# Catalytic hydration of mono and dinitriles using nickel(0) and PTSA

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## ABSTRACT

The catalytic hydration of mono and dinitriles (dicyanoalkanes, DCAs) using nickel(0) catalysts of the type, [(dippe)Ni($\eta^2$-*N,C*–R)] (R = –Me,–Ph,–(CH$_2$)$_2$–CN,–(CH$_2$)$_4$–CN) and *p*-toluenesulfonic acid monohydrate (PTSA) as a co-catalyst, is reported. In the cases where DCAs (adipo and succinonitrile) were used, both the activity and the selectivity for the process were affected by length of the internal chains of the substrates. A competitive decomposition of the amide products was observed to be favoured to a greater extent in the case of succinonitrile, resulting in extensive carbonization and formation of ammonia. The carbonaceous by-products were analysed by scanning electron microscopy (SEM). The use of nickel(II) sources was addressed in the presence and in the absence of PTSA, with the aim of comparing their reactivity with that displayed by nickel(0) catalysts. The results obtained from these studies suggest that activity of the catalyst is affected by the oxidation state of the metal, the use of nickel(0) compounds resulting in better catalyst performance overall.

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## 1. Introduction

The direct preparation of amides by hydration [1] of nitriles is a process that has long been pursuit by chemists and exhibits considerable synthetic relevance both from the fundamental [2] and commercial [3] viewpoints. The readiness of the reaction is hampered by the low reactivity of the nitrile which is thermally stable and in the past, this contributed for a widespread use of harsh reaction conditions to promote its hydration [4], often resulting in poor selectivity for the amide. Alternative strategies involving enzymatic [5] and metal [6] catalyzed processes have been the subject of intense research over the course of the last 30 years and significant progress in both selectivity and catalyst efficiency has been achieved as a result of these efforts [7].

During the same period of time, our group has become deeply involved in the chemistry of nickel(0) compounds that exhibit $\eta^2$-coordination from a variety of different nitriles [8] and previously we have published our results on the catalytic hydration of benzo (BN) and acetonitrile (AN) [8g] using such type of compounds as catalysts, more recently extended for the catalytic hydration of 1,2-, 1,3-, and 1,4-dicyanobenzenes (DCBs) [8f].

In the current work we have extended these studies to the catalytic hydration of dicyanoalkanes (DCAs) which are valuable substrates for the industrial sector [9]. A discussion concerning the use of *p*-toluensulfonic acid (PTSA) as a co-catalyst for the hydration of BN, AN and AdN is presented as well.

## 2. Experimental

### 2.1. General considerations

Unless otherwise noted, all manipulations were performed using standard Schlenk and glovebox techniques under high purity argon (Praxair, 99.998%) in an MBraun glovebox (<1 ppm, H$_2$O and O$_2$). Stainless steel autoclaves (T316SS) Parr Series 4590, 4561 M, Bench Top Mini Reactors (100, 300 mL) and 4750 Parr vessels (125 mL) were used for catalysis experiments. Liquid substrates were reagent grade and were degassed using the freeze-thaw method prior to their use. AN (J.T. Baker) was refluxed over calcium hydride (CaH$_2$) until dryness [10], distilled under inert atmosphere and stored over 3 Å molecular sieves in a glovebox. Anhydrous BN, SuN and AdN were purchased from Aldrich and were used as received. All water used was distilled. Solvents (J.T. Baker) were reagent grade and were dried and purified by distillation from benzophenone ketyl solutions (THF and Hexanes). Deuterated solvents for NMR experiments were purchased from Cambridge Isotope Laboratories and stored over 3 Å molecular sieves in the glovebox. The chelating bisphosphine ligand, dippe [11] was synthesized from 1,2-bis(dichlorophosphino)ethane (Aldrich) and the corresponding isopropylmagnesium chloride THF solution (2.0 M, Aldrich). [(dippe)NiH]$_2$ (**1**) was prepared from an hexanes slurry of [(dippe)NiCl$_2$] [12] using Super-Hydride,

