumina on the catalytic performance of NiAl and CoAl samples is in some extent debatable because, depending on the nature and amount of the metallic active sites, the preparation method as well as the reaction conditions, different behaviors were noted. For instance,
⁴⁰ Volpe et al. [59] reported that alumina support manifests the

same effect on the catalytic behavior as silica. Thus, copper supported on alumina and silica by impregnation showed similar selectivity to CNOL (51-73 and 48-75 % for Cu/Al₂O₃ and Cu/SiO₂, respectively at 15-30 % CNA conversion; the reaction 45 was performed at 1 MPa and iso-propanol as solvent). Lashdaf et al. [61] showed that platinum catalysts supported on silica by gasphase deposition and impregnation are more active in the hydrogenation of CNA that those on alumina, prepared by the same routes (the reaction was performed at 10 bar and iso-50 propanol as solvent). In a study on alumina-supported platinum catalysts, Arai et al. [62] found that the catalysts, reduced with sodium tetrahydroborate at 30 °C, display high selectivity to cinnamyl alcohol (78 % at 50 % CNA conversion) in comparison with the catalysts reduced with hydrogen at 400 °C, that did not 55 display selectivity to cinnamyl alcohol. Szollozi et al. [63] revealed that the activity and the selectivity to cinnamyl alcohol was lower with platinum on alumina (e.g., 32 x 10³ mol.g⁻¹_{Pt}h⁻¹ and 47 % CNOL) than platinum on silica (e.g., 72 x 10³ mol.g⁻ ¹_{Pt}h⁻¹ and 79 % CNOL), when the catalysts are submitted to 60 sonication under hydrogen for 10 min previous the reaction. The next example is more suitable to our situation due to the similar reaction conditions. In this case, the comparison is made between copper supported on alumina by impregnation and Cu-Al mesoporous material prepared by direct synthesis [64]. The 65 authors found that the Cu-impregnated alumina exhibited selectivity to CNOL of 30 % at 35 % CNA conversion while for Cu-Al mesoporous catalysts, a selectivity to CNOL of 55 % at the same iso-conversion was noted. On the basis of these studies, a beneficial effect of reduction from cation incorporated into the

alumina lattice to generate strong metal interaction with residual

alumina support to give improved selectivities can be pointed out.



Fig. 8 CNA conversion vs time and selectivity to reactions products for CoAl samples after reduction at 500 and 700 °C (Test conditions: $T_{reaction} = 150$ °C, s 0.265 g catalyst; 1 ml of CNA, 25 mL propylene carbonate as solvent, H₂ flow = 1 L h⁻¹, stirring rate = 900 rpm).

According to TPR and in-situ XRD after temperatureprogrammed reduction, the total reduction of cobalt take place at 700 °C, reason why the hydrogenation of cinnamaldehyde on CoAl sample was also carried out after reduction at 700 °C. The 10 conversion curve and selectivity to CNOL are displayed together with those recorded after reduction at 500 °C in Fig. 8. As observed, the activity is twice the activity obtained after reduction at 500 °C suggesting the generation of a higher number of active sites by reduction at higher temperatures (*i.e.*, 700 °C). Also, the 15 selectivity to CNOL increased with ~ 15 % while the selectivity to HCNA decreased suggesting that the adsorption of the

- carbonyl bond is further favored over the olefin bond. This improvement in the chemoselectivity can be related to the modification of adsorption site density with metal particle size. It 20 is assumed that upon reduction of the sample at 700 °C the
- particle size slightly increased as compared to the sample reduced at 500 °C because of particle sintering. Indeed, previous studies demonstrated that as compared with small particles, large cobalt particles are more favourable to the CNA adsorption *via* C=O 25 bond due to a higher proportion of dense Co (111) faces [**58**, **65**].
- It is also interesting to note that the high CNOL selectivity obtained over CoAl is maintained up to high CNA conversions (Fig. 8, i.e., ~60% at 90% conversion), suggesting that during the reaction the adsorption of unsaturated alcohol on the catalyst
- ³⁰ surface is weaker than the adsorption of saturated or unsaturated aldehyde.
- For a catalyst, the stability during several catalytic tests is very important for the economy of the process. Therefore, several catalytic runs with recycled catalysts were performed and the
- ³⁵ catalytic activities were evaluated (Fig. 9). It can be observed that the catalytic performances of both catalysts are not essentially changed over the three catalytic runs demonstrating their good stability and reusability.



40 Fig. 9 Recycling tests for NiAl and CoAl samples.

As a conclusion, this study shows the interest to use binary precursors of NiAl and CoAl LDHs to prepare metallic catalysts with controlled and stable catalytic performances in terms of both activity and chemoselectivity.

