Catalytic response and stability of Ni/Alumina prepared from layered double hydroxides for the hydrogenation of

5-hydroxymethyl furfural in water

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**Abstract:** The catalytic response of Ni on alumina obtained from Ni-Al layered double hydroxides was studied for the liquid phase hydrogenation of hydroxymethyl furfural to tetrahydrofuran-2,5-diyldimethanol in water. The successive calcination and reduction of the precursors caused the removal of interlayer hydroxyl and carbonate groups and the reduction of Ni2+ to Ni0. Four reduced mixed oxide catalysts were obtained, consisting of different nickel metal (47-68 wt%) on an Al-rich amorphous component. The catalytic activity was linked to Ni content while selectivity was mainly affected by reaction temperature. Tetrahydrofuran-2,5-diyldimethanol is formed in a stepwise manner at low temperature (353 K) while 3-hydroxymethyl cyclopentanone is generated at higher temperature. Coke formation causes deactivation, however catalytic activity can be regenerated with heat treatment. The results establish Ni on alumina as a promising catalyst for the production of tetrahydrofuran-2,5-diyldimethanol in water.

Introduction

As the production of biofuels and bioenergy from biomass remain economically challenging, there is a growing demand for the co-production of value added chemicals in order to render the process cost-effective. Cellulose and hemicelluloses, the two major components of lignocellulosic biomass, can be broken down and converted to monosaccharides.[[1](#_ENREF_1)] The subsequent dehydration of six carbon sugars can generate 5-hydroxymethyl furfural which is regarded as a primary renewable building block.[[2-5](#_ENREF_2)] The hydrogenolysis of biomass and the subsequent dehydration are mainly carried out in water, however the extraction of furanic products remains challenging.[[3](#_ENREF_3),[6](#_ENREF_6),[7](#_ENREF_7)] Therefore the use of water as solvent for the subsequent transformation of 5-hydroxymethyl furfural is of great importance and these reactions require heterogeneous catalysts that exhibit high activity, selectivity and stability in aqueous solution.

The conversion of 5-hydroxymethyl furfural into value added chemicals has received increasing interest over the last decade [[2](#_ENREF_2),[3](#_ENREF_3),[8](#_ENREF_8),[9](#_ENREF_9)] where a wide variety of heterogeneous metal (i.e., Ni, Cu, Pd, Pt, Ru) supported catalysts have been studied.[[10](#_ENREF_10),[11](#_ENREF_11)] While most research focused on C-O hydrogenolysis (e.g., dimethyl furan) and ring opening products (e.g., hexanetriol, C5-C6 polyols), there are fewer reports on the selective hydrogenation of 5-hydroxymethyl furfural towards tetrahydrofuran-2,5- diyldimethanol (Figure 1). This chemical finds application as a solvent (e.g., for the dehydration of fructose), a building block for the synthesis of polymers (e.g., synthesis of polyestersvia caprolactone)[12] and high-value chemicals (e.g., 8-oxa-3-aza-bicyclo(3.2.1)octane hydrochloride).[[13](#_ENREF_13)]

A number of factors have been proposed to influence the catalytic response, including the nature of the catalysts and reaction conditions, i.e., the solvent,[[14](#_ENREF_14)] pH (acidic or neutral),[[15](#_ENREF_15)] hydrogen partial pressure,[[16](#_ENREF_16)] temperature,[[16](#_ENREF_16)] metal, isoelectric point, acid and basic properties of the support.[[7](#_ENREF_7),[15](#_ENREF_15)] Indeed, the nature of the metal affects selectivity where Cu and Ru based catalysts can be selective for C-O hydrogenolysis with formation of dimethyl furan[[17](#_ENREF_17),[18](#_ENREF_18)] while polymerisation of the intermediate (furan-2,5-diyldimethanol, Figure 1) occurs over Pd and Pt catalysts.[[15](#_ENREF_15)]

On the other hand, incorporation of Ni on Pd/SiO2 and Co-Al mixed oxide catalysts results in concomitant hydrogenation of the ring and formation of the saturated tetrahydrofuran-2,5-diyldimethanol derivative (THFDM), with a 96% yield over Ni-Pd/SiO2[[11](#_ENREF_11)] and 89% over Ni-Co-Al mixed oxides.[[16](#_ENREF_16)] It is worth noting that Raney nickel[12,13,19] exhibits 100% selectivity towards THFDM, however it is less active than the other supported Ni (e.g. Ni-Pd/SiO2) for this reaction.[[11](#_ENREF_11),[16](#_ENREF_16)] It has also been shown that supports with high isoelectric point (e.g. Al2O3) favour hydrogenation of the ring while supports exhibiting Brönsted acidity, such as SiO2, generate polyols and polymers via ring opening.[15,20] Despite these reports[11,13,15,16,20] which suggest that Ni metal and alumina favour the formation of tetrahydrofuran-2,5-diyldimethanol, the hydrogenation of 5-hydroxymethyl furfural over Ni on alumina has not been studied in a systematic manner.

The environment can cause degradation of heterogeneous catalysts and stability in water remains challenging as changes in physical structure easily occur.[21] The studies over Raney nickel were conducted in organic solvents such as alcohols (e.g., ethanol)[19] and ethyl acetate[[13](#_ENREF_13)]. Nakagawa et al.[[11](#_ENREF_11)] tested Ni-Pd/SiO2 as a catalyst for the same reaction in water and they observed that 16% of Ni leached into the liquid phase after 2h.

Raney nickel can exhibit 100% selectivity towards tetrahydrofuran-2,5-diyldimethanol. However, its preparation requires dissolving nickel with molten aluminium, quenching and treatment of the alloy with NaOH (*ca.* 5 M) in order to leach Al out. As a result, a large amount of concentrated NaOH is used during synthesis, the material is pyrophoric and its chemical composition cannot be easily controlled. Therefore, catalysts that are easier to synthesise and handle are required, if the hydrogenation of 5-hydroxymethyl furfural is to be carried out in a more environmentally benign process using water as the solvent. The use of water as a solvent in sustainable chemical processes is preferred as it is non-toxic, non-flammable, low cost, renewable and widely available.[22,23]

There has been a growing interest, in recent years, in the synthesis of mixed oxides by thermal pre-treatment of layered double hydroxides and their use for hydrogenation reactions.[24] The mixed oxides obtained can exhibit distinct properties compared to traditional impregnated metal catalysts including small crystallite size, large surface area, good stability, high metal loading, basic properties and distinct catalytic performance.[25-27] After reduction, the catalysts display well dispersed metallic particles on the surface and enhanced metal-oxide interaction.[24] Hence the supported nickel catalysts used in this study were derived from Ni-Al layered double hydroxides.