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similarly to the procedure informed in the literature [13]. Neutral alumina was used for the preparation of complex **1** and was dried under vacuum at 200 °C for 48 h. NiCl$_2$·6H$_2$O (Baker) and *p*-toluenesulfonic acid monohydrate (Aldrich) were used as received. All complexes and organics produced in this work were purified by crystallization or column chromatography. Reactor vessels for catalysis were charged in a glovebox. The amount of nitrile used in each run was calculated with respect to the corresponding mol percent of nickel(0) catalyst, [(dippe)Ni($\eta^2$-*N,C*–R)] (R = –Me,–Ph,–(CH$_2$)$_2$–CN,–(CH$_2$)$_4$–CN) prepared in situ. The –CN functions within each dinitrile were considered as independent entities. The hydration products were recovered from the reactor vessels using hot ethanol washings or acetone. The crude products were quantified once dried and were purified either by filtration through a frit using alumina (acetamide and benzamide) or by column chromatography (5-cyanovaleramide and adipamide) prior to their complete analytical and spectroscopic characterization. NMR spectra of complexes and products were recorded at ambient temperature using either 300 MHz Varian Unity or 400 MHz Varian INOVA spectrometers. $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of nickel(0) complexes were obtained at room temperature from concentrated THF-$d_8$ and benzene-$d_6$ solutions (100 mg) of the pure compounds under inert atmosphere using thin wall (0.38 mm) WILMAD NMR tubes equipped with J Young valves. The $^1$H and $^{13}$C{$^1$H} NMR spectra of purified hydration products were obtained from concentrated CDCl$_3$ or DMSO-$d_6$ solutions. $^1$H and $^{13}$C{$^1$H} chemical shifts ($\delta$, ppm) are reported relative to the corresponding residual proton or deuterium resonances in the deuterated solvent and $^{31}$P{$^1$H} NMR spectra are reported relative to external 85% H$_3$PO$_4$. All calculated $^1$H and $^{13}$C{$^1$H} NMR spectra were obtained using ACD/HNMR [14] and ACD/CNMR Predictor [15] from optimised chemical structures calculated using ACD/ChemSketch [16]. Elemental analyses and mass spectra (MS-EI$^+$) of the purified organics were carried out by USAI–UNAM using an EA 1108 FISONS Instruments analyser and a Jeol SX-102A mass spectrometer, respectively. Elemental and mass spectrometric analyses of pure compounds **2**–**4** yielded irreproducible results due to extreme oxygen sensitivity and are not reported. Infrared spectra of the organic products were obtained using a PerkinElmer 1600 FT spectrophotometer. A scanning electron microscope Jeol JSM 5900 LV was used for the analysis of the carbonaceous materials. Ammonia generated during catalysis experiments was bubbled after reaction into concentrated hydrochloric acid and the produced ammonium chloride (NH$_4$Cl) analyzed by X-ray powder diffraction (Powder XRD). All Powder XRD analyses were performed using graphite monochromatized Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å) in a Siemens D5000 diffractometer. Experimental melting points were obtained by closed capillary methods using an Electrothermal Digital Melting Point Apparatus. All conversions in this work are determined according to the total product obtained (in mol) divided by total substrate. Turnover numbers (TON) for the catalytic hydrations were calculated with respect to total water incorporated per mole of isolated product over total nickel(0) unless otherwise stated, e.g., {[(mol of 5-cyanovaleramide) × (1 H$_2$O)] + [(mol of adipamide) × (2 H$_2$O)]}/[mol of [Ni(0)]. Turnover frequencies (TOF) are calculated as TON over reaction time (TON/h). All catalysis experiments were performed by duplicate.