45 Conclusions

Highly dispersed and thermostable nickel and cobalt nanoparticles showing high performance in cinnamaldehyde hydrogenation were prepared from NiAl takovite-like LDH precursors and related materials. The lamellar structure of the 50 LDH precursors was confirmed by XRD while DR UV-vis indicated the incorporation of the two cations in octahedral coordination in the brucite-like sheets. The calcination of the samples generated external NiO and Co_3O_4 oxides phases amorphous alumina and perhaps cobalt and nickel. The TPR and $_5$ *in situ* XRD results for the calcined NiAl sample indicated a

- strong interaction between nickel and alumina, which resulted in limited sintering of evolved nickel nanoparticles in the high-temperature range of 600-800 °C (*i.e.*, the crystallite size of Ni⁰ nanoparticles only slightly increased with temperature from 3.6 to
- ¹⁰ 5.8 nm). Likewise, a very strong interaction between cobalt and alumina was evidenced for the CoAl sample, with no detectable sintering of generated cobalt nanoparticles in the hightemperature range (*i.e.*, the crystallite size of Co⁰ nanoparticles was below the XRD detection limit (< 3 nm) even after reduction ¹⁵ at 800 °C). Materials derived from the studied HDL systems are
- found to be performance catalysts for the hydrogenation of cinnamaldehyde. Thus, at similar reduction temperature (*i.e.*, 500 °C), NiAl catalyst presented much higher overall activity than CoAl, though the activity of CoAl can be enhanced by reduction
- ²⁰ at higher temperature (*i.e.*, 700 °C). NiAl was highly chemoselective for the hydrogenation of C=C bond (selectivity to hydrocinnamaldehyde of ~95% at complete conversion of cinnamaldehyde), whereas CoAl was chemoselective for the hydrogenation of C=O bond (selectivity to cinnamyl alcohol of ²⁵ ~60% at ~50% conversion of cinnamaldehyde), indicative of composition-dependent chemisorption modes of CNA molecules on the catalytic active sites. Improvement in the chemoselectivity of CoAl to cinnamyl alcohol (~70 % at ~50 % conversion of cinnamaldehyde) was further achieved by reduction at 700 °C. ³⁰ Finally, it can be concluded that effective and low cost hydrogenation catalysts with chemoselective properties can be prepared from takovite-like LDH precursors and related

Acknowledgment.

materials.

Published on 10 October 2013. Downloaded by Yale University Library on 10/10/2013 18:05:07

³⁵ This work was partially supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-0403. C.R. acknowledges the project CUANTUMDOC "Doctoral Studies for European Performances in Research and Innovation" ID79407 funded by

⁴⁰ the European Social Fund and Romanian Government.

Notes and references

 ^a Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71A D. Mangeron Bvd, 700050, Iasi, Romania, Fax: +40 - 232 271 311; Tel: +40 - 232 278683; E-mail:
 <u>bdragoi@tuiasi.ro</u>

^b Université de Poitiers, UMR 7285 CNRS, IC2MP, 4 Rue Michel Brunet, 86022 Poitiers, France

^c Dipartimento di Chimica, Universita della Calabria, via P. Bucci 87036, Arcavacata di Rende (Cosenza), Italy

- 1. P. Mäki-Arvela, J. Hajek, T. Salmi, D.Y. Murzin, *Appl. Catal., A*, 2005, **292**, 1.
- S. Handjani, E. Marceau, J. Blanchard, J.-M. Krafft, M. Che, P. Mäki-Arvela, N. Kumar, J. Wärn, D.Y. Murzin, *J. Catal.*, 2011, 5 282, 228.
- 3. P. Zucca, M. Littarru, A. Rescigno, E. Sanjust, *Biosci. Biotechnol. Biochem.*, 2009, **73**, 1224.
- 4. US Pat. 5129951A, 1991.