In this work, the catalytic response of Ni on alumina catalysts for the hydrogenation of 5-hydroxymethyl furfural in water is presented. The catalysts are prepared from layered double hydroxides of readily available non-noble metals under mild conditions in water. The effect of catalysts composition and reaction conditions is also systematically investigated; the chemical kinetics of this reaction and the catalytic stability of the catalysts are also considered.

Results and Discussion

**1. Characterisation Measurements**

**1.1. Layered double hydroxides precursors:**

Layered double hydroxides are composed of hydroxide brucite-like sheets where two metals (M2+, M3+) occupy octahedral sites; the presence of M3+ cations generate a net positive charge which is balanced by interlayers composed of anions and water.[28] In this work, M3+ = Al3+, M2+ = Ni2+ have been introduced as cations, whereas CO32- is the charge balancing anion; their general formula can be written as [Ni(II)1-xAl(III)x(OH)2][CO32-]x/2∙mH2O. The precursors were synthesised by precipitation of aqueous solution of NiCl2.6H2O and AlCl3.6H2O with urea, based on the method of Costantino *et al*.[29] The change in temperature (from 295 K to 368 K, at 1 K min-1) results in the decomposition of urea.[30]

(1)

The pH progressively increased to *ca.* 8.5 which is suitable to precipitate the metal hydroxides. The urea hydrolysis takes place slowly and uniformly, so the precipitation is carried out under a low degree of supersaturation.[31] The predominant species in the carbonate equilibria at final pH (~8.5) is hydrogen carbonate,[32] providing the required interlayer anion. Four layered double hydroxides (NiAl-P) were made with different Ni-Al ratios (x = 0.24, 0.28, 0.36, 0.47); the increasing X number (NiAl-XP) relates to the increasing Al content (x, Table 1). The crystalline structure and textural properties were investigated by ICP, XRD, CHN, TGA, SEM-EDX, FT-IR and nitrogen physisorption.

The XRD pattern of Ni-Al precursors (taking the sample with the lowest Al content, NiAl-1P, as representative, Figure 2a) shows 7 peaks (2*θ* = 13-78°) that are characteristic of nickel aluminium layered double hydroxides.[33] The degree of crystallinity and textural properties depend on various reaction parameters such as pH, temperature, concentration and aging of the precipitate.[26,34] The samples present good crystallinity in agreement with the work of Costantino et *al*,[29] who reported improved crystallinity with longer digestion time (>36 h) at temperatures of 363-373 K.

The infrared spectra (taking NiAl-1P as representative, Figure S1) show a broad band at 3530 cm-1 which is mainly attributed to Al coordinated OH groups with small contributions of hydrogen-bonded interlayer water, CO32--H2O bridging and hydroxyl coordinated by both Ni and Al.[35] The region between 1200-1800 cm-1 is characterised by the bending mode of interlayer water around 1655 cm-1 (1640-1700 cm-1)[35] and interlayer carbonate at 1366 cm-1 (1350-1400 cm-1)[35] These results confirm the presence of H2O and CO32- in the interlayer and are in agreement with hydroxide sheets.

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| **Table 1.** Composition, Al ratio (x), BET surface area (SA), lattice parameter (*a*, *c*) and crystallite size (*d*LDH) associated with the precursors | | | | | | |
| Catalysts | Composition[a] | Al ratio  (x)[b/c] | SA[d]  (m2 g-1) | *a[e]*  (Å) | *c[e]*  (Å) | *d*LDH[f]  (nm) |
| NiAl-1P | Ni0.76Al0.24(OH)2(CO3)0.12∙0.64H2O | 0.24/0.26 | 65 | 3.061(1) | 23.46(1) | 10(1) |
| NiAl-2P | Ni0.72Al0.28(OH)2(CO3)0.14∙0.58H2O | 0.28/0.28 | 67 | 3.057(1) | 23.52(1) | 10(1) |
| NiAl-3P | Ni0.64Al0.36(OH)2(CO3)0.18∙0.45H2O | 0.36/0.34 | 84 | 3.048(1) | 23.37(1) | 10(1) |
| NiAl-4P | Ni0.53Al0.47(OH)2(CO3)0.23∙0.30H2O | 0.47/0.51 | 107 | 3.037(1) | 23.06(1) | 10(1) |
| [a]based on ICP, CHN and TGA analysis  [b]from ICP analysis after digestion in HCl  [c]from SEM-EDX  [d] BET surface area calculated from N2 adsorption-desorption isotherms  [e]based on space group, errors report to 3*σ*  [f]based on Double-Voigt approach, errors report to 1*σ* | | | | | |  |

The analysis by ICP of Al and Ni contents of the supernatant (< 0.1% metal in solution) and the precursors after digestion (xAl, Table 1) verified that complete precipitation of the metal hydroxides occurred. The CHN results were in agreement (±5%) with the theoretical amount of CO32- and H2O in the interlayer (according to Miyata formula)[36]; the compositions of the four layered double hydroxides are presented in Table 1.

XRD patterns over a larger 2*θ* range (10°-120°)and with an internal standard were measured in order to determine the lattice parameters (*a*, *c*, Table 1); they were obtained by fitting the patterns with a rhombohedral symmetry unit cell. *c* corresponds to three times the thickness of a unit layer; hence it is related to the interlayer and depends on factors such as the nature and concentration of the anion, the state of hydration, the strength of hydrogen bond between the anions and the hydroxyl groups.[28] *a* is associated with the cation-cation distance in the hydroxide layer; as the radius of Al3+ (0.50 Å) is smaller than Ni2+ (0.69 Å), the parameter *a* decreases with increasing Al content (x). Applicability of Vegard’s law can be tested (Figure 1b) with,

(2)

Where x and (*a*Ni, *a*Al) correspond to the molar fraction of Al and the lattice parameters of the pure constituents, respectively. The linear fitting confirms the validity of Vegard’s law; moreover the extrapolation of *a*Ni (x = 0, *a*Ni = 3.08 Å) is close to that of brucite-like Ni(OH)2 (3.11 Å).[37]

A representative SEM image is presented in Figure 3(a) where the lamellar/platelet morphology observed for the four samples is characteristic of well-developed layered structure. EDX measurements confirmed the homogeneity of the samples and the Al ratios (Table 1) are close (± 8%) to ones obtained by ICP. The BET surface areas (SA = 65-107 m2 g-1, Table 1) are within the range of values reported in the literature for Ni-Al layer double hydroxides (15-98 m2 g-1)[38-40] and increase with the Al content while the crystallite’s size (*d*LDH = 10 nm) remains constant.