### 2.2. Preparation of [(dippe)Ni{$\eta^2$-N,C–(CH$_2$)$_2$–CN}] (2)

[(dippe)NiH]$_2$, **1** (0.100 g, 0.156 mmol) was dissolved at room temperature in dry THF (5 mL) using a vial in a glovebox and to it was added 2 equiv. of SuN (0.025 g, 0.312 mmol). The mixture resulted in the evolution of hydrogen gas and a colour change

from deep red to dark yellow. The system was stirred for the next 15 min allowing the gas to vent away into the glovebox and the remaining solution taken to dryness using the vacuum line. The remaining brown residue was dried under vacuum (*P* < 30 mTorr) for the next 6 h. Yield: 96% (0.124 g, 0.298 mmol) of a dark brown solid. NMR spectra for **2** in THF-$d_8$, $^1$H: $\delta$ (ppm) 3.1 (*t*, $^3J$ = 7.5 Hz, 2H, CH$_2$), 2.8 (*t*, $^3J$ = 7.5 Hz, 2H, CH$_2$), 2.1 (*br septuplet*, $^3J$ = 7 Hz, 2H, CH), 2.03 (*br septuplet*, $^3J$ = 7 Hz, 2H, CH), 1.6 (*m*, 4H, CH$_2$), 1.2–1.05 (*m*, 24H, CH$_3$). $^{13}$C{$^1$H}: $\delta$ (ppm) 164.6 (*dd*, $J_1$ = $^2J_{C–P-trans}$ = 29 Hz, $J_2$ = $^2J_{C–P-cis}$ = 9 Hz, coordinated-CN), 119.3 (*s*, uncoordinated-CN), 26.5 (*t*, $^1J_{C–P}$ = 17.6 Hz, CH), 25.07 (*dd*, $J_1$ = 17.8 Hz, $J_2$ = 5 Hz, CH$_2$), 22.4 (*dd*, $J_1$ = 21.4 Hz, $J_2$ = 19.9 Hz, CH$_2$), 20.5 (*dd*, $J_1$ = 19.9 Hz, $J_2$ = 15.4 Hz, CH$_2$), 19.6 (*d*, $^2J_{C–P}$ = 8 Hz, CH$_3$), 19.2 (*d*, $^2J_{C–P}$ = 7.8 Hz, CH$_3$), 18.7 (*d*, $^2J_{C–P}$ = 3.1 Hz, CH$_3$), 18.6 (*d*, $^2J_{C–P}$ = 1.8 Hz, CH$_3$), 15.8 (*br d*, *J* = 4.6 Hz, CH$_2$). $^{31}$P{$^1$H}: $\delta$ (ppm) 84.4 (*br d*, $^2J_{P–P}$ = 68 Hz), 70.1 (*br d*, $^2J_{P–P}$ = 68 Hz).

### 2.3. Preparation of [(dippe)Ni{$\eta^2$-N,C–(CH$_2$)$_4$–CN}] (3)

The preparation of **3** was performed following the same procedure described for **2**, using **1** (0.100 g, 0.156 mmol) and 2 equiv. of AdN (36 μL, 0.316 mmol) in dry THF (5 mL). Yield: 95% (0.131 g, 0.295 mmol) of a dark brown solid. NMR spectra for **2** in THF-$d_8$, $^1$H: $\delta$ (ppm) 2.8 (*m*, 2H, CH$_2$), 2.4 (*br t*, $^3J$ = 7 Hz, 2H, CH$_2$), 2.1–1.97 (*m*, 4H, CH), 1.85 (*br quintet*, $^3J$ = 7 Hz, 2H, CH$_2$), 1.77 (*br quintet*, $^3J$ = 7 Hz, 2H, CH$_2$), 1.59 (*m*, 4H, CH$_2$), 1.2–1.03 (*m*, 24H, CH$_3$). $^{13}$C{$^1$H}: $\delta$ (ppm) 165.7 (*dd*, $J_1$ = $^2J_{C–P-trans}$ = 25.5 Hz, $J_2$ = $^2J_{C–P-cis}$ = 9.5 Hz