- 5. X. Han, R. Zhou, B. Yue, X. Zheng, *Catal. Lett.*, 2006, **109**, 157.
- 60 6. H.-D. Jakubke, H. Jeschkeit, Concise Encyclopedia Chemistry, Walter de Gruyter & CO., Berlin,1993, Pp. 506.
 - J.A. Goodall, J. Lyall, R.J. McBride, J.B. Murray, G. Smith, J. Clin. Pharm. Therap., 1980, 5, 323.
- G.R. Bertolini, C.I. Cabello, M. Muñoz, M. Casella, D. Gazzoli, I.
 Pettiti, G. Ferraris, J. Mol. Catal. A: Chem., 2013, 366, 109.
 - V.R. Landaeta, F. López-Linares, R. Sánchez-Delgado, C. Bianchini, F. Zanobini, M. Peruzzini, J. Mol. Catal. A: Chem., 2009, 301, 1.
 - A.M. Raspolli Galletti, L. Toniolo, C. Antonetti, C. Evangelisti, C. Forte, *Appl. Catal.*, A, 2012, 447-448, 49.
- 70 11. Y. Zhang, S. Liao, Y. Xu, D. Yu, Appl. Catal., A, 2000, 192, 247.
- L. Zhang, J.M. Winterbottom, A.P. Boyes, S. Raymahasay, J Chem. Technol. Biotechnol., 1998, 72, 264.
- B.F. Machado, S. Morales-Torres, A.F. Pérez-Cadenas, F.J. Maldonado-Hódar, F. Carrasco-Marín, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, *Appl. Catal.*, A, 2012, 425-426, 161.
- A.K. Prashar, S. Mayadevi, R. Nandini Devi, *Catal. Commun.*, 2012, 28, 42.
- X. Zhang, Y.C. Guo, Z. Cheng Zhang, J.S. Gao, C.M. Xu, J. Catal., 2012, 292, 213.
- 80 16. C. Milone, J. Catal., 2004, 222, 348.
- 17. J. Lenz, B.C. Campo, M. Alvarez, M.A. Volpe, J. Catal., 2009, 267, 50.
- M.L. Toebes, F.F. Prinsloo, J.H. Bitter, A. Jos van Dillen, K.P. de Jong, J. Catal., 2003, 214, 78.
- 85 19. A.-M. Simion, T. Arimura, C. Simion, C. R. Chim., 2013, 16, 476.
- 20. B.M. Reddy, G.M. Kumar, I. Ganesh, A. Khan, J. Mol. Catal. A: Chem. 2006, 248, 80.
- 21. H. Li, H. yang, H Li, J. catal., 2007, 251, 233.
- W. Lin, H. Cheng, L. He, Y. Yu, F. Zhao, *J. Catal.*, 2013, **303**, 110.
 R.S. Disselkamp, T.R. Hart, A.M. Williams, J.F. White, C.H. Peden, *Ultragonics Superchartics*, 2005, **12**, 210.
- Ultrasonics Sonochemistry, 2005, 12, 319.
 24. K.J.A. Raj, M.G. Prakash, T. Elangovan, B. Viswanathan, Catal. Lett., 2012, 142, 87.
- 25. K.-Y. Jao, K.-W. Liu, Y.-H. Yang, A.-N. Ko, J. Chin. Chem. Soc., 2009, 56, 885.
- A. Ungureanu, D. Meloni, B. Dragoi, M. Casula, A. Chirieac, V. Solinas, E. Dumitriu, *Environ. Eng. Manag. J.* 2010, 4, 461; B. Dragoi, A. Ungureanu, D. Meloni, M. Casula, A. Chirieac, A. Sasu, V. Solinas, E. Dumitriu, E. *Environ. Eng. Manag. J.* 2010, 9, 1203;
 A. Chirieac, B. Dragoi, A. Ungureanu, A. Moscu, C. Rudolf, A.
 - Sasu, E. Dumitriu, *Environ. Eng. Manag. J.* 2012, 11, 47.
 27. J. Barrault, A. Derouault, G. Courtois, J.M. Maissant, J.C. Dupin, C. Guimon, H. Martinez, E. Dumitriu, *Appl. Catal.*, A, 2004, 262 43.
- 28. J.T. Kloprogge and R.L. Frost, in *Layered Double Hydroxides:* Present and Future, ed. V. Rives, Nova Science Publishers, New York, 2001, pp. 164.
 - 29. Ger. Pat 2 024 282, 1970
 - B. Dragoi, A. Ungureanu, A. Chirieac, V. Hulea, E. Dumitriu, Acta Chim. Slov., 2010, 57, 677.
- 110 31. J. M. Fernandez, C. Barriga, M. A. Ulibarri, F. M. Labajos, V. Rives, *Chem. Mater.* 1997, 9, 312.
 - 32. F. Cavani, F. Trifirò, A. Vaccari, Catal. Today, 1991, 11, 173.
- 33. N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Reed Educational and Professional Publishing Ltd., Oxford, 1997, pp. 115, 1115, 1148.
- M. Crivello, C. Perez, E. Herrero, G. Ghione, S. Casuscelli, E. Rodriguez-Castellon, *Catal. Today* 2005, 107, 215.
- 35. H. T. Gomes, P. Selvam, S. E. Dapurkarc, J. L. Figueiredo, J. L. Faria, *Microporous and Mesoporous Mater.*, 2005, **86**, 287.
- 120 36. M. J. Holgado, V. Rives, M. S. San Román, Appl. Catal., A, 2001, 214, 219.
 - Z. Sojka, F. Bozon-Verduraz, M. Che, in *Handbook of Heterogeneous Catalysis*, eds. G. Ertl, H. Knözinger F. Schüth J. Weitkamp, Wiley-VCH, Weinheim, 2nd edn., 2008, vol. 2, pp 1039 1046.
 - L.Y. Mostovaya, T.S. Petkevich, L.A. Kupcha, J. Appl. Spectrosc., 1989, 51, 1298.
 - M. Herrero, P. Benito, F.M. Labajos, V. Rives, J. Solid State Chem., 2007, 180, 873.