**1.2. Catalysts pre-treatments:**

The thermogravimetric analysis (TGA) curves of the four systems are shown in Figure 2c. The first mass loss can be attributed to dehydration and partial dehydroxylation while the second step is due to the loss of interlayer hydroxyl and carbonate groups.[41] NiAl-4P has the lowest amount of water and highest quantity of carbonate in the interlayer (see composition, Table 1), hence it has the lowest mass loss during the first step and the highest during the second step. The four layered double hydroxides present similar temperatures for the two steps (*ca.* 373 K, 550 K). The loss of the interlayer groups is associated with an increase of the surface area by 50-80%. Based on TGA results, all samples were calcined at 773 K (denoted as NiAl-C). The XRD patterns of NiAl-C after calcination (taking NiAl-1C as representative, Figure 2a), present 3 peaks (2*θ* = 43-75°) that are characteristic of cubic nickel oxides. There was no detectable signal due to aluminium oxide (e.g., Al2O3) or spinel (e.g., NiAl2O4); this is not surprising as higher calcination temperatures (> 1100 K) are usually required for their formation.[42] So the samples are composed of a mixture of an Al-rich amorphous component and a NiO-like oxide. The decrease of the NiO lattice parameters (*a*, Table 2) with increasing Al content and the lower values compared to pure NiO (4.177 Å) suggest that Al3+ is incorporated into the lattice, in agreement with the literature.[26] The substitution of a divalent host (Ni2+) by a trivalent cation (Al3+) is compensated by the formation of cation vacancies to balance the charge.[43] The introduction of Al3+ is associated with a slight decrease in NiO mean crystallite size (from 6 to 4 nm). The Al-rich amorphous phase contributes significantly to the surface area of the calcined samples as it increases (Table 2) with a decreasing Ni content.

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| **Table 2.** Ni content (wt%), surface area (SA), lattice parameter (*a*) and mean NiO crystallite size (*d*NiO) after calcination; H2 consumed and maximum temperature (*T*max) during TPR of the calcined samples | | | | | | |
| Catalysts | Ni[a]  (%w/w) | SA[b]  (m2 g-1) | *a*[c]  (Å) | *d*NiO[d]  (nm) | H2-TPR | |
| H2 (mmol g-1) | *T*max (K) |
| NiAl-1C | 68 | 117 | 4.159(1) | 6.2(6) | 11.5(2) | 819 |
| NiAl-2C | 61 | 121 | 4.155(1) | 5.1(4) | 10.9(2) | 828 |
| NiAl-3C | 58 | 142 | 4.149(1) | 4.3(5) | 9.5(2) | 850 |
| NiAl-4C | 47 | 162 | 4.145(1) | 3.7(6) | 8.1(2) | 859 |
| [a]based on ICP analysis after digestion in HCl  [b]BET surface area calculated from N2 adsorption-desorption isotherms  [c]based on space group, errors report to 3*σ*  [d]based on Double-Voigt approach, errors report to 1*σ* | | | | | | |

The H2-TPR of the four calcined samples generated the profiles shown in Figure 2dwhere positive peaks, corresponding to H2 consumption, are evident. The amounts of H2 consumed (per gram of material) are included in Table 2 and correspond (± 4%) to the amount of H2 required for the complete reduction of Ni2+ to Ni0. The temperatures of the peaks at maximum signals (*T*max) are included in Table 2 and over the range 819-859 K. The introduction of Al3+ into the NiO lattice enhance the stability of Ni2+ and therefore hinder its reduction; this is a well-established phenomenon[26,42] and explains the shift of *T*max to higher temperature with increasing aluminium content. Finally, the calcined samples were reduced under H2 (at 773 K) and passivated; after these pre-treatments, the samples are denoted as NiAl-R.

**1.3. Reduced mixed oxides catalysts:**

The composition of the four catalysts (Table 3) was determined by ICP, CHN and TGA analysis. As expected, the Al bulk ratios of the reduced catalysts are similar (± 5%) to the ones of the precursors (NiAl-P, Table 1).The XRD patterns of NiAl-R (taking NiAl-1R as representative, Figure 2a) present 2 peaks (2*θ* = 52-61°), which can be attributed to cubic nickel metal (ICDD 04-0850). The samples must consist of nickel particles dispersed on an Al-rich amorphous component, since no Al-containing phases were observed in the diffraction patterns. Ni0 mean crystallite sizes (*d*Ni, Table 3) are in the range of 10-14 nm, where an increase in Ni loading is associated with an increase in crystallite size. Ni0 mean crystallite sizes of the reduced samples NiAl-R are twice the size of NiO crystallites (NiAl-C, *d*NiO, Table 2); however the presence of Al3+ in NiO lattices after calcination may broaden the peaks due to strain and a direct comparison between crystallite sizes might not be valid.

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| **Table 3.** Composition, Ni content (wt%), BET surface area (SA), total pore volume (PV), mean pore diameter (*d*pore), lattice parameter (*a*), mean Ni crystallite size (*d*Ni) and isoelectric point associated with the reduced catalysts | | | | | | | | |
| Catalysts | Composition[a] | Ni[a]  (%w/w) | SA[b]  (m2 g-1) | PV[b]  (cm3 g-1) | *d*pore*[b]*  (nm) | *a[c]*  (Å) | *d*Ni[d,e]  (nm) | IEP |
| NiAl-1R | Ni0.76Al0.24O0.79H0.28 | 68 | 89 | 0.25 | 10 | 3.5227(3) | 14(1)[d] | 10.0(2) |
| NiAl-2R | Ni0.73Al0.27O0.97H0.24 | 60 | 101 | 0.25 | 10 | 3.5226(4) | 13(1)[d] | 10.2(2) |
| NiAl-3R | Ni0.64Al0.36O0.96H0.33 | 56 | 113 | 0.27 | 9 | 3.5241(4) | 12(1)[d] | 10.3(2) |
| NiAl-4R | Ni0.53Al0.47O1.10H0.39 | 47 | 129 | 0.28 | 9 | 3.5217(8) | 10(1)[d]/9(3)[e] | 10.1(2) |
| [a]based on ICP, CHN and TGA analysis  [b] BET surface area calculated from N2 adsorption-desorption isotherms  [c]based on space group, errors report to 3*σ*  [d]based on Double-Voigt approach, errors report to 1*σ*  [e]from TEM, errors report to 1*σ* | | | | | | | | |

The morphology of the catalysts was investigated by SEM and TEM imaging. Despite the modifications to the composition during pre-treatment, the reduced catalysts (Figure 3b) present a similar lamellar/platelet structure to that of the precursor layered double hydroxides (Figure 3a); the retention of the morphology after calcination and reduction has already been reported elsewhere.[28,44,45] TEM-EDX analysis was conducted on NiAl-4R as representative; the results obtained suggest that the samples have a good homogeneity (xAl = 0.43 ± 0.03) and the value obtained is in agreement with the ICP result (xAl = 0.47). Chlorine precursors were used for the synthesis of the catalysts however no chlorine was detected by SEM-EDX analysis (Figure S2). This shows that washing with H2O followed by treatment with NH4HCO3 (see experimental section) was enough to remove any residual chlorine. This result is important as chlorine is known to increase metal atom mobility on the support and cause sintering.[46] TEM was also employed to determine the Ni particle size distribution and a representative TEM image (for NiAl-4R) is presented in Figure 3c, showing dispersed pseudo-spherical particles in the 2-16 nm size range (Fig. 3d). An essentially equivalent mean size (*d*Ni) was obtained from the measurements with XRD (10 nm) and TEM (9 nm) analysis (Table 3).

The calcination and reduction of layered double hydroxides (NiAl-P → NiAl-R) was associated with an increase in surface area by 20 to 50%. Moreover, the surface area (SA) and total pores volume (PV) of the reduced mixed oxide increases with decreasing Ni loading (Table 3). The four catalysts exhibit an average pore size of 9-10 nm. The isoelectric points (IEP) were measured; the values obtained are listed in Table 3 and a representative curve of the zeta potential versus pH is shown in Figure S3. The four catalysts present a similar isoelectric point (pH = 10.2 ± 0.2) which is in agreement with the literature where values in the range 8.5-10.0 have been reported for aluminium oxide, bohemite and aluminium hydroxide.[47] We could not find any values reported for Ni metal, however IEP between 7.5 and 10.5 have been measured for NiO.[47]

To summarise, four catalysts precursors were synthesised by precipitation with urea. XRD, ICP, CHN, SEM-EDX and IR measurements confirm the full precipitation and formation of layered double hydroxides Ni(1-x)Alx(OH)2(CO3)x/2.mH2O, with 0.24 ≤ x ≤ 0.47 and 0.3 ≤ m ≤ 0.7. The successive calcination and reduction of the precursors generated reduced mixed oxides compounds. This method of preparation allowed us to synthesis four Ni on alumina catalysts with well dispersed nickel metal particles and high Ni contents (between 47 wt% and 68 wt%).

**2. Catalytic results:**

***2.1. Kinetic and mechanistic aspects:***

The hydrogenation of 5-hydroxymethyl furfural (HMF) using water as solvent (T = 353 K, PH2 = 20 bars), generated a mixture of furan-2,5-diyldimethanol (FDM) and tetrahydrofuran-2,5-diyldimethanol (THFDM) over the four Ni-Al catalysts (NiAl-R, Figure 4a). Control experiments employing γ-Al2O3 or the precursors before (NiAl-P) and after calcination (NiAl-C) did not result in any conversion, suggesting that it is the presence of Ni0 particles, formed after reduction of the precursors, which allows for H2 uptake on the surface and catalyses the hydrogenation of HMF.

Reaction conditions were chosen in order to avoid mass transfer limitations. Indeed, the stirring speed and particle size tests were conducted with NiAl-4R (Figure S4) in order to probe the absence of mass transfer resistance of the reactants from the gas to the liquid phase (for H2), from the bulk liquid to the catalyst surface (for HMF and H2) and internal diffusion resistance.[48] The average pore sizes of the four catalysts (9-10 nm, Table 3) are 10 times larger than the long axis of HMF (9 Å);[49] hence the pores are sufficiently wide not to impede the passage of the reactant and products of similar size. Moreover, the stoichiometric ratio of H2 to reactant (for converting HMF to THFDM) is above 100. Therefore, applicability of a pseudo-first order treatment can be tested using the relationship,

(3)

Where *C*HMF and *C*HMF,0 represent the concentrations of HMF at time *t* and *t* = 0. The linear relationship between ln(*C*HMF) and *t* (Figure 4(b)) for the four catalysts confirms the adherence to pseudo-first order behaviour. Assuming that deactivation is negligible in these conditions (*t* < 18 min and conversion under 32%), the initial rate constants (*k*, min-1), listed in Table 4, represent a measure of the intrinsic catalysts activity. We did not observe any induction period associated with catalysts activation, therefore the passivation layer (and its removal) deos not significantly affect the catalytic response. As shown in Table 4, the rate constant k increases with Ni loading (Table 3) and the four catalysts exhibit equivalent (± 6%) specific rate (*k*’) per mass of Ni. The rate constants were converted to specific values (*k*’’) using Ni surface areas (*S*Ni, see experimental section) and are included in Table 4. While previous studies did not find a clear relation between the activity and the metal particles size (e.g., Pd[50]), our results suggest an increase in specific values (*k*’’) with increasing *d*Ni. To the best of our knowledge, this is the first example in which kinetic rates are presented for the hydrogenation of HMF over metal supported catalysts.

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| **Table 4.** Rate constant (*k*) and specific rate constant per mass of Ni (*k*’) and per Ni surface area (*k*’’) for the hydrogenation of HMF at 353 K and PH2 = 20 bars | | | |
| Catalysts | *k* (min-1) | *k*’ (gNi-1 min-1) | *k*’’ (mNi-2min-1) |
| NiAl-1R | 0.032 | 1.5 | 32 |
| NiAl-2R | 0.026 | 1.4 | 28 |
| NiAl-3R | 0.025 | 1.5 | 27 |
| NiAl-4R | 0.022 | 1.5 | 22 |

Typical temporal dependence of the reactant and products molar yields (*Y*) for the catalytic hydrogenation of HMF (353 K, 20 bars) over NiAl-R is shown in Figure 4(c). The hydrogenation of the aldehyde group generates FDM which is then further reduced to the fully saturated THFDM derivate via the hydrogenation of the furan ring. It has been reported that hydrogenation over Ni-Pd/SiO2[[11](#_ENREF_11)] can also proceed in a reverse order (i.e., initial reduction of the furan ring). However, we did not detect the associated saturated aldehyde by GC-MS, suggesting that this reverse mechanism does not take place under our reaction conditions. In aqueous solution, the hydrogenation of HMF can also produce ring opening products such as levulinic acid.[51] Moreover cross-polymerisation reactions can lead to the production of soluble polymers and insoluble brown humins.[52] But based on analytical results (GC and NMR) no products associated with ring opening or hydrogenolysis (C-O or C-C) were formed under our reaction conditions.Our results are in agreement with the literature where catalysts with a high isoelectric point (> 7)[[5](#_ENREF_5)] and Ni metal[[11](#_ENREF_11)] favour the complete hydrogenation of the furan ring. Moreover, Ni catalysts are commonly used for alkene (e.g., propadiene) or total alkyne (e.g., propyne) hydrogenation reactions.[53] The presence of Ni must favour the adsorption of the intermediate (FDM) with its molecular plane parallel to the surface, which facilitates the hydrogenation of the ring.[[16](#_ENREF_16)]

Figure 5(a)presents the selectivity (*S*) obtained towards FDM and THFDM as a function of HMF conversion (*X*); this figure combines data obtained over the four catalysts, where the mass of catalyst was varied in the range 0.01 g ≤ *m* ≤ 0.06 g and samples were taken every 40 min up to 6 h. The collected data points overlay one another, suggesting that the selectivity is independent of the catalyst’s composition, initial mass of catalysts and time but varies consistently with *X*. HMF is first converted to FDM, as *S*FDM = 100% when *X* < 5%. FDM is then progressively converted to THFDM and *S*THFDM = 40% when *X* ~ 98%.

Therefore, the hydrogenation of HMF generates FDM (step 1, Figure 4(a)) which is then hydrogenated to THFDM (step 2). We also consider in this model, the possibility of a direct hydrogenation of HMF to THFDM (step 3):

(4)

(5)

where *k*i is the pseudo-first order rate constant of step *i* and Y*j* is the yield of the compound *j*.By combination of equations 4 and 5:

with (6)

Which, after integration gives,

(7)

where *C* is a constant. The applicability of this mechanism is assessed in Figure 5(b) and the model fit the experimental data (R = 0.9989). The values of *A* (0.912 ± 0.005) and *B* (0.138 ± 0.003) were determined by non-linear mathematical fitting, where

and (8)

The ratio *k*3/*k*1 (= 0.09) << 1 indicates the strictly stepwise formation of THFDM while *k*1/*k*2 (= 6.60) >> 1 suggests that the hydrogenation of FDM to THFDM is the rate determining step. This could be due to a competitive adsorption of FDM with HMF on the catalyst surface; the stronger adsorption of HMF would hinder the reaction of the intermediate, FDM. This is coherent with results obtained for the hydrogenation of furfural over Ni catalysts,[54] where the authors observed that the rate determining step was the attack of adsorbed hydrogen on the furan ring of the intermediate (furfuryl alcohol) due to the competitive adsorption of furfural with furfuryl alcohol on the surface.

Figure 5(a)includes the selectivity associated with the two products up to 98% conversion of HMF; once full conversion is reached, FDM is further converted to THFDM and higher yields of THFDM are achieved.Figure 6 represents the final composition of the solution after 6 h over varying mass (*m*) of NiAl-4R. A rate of THFDM production (*R*THFDM) can be extrapolated from the linear regression of *Y*THFDM = f(*m*) with, *R*THFDM = 32 mmolTHFDM gNi-1. High yields of THFDM (> 99%) were achieved at longer reaction time (8-12 h) or when increasing the mass of catalyst, as confirmed by GC and NMR (Figure S5). Overall, above 99% yield is achieved in water using our Ni/alumina catalysts (NiAl-R). A result that has not been previously observed in water as studies over Raney nickel operated in organic solvents.[12,13,19]

***2.2. Stability testing:***

By preventing pollution at source, waste formation can be reduced or eliminated and waste treatment circumvented. As most bio-based chemicals can be used in food, cosmetic and pharmaceutical industry, metals have to be completely removed from the solution after reaction; so when leaching occurs, expensive separation and purification steps (e.g., ion-exchange, filtering) have to be conducted. So the design of a selective process with catalysts resistant to leaching is essential.

The stability of the catalysts was investigated using NiAl-4R as representative. Reaction conditions were chosen in order to stay below 100% conversion. After reaction, the catalyst was recovered and dried at 393 K under N2. Three consecutive runs were conducted (run 1, run 2, run 3) and the composition of the reaction solution after 6 h is presented in Figure 7. The results show that the conversion decreased from *ca.* 80% to 50% after 3 runs. The process of deactivation can be both of chemical and physical nature where the main causes include sintering, phase transformation, leaching, coking and poisoning.[55] In order to assess the cause of deactivation, the used catalyst (after run 3) was characterised (Table 5).

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| **Table 5.** Mean Ni crystallite size (*d*Ni), amount of Ni (wt%) leached in solution, carbon and hydrogen content of NiAl-R and mass loss during TGA | | | | | |
| NiAl-4R | *d*Ni[a]  (nm) | Ni[b] (wt%)  leached | C[c]  (wt%) | H[c]  (wt%) | mass loss[d]  (wt%) |
| Before run 1 | 10(1) | - | 0.2 | 0.6 | 4 |
| After run 3 | 10(1) | <0.002 | 8.2 | 2.2 | 29 |
| [a]based on Double-Voigt approach, errors report to 1*σ*  [b]based on ICP analysis of the solution after turnover  [c]based on CHN analysis  [d]based on TGA analysis, after heating to 975 K under Ar | | | | | |

The XRD pattern of the catalyst after turnover does not show any additional peaks or changes in peak intensities, indicating no noticeable phase transformation. For supported metals, sintering occurs via migration and coalescence of crystallites with a concomitant increase of the crystallite dimension.[55] However, mean Ni crystallite size does not change before and after turnover (*d*Ni = 10 nm, Table 5), suggesting that sintering does not occur. The possibility of Ni leaching during the reaction was also assessed; the content of Ni in solution after turnover was measured by ICP and the results obtained were close to the detection limit of 5 ppb, i.e. less than 0.002 wt% of Ni leached in the reaction solution. Catalyst was filtered off from the reaction mixture and the latter was left under H2 at 353 K for another 12 h; no further conversion was observed. These results confirm that Ni is not leaching into the liquid phase and clearly demonstrate the heterogeneous nature of our catalytic system. It should be reminded that Nakagawa *et al* observed 16% of Ni leached into the liquid phase after conducting the hydrogenation of HMF over Ni-Pd/SiO2 for 2 h in water.[[11](#_ENREF_11)]

Poisoning usually refers to the obstruction of active sites by molecules/impurities strongly chemisorbed on the surface. The formation of coke results from the condensation, polymerisation and decomposition of molecules on the surface. Elemental analysis (Table 5) showed an increase in carbon (8.0 wt%) and hydrogen (1.6 wt%) content after 3 runs. The respective TGA curves, measured under Ar, are shown in Figure S6. A total loss of 29 wt% was observed (at 975 K) for the catalyst after 3 runs, indicating the presence of organics bound onto the surface. A loss of activity due to the formation of polymer on the surface has previously been reported for the hydrogenation of furanic compounds. Indeed, fast deactivation of Cu-based catalysts has been reported for the hydrogenation of furfural due to thermal polymerisation and coking of furfuryl alcohol.[56] During the hydrogenation of HMF, it has been reported that polymers may form through the loss of formaldehyde from FDM, followed by polymerisation.[[15](#_ENREF_15)]

The TGA results suggest that a heat treatment at 773 K should be sufficient to remove the organic impurities. To this end, the catalyst was regenerated by calcination and reduction at 773 K, resulting in significant restoration of catalytic activity. As presented in Figure 7, a conversion of *ca.* 75% was observed after catalyst’s regeneration (run 4) which is relatively close to the one obtained after the first run (*ca.* 80%, run 1). Table 6 summarises the amount of HMF consumed at the end of each run per mass of catalyst (*R*HMF) where the values obtained follow the trend observed in Figure 7. However it is interesting to relate the consumption of HMF to the mass of Ni (*R’*HMF). Indeed, due to the presence of organics on the surface, the amount of Ni after 3 runs is lower (Table 6, based on ICP), while *R’*HMF is the same for run 3 and run 4. This confirms the removal of the organics from the surface during the heat treatment.

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| **Table 6.** Ni content (wt%); HMF consumed per mass of catalyst (*R*HMF) and mass of Ni (*R*’HMF) after 6 h reaction; *Ci*HMF ~0.04 mol L-1; *m*catalyst = 0.015 g; T = 353 K, PH2 = 20 bars | | | |
| NiAl-4R | Ni[a] (wt%) | *R*HMF  (mmolHMF gcatalyst-1) | *R’*HMF  (mmolHMF gNi-1) |
| Run 1 | 47 | 98 | 209 |
| Run 3 | 33 | 61 | 185 |
| Run 4 | 47 | 87 | 184 |
| [a]based on ICP analysis after digestion in HCl | | | |

***3.2.3. Effect of reaction conditions:***

The reaction temperature is known to affect catalyst selectivity; when operating at higher temperature (410-450 K) over acid catalysts, cyclopentanone derivatives are predominately form in aqueous solution (e.g., Au/Nb2O5)[57] while the use of an alcohol favours etherification (e.g., Sn-beta zeolite,[58] PtSn/Al2O3[59]). An increase of temperature from 353 K to 413 K was associated with a shift of selectivity towards the ring rearrangement of HMF to a cyclopentanone derivative, 3-hydroxymethylcyclopentanone (HCPN, Figure 8a). This is an important chemical intermediate for the production of pharmaceuticals, insecticides and rubber chemicals.[57]

The ring rearrangement of furfural and furfural alcohol to cyclopentanone has been studied to a limited extent over supported Pt, Pd, Ru and Ni-Cu catalysts.[60,61] These reports suggest that the presence of water, excess of H2 and high temperature (e.g., 433 K) are required.[60,61] First, furfural is catalytically hydrogenated to furfuryl alcohol. Then, a carbocation is created via the scission of the C-O bond of the furfuryl alcohol. This carbocation is produced in excess of hydrogen and is stabilized by strong interaction with the metal surface. The additional interaction with co-adsorbed water generates cleavage of the C-O bond and rearrangement to cyclopentanone.[60,61] There is only one study reporting the conversion of HMF to HCPN[57] where the reactions were conducted over Au, Pt, Pd, Ru supported on Nb2O5, at 413 K. They proposed a similar reaction mechanism, in which the hydrogenation of the aldehyde to the alcohol initially takes place (with formation of FDM), followed by ring opening which generates 1-hydroxyl-2,5-hexanedione (HHD, Figure 8a); HCPN is then formed by intramolecular aldol condensation of this intermediate. They attributed the high yield achieved over Au/Nb2O5 (86%) to the presence of Lewis acidic sites which favour ring rearrangement.

Figure 8b presents the concentration of products with time, for the hydrogenation of HMF over NiAl-4R at 413 K. The first intermediate, FDM, is formed after hydrogenation of the C=O bond (step 1). Then there is a competitive reaction between the full hydrogenation of the ring (with formation of THFDM, step 2, as previously discussed for lower T) and ring opening (with formation of HHD, step 3). The following aldol condensation results in the formation of HCPN (step 4). Formation of HCPN and the linear intermediate HHD was verified by GC-MS (Figure S7) and NMR (Figure S8), in complete agreement with the reaction pathway described in the literature.[57,60,61] The concentration of FDM follows the expected time dependence for reaction intermediate: first it increases with time (1-2 h) but then decreases as it is consumed and converted to products (THFDM and HCPN). The reaction conditions used (i.e., water, excess of H2, high temperature) favour the aldol condensation and formation of HCPN, in agreement with the literature.[60,61] We thus report for the first time the synthesis of HCPN over Ni catalysts, as opposed to the use of noble metal catalysts[57]. Hence this is the first study conducted over a base metal catalyst where yields up to 80% were achieved after 6 h reaction (Figure 8b).

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| **Table 7.** Effect of temperature, pressure and mass of catalyst on conversion (X) and yields of products for the hydrogenation of HMF over NiAl-4R; results after 6 h reaction | | | | | | | | |
| Reaction | T  (K) | PH2  (bar) | mcatalyst  (mg) | X  (%) | YFDM  (%) | YTHFDM  (%) | YHHD  (%) | YHCPN  (%) | |
| A | 353 | 20 | 31 | 96 | 25 | 71 | 0 | 0 | |
| B | 393 | 20 | 35 | 100 | 5 | 26 | 5 | 64 | |
| C | 413 | 20 | 35 | 100 | 0 | 8 | 11 | 81 | |
| D | 413 | 20 | 10 | 53 | 11 | 3 | 2 | 37 | |
| E | 413 | 3 | 30 | 49 | 21 | 3 | 3 | 22 | |
| F | 413 | 56 | 30 | 100 | 0 | 16 | 15 | 69 | |

Table 7 summarises the effect of temperature and pressure on the catalytic results. Entry A corresponds to the result presented above at 353 K where a mixture of FDM and THFDM is obtained. Increasing the temperature (entry B, 393 K) results in two competitive reactions: hydrogenation of the ring (step 2) and ring opening (step 3, followed by step 4), with the former becoming predominant at 413 K (entry C). When operating at 413 K, a decrease of initial mass of catalyst (entry D) is associated with a decrease in conversion where HCPN is still the major product. The partial pressure of H2 (*P*H2) was varied in order to assess a possible effect on selectivity. At lower pressure (*P*H2 = 3 bars, entry E), the conversion is lower and higher concentration of intermediates (FDM) is observed. On the contrary, higher pressure (*P*H2 = 56 bars, entry F) favours the formation of THFDM (step 2) over HCPN. When running the reaction at even higher temperature (> 433 K), cross-polymerisations take place leading to the production of insoluble brown Humin. Therefore selectivity depends mainly on temperature and conversion and to some extent on H2 partial pressure; we observed that the hydrogenation of HMF towards THFDM is favoured with an increase in pressure and a decrease in temperature.

Conclusions

We report the synthesis of Ni on alumina catalysts derived from Ni-Al layered double hydroxides and their use to promote the selective liquid phase hydrogenation of 5-hydroxymethyl furfural to tetrahydrofuran-2,5-diyldimethanol in water. The layered double hydroxides were successfully synthesised by precipitation with urea and full precipitation occurred. The XRD patterns were fitted with the space group (rhombohedral symmetry), revealing that the lattice parameter *a* decreased with increasing Al content, following Vegard’s law. Calcination of the precursors caused the removal of interlayer hydroxyl and carbonate groups and formation of NiO particles. The following reduction of Ni2+ to Ni0 occurs during pre-treatment with H2 at 773 K and is hindered by the presence of Al3+ incorporated into NiO lattice. The four reduced mixed oxide catalysts exhibit high Ni contents (up to 68%) and present a lamellar structure with well dispersed nickel metal nanoparticles (*d*Ni = 10-14 nm) on an Al-rich amorphous component. We demonstrate the applicability of first order reaction kinetics for HMF conversion to THFDM and observe that the respective rate constants per mass of Ni are equivalent for the four catalysts. Stability tests show that Ni is not leaching and sintering does not take place after 3 consecutive runs. The decrease in conversion is associated with the formation of coke resulting from polymerisation; the removal of the coke by heat treatment regenerates the activity. We also establish that selectivity depends mainly on temperature and conversion and to some extent on H2 pressure. We achieved 100% yield of the target tetrahydrofuran-2,5-diyldimethanol when working at 353 K in water; the use of higher temperature generated the formation of 3-hydroxymethylcyclopentanone, an important intermediate chemical.

Experimental Section

***Catalyst Preparation***

Four catalyst precursors Ni(1-x)Alx(OH)2(CO3)x/2.mH2O, with 0.24 ≤ x ≤ 0.47 and 0.3 ≤ m ≤ 0.7, were prepared by co-precipitation with urea, based on Costantino *et al.* method [29]. A known mass of powder urea (Sigma) was placed in a reaction flask (250 mL) with distilled water (50 mL). A mixture of 1.5 M aqueous solutions of AlCl3∙6H2O (Fluka, ≥ 99.0 wt% purity) and NiCl2∙6H2O (Aldrich, 99.9 wt% purity) were added. The volumes of the solutions and the mass of urea were appropriately chosen to have the Al ratios (x) = nAl/(nNi + nAl) in the range 0.24-0.47 and nurea/(nNi + nAl) = 3.3. The flasks were placed in a Radley Carousel 6 Plus station, stirred at 750 rpm and heated to 368 K at 1K min-1 under reflux. After aging for 65 h, the solutions were cooled to ambient temperature and filtered. The precipitated materials were left in suspension with NH4HCO3 for 5 h (to remove any residual Cl), then filtered, washed and dried at 2 K min-1 to 353 K for 3 h. The solids were then ground and dried at 2 K min-1 to 393 K for 5 h; the precursors are denominated NiAl-XP, with X = 1, 2, 3 and 4; The number X relates to the Al contents (x) where NiAl-1P corresponds to the precursor with the lowest Al content. The samples were placed in a furnace (0.35 g of powder per crucible) and successively calcined (under air, 75 mL min-1, NiAl-XC) and reduced (under pure H2, 100 mL min-1) at 5 K min-1 to 773 K for 5 h; the catalysts were then passivated (<1% v/v O2/N2, 100 mL min-1) at room temperature for 3 h (NiAl-XR).

***Catalysts Characterization***

Total surface area (SA), pore volume (PV) and pore size distribution of the precursors and catalysts were determined by volumetric N2 adsorption at 77 K, with a Tristar II micromeritics. Thermal gravimetric analysis (TGA) were measured with a Q500 TA Instruments; *ca.* 10 mg of samples heated to 1023 K at 5 K min-1 under 50 mL of air or Ar and changes in mass were recorded. Temperature programmed reduction (TPR) was measured using the commercial CHEM-BET 3000 (Quantachrome) unit; 50 mg of samples were loaded into a Quartz cell, heated in 30 mL min-1 5% v/v H2/N2 at 5 K min‑1to 773-1073 K and changes in H2 consumption were monitored by TCD. Carbon and hydrogen contents of the materials were determined by microanalytical procedures using a Thermo EA1112 Flash CHNS Analyser.Al and Ni contents of the catalysts and solutions were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) after digesting 25 mg of the material in 10 mL of HCl (37%) for 4h and diluting it with water (1/10 v/v).

The precursors and catalysts were sputter coated with gold and images were recorded with a Hitachi S-4800 Field-Emission Scanning Electron Microscope; Ni, Al and Cl content were obtained by SEM-EDX. A small amount of sample was deposited on the carbon film of a copper grid and Ni particle size distribution was obtained using a JEOL 2100 Transmission Electron Microscopy (TEM).

The precursors were ground and combined with oven dried KBr and pressed into a disc. The spectra of the samples were recorded by accumulating 64 scans at 4 cm-1 resolution between 400 and 4000 cm-1 using a Fourier Transform Infrared (FT-IR) Bruker Tensor 27.

Powder X-ray diffractograms (XRD) data were collected in reflection geometry on a Panalytical X’Pert Pro diffractometer with Co K*α1* radiation (λ = 1.7890 Å). Samples were scanned at 0.023º s-1 over the range 10º ≤ 2*θ* ≤ 80º for phase identification using the reference standards, i.e. Ni (Card No. 73-1519), NiO (70-0989). Samples were mixed with LaB6 as an internal standard and the powders were scanned over the range 10º ≤ 2*θ* ≤ 120º for whole pattern fitting; the lattice parameters of the materials were obtained performing Pawley refinement using Topas academic software, with the cell parameter of LaB6 (space group ; *a* = 4.15700 Å) fixed. The mean crystallite sizes (*d*Ni) were determined using the Double-Voigt approach based on the method of Balzar et al. [62,63] and assuming a mono-disperse system of spheres. Specific Ni surface areas were obtained with,

(9)

With ρ the Ni specific mass.

The isoelectric points (IEP) were determined by measuring the change in zeta potential as a function of pH. In each case, *ca.* 10 mg of catalyst was dispersed in 10mL of distilled water; the zeta potentials were obtained by measuring the electrophoretic mobility of the particle using a Malvern Zetasizer Nano ZSP Instrument. The pH was controlled with a MPT-2 titrator (adding HCl or NaOH, 0.025 M) and 10 measurements were conducted between pH 6 and 12.

*2.3. Catalytic testing*

Reactions were carried out in a batch stirred stainless steel Parr 5000 reactor. In a typical experiment 0.01-0.14 g of catalyst and 45 mL aqueous solution of reactant (C = 0.02-0.04 M) were charged in a glass liner. The reactor was then closed, flushed under N2, stirred (600 rpm) and heated to reaction temperature (353-413 K). After stabilisation of the temperature (ca. 1 h), H2 was added and the reactor was kept under constant pressure (5-60 bars). The product composition and identification was determined using an Agilent Technologies 7890A gas chromatograph equipped with FID and an 6890N GC equiped with 5973 MSD agilent, respectively. A DB-WAXetr 60 m × 0.25 mm *i.d.*, 0.25 μm film thickness capillary column (Agilent J&W) was employed in both. Repeated reactions with different samples from the same batch of catalyst delivered a product composition that was reproducible to within ± 5%. A blank test conducted without catalyst did not result in any detectable conversion. 5-Hydroxymethyl furfural (Sigma, ≥ 99 wt% purity) was used as received without further purification. furan-2,5-diyldimethanol (Manchester organics) and tetrahydrofuran-2,5-diyldimethanol (Ambinter) were used for identification and calibration of products.

5-hydroxymethyl furfural (HMF) conversion (X) at time *t* was calculated as

(10)

*C*HMF,in and *C*HMF are the initial concentrations initial and at time *t* of HMF in solution, respectively. The selectivity (*S*) and yield (*Y*) with respect to furan-2,5-diyldimethanol (FDM), as an example, are given by,

& (11)

Identification of tetrahydrofuran-2,5-diyldimethanol and 3-hydroxymethyl cyclopentanone were verified by 1H and 13C NMR using a Bruker Avance III HD NMR spectrometers operating at 400 MHz proton frequency. Water was removed from the solutions with a rotary evaporator and the compounds left were diluted in DMSO; chemicals shifts are reported relatively to residual solvent.

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**Keywords:** Hydrogenation • 5-Hydroxymethyl-furfural • Layered compounds • Nickel • water

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**Table of Contents**

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| FULL PAPER | | | | |
| **Water as a solvent?** The hydrogenation of 5-hydroxymethyl furfural over Ni/alumina catalyst can result in exclusive formation of tetrahydrofuran-2,5-diyldimethanol. The effect of water, reaction conditions and catalysts composition on the catalytic response and stability were investigated. |  |  |  | Author(s), Corresponding Author(s)\*  Page No. – Page No.  Title |

**Figure Captions:**

**Figure 1.** Reaction pathway for the transformation of 5-hydroxymethyl furfural to some of the targeted compounds in the literature.

**Figure 2.** (a) XRD patterns of NiAl-1 precursor (black), calcined (red) and reduced (blue); (b) lattice parameters *a* of the precursors in function of Al bulk molar ratio (x) where the linear fit obey Vegard’s law; (c) TGA profiles and (d) H2-TPR profiles (with temperature ramp in dotted line) generated for the precursors (c) and calcined (d) samples of NiAl-1 (red), NiAl-2 (blue) NiAl-3 (green) and NiAl-4 (black). *Note*: the main planes associated with Ni (♦), NiO (●) and hydrotalcite (▲) are identified in (a).

**Figure 3.** Representative SEM (a) and TEM (b,c) images, associated with Ni particle size distribution (d) for NiAl-4P (a) and NiAl-4R (b,c,d).

**Figure 4.** (a) Reaction pathway observed for the hydrogenation of HMF, at 353 K and PH2 = 20 bars; (b) Logarithm of HMF concentration (*C*HMF) with time (*t*), over 0.03 g of catalyst (NiAl-R), C*i*HMF ~0.04 mol L-1. (c) Concentration (C) of HMF, FDM and THFDM as a function of time, for the hydrogenation of HMF (C*i*HMF ~0.04 mol L-1) over 0.04 g of NiAl-4R.

**Figure 5. (a)** Selectivity towards FDM (SFDM, red) and THFDM (STHFDM, black) with conversion of HMF (for X < 0.99) over the four catalysts. **(b)** YFDM in function of YHMF and fitting associated with equation 7 (for YHMF > 0.01).

**Figure 6.** Conversion of HMF (X, blue), yields of FDM (YFDM, red) and THFDM (YTHFDM, black) in function of the mass of NiAl-4R after 6 h reaction; T = 353 K, PH2 = 20 bars, *Ci*HMF ~0.04 mol L-1.

**Figure 7.** Yields of FDM (YFDM) and THFDM (YTHFDM) after 6h reaction over NiAl-4R; T = 353 K, PH2 = 20 bars, *Ci*HMF ~0.04 mol L-1, mcatalyst = 0.015 g

**Figure 8.** (a) Reaction pathway observed and (b) concentrations of HMF, FDM, THFDM, HHD and HCPN in function of time, for the hydrogenation of HMF (Ci ~ 0.04 mol L-1) over 0.035 g of NiAl-4R; T = 413 K, PH2 = 20 bars.