- 40. L. Ji, J. Lin, H. C. Zeng, J. Phys. Chem. B, 2000, 104, 1783.
- 41. K. Lee, W. Lee, Zeolitic Mater., 2002, 3, 8.
- 42. N. Sahli, C. Petit, A.C. Roger, A. Kiennemann, S. Libs, M.M., Bettahar, *Catal. Today*, 2006, **113**, 187.
- 5 43. S. Velu, K. Suzuki, M.P. Kapoor, S. Tomura, F. Ohashi, T. Osaki, *Chem. Mater.*, 2000, **12**, 719.
- 44. V. Rives, M.A. Ulibarri, A. Montero, *Appl. Clay Sci.*, 1995, 10, 83.
- P. Benito, F. M. Labajos, J. Rocha, V. Rives, *Microporous and Mesoporous Mater.*, 2006, 94, 158.
- 10 46. V. Rives, in Layered Double Hydroxides: Present and Future, ed. V. Rives, Nova Science Publishers, New York, 2001, pp. 243.
- 47. J.W. Lee, T. Ahn, J.H. Kim, J.M. Ko, J.-D. Kim, *Electrochim. Acta.*, 2011, **56**, 4849.
- 48. X. Ke, J. Cao, M. Zheng, Y. Chen, J. Liu, G. Ji, *Mater. Lett.*, 2007, **61**, 3901.
 - 49. M.A. Ulibarri, J.M. Fernandez, F.M. Labajos, V. Rives, *Chem. Mater.*, 1991, **3**, 626.
 - 50. Z. Wen, F. Zheng, Z. Jiang, M. Li, Y. Luo, J. Mater. Sci., 2013, 48, 342.
- 20 51. Z. Li, X. Xiang, L. Bai, F. Li, Appl. Clay Sci., 2012, 65-66, 14.
 - J. Newnham, K. Mantri, M.H. Amin, J. Tardio, S.K. Bhargava, *Inter. J. Hydrogen Energy*, 2012, 37, 1454.
 - 53. P. Claus, Top. Catal., 1998, 5, 51.
- 54. C. Mohr, P. Claus, *Sci. Prog.*, 2001, **84**, 311.
- 25 55. P. Claus, Y. Onal, in *Handbook of Heterogeneous Catalysis*, eds. G. Ertl, H. Knözinger F. Schüth J. Weitkamp, Wiley-VCH, Weinheim, 2nd edn., 2008, vol. 2, pp 3316 3319.
 - 56. F. Delbeq, P. Sautet, J. Catal., 1995, 152, 217
 - 57. U.K. Singh, M.A. Vannice, J. Catal., 2001, **199**, 73.
- 30 58. Y. Nitta, K. Ueno, T. Imanaka, Appl. Catal., 1989, 56, 9.
 - A. Ungureanu, B. Dragoi, A. Chirieac, C. Ciotonea, S. Royer, D. Duprez, A.S. Mamede, E. Dumitriu, ACS Appl. Mater. Interfaces, 2013, 5, 3010.
- 60. V. Gutierrez, M. Alvarez, M.A. Volpe, *Appl. Catal.*, *A*, 2012, **413**-35 **414**, 358
 - M. Lashdaf, J. Lahtinen, M. Lindbla, T. Venalainen, A.O.I. Krause, *Appl. Catal.*, A, 2004, 276, 129.
 - 62. M. Arai, K. Usui, Y. Nishiyama, Chem. Commun., 1993, 1853.
 - G. Szollosi, B. Torok, G. Szakonyi, I. Kun, M. Bartok, *Appl. Catal.*, A, 1998, **172**, 225.
 - 64. S. Valange, A. Derouault, J. Barrault, Z. Gabelica, J. Mol. Catal A: Chemical, 2005, **228**, 255.
 - C. Ciotonea, B. Dragoi, A. Ungureanu, A. Chirieac, S. Petit, S. Royer, E. Dumitriu, *Chem. Commun.*, 2013, 49, 7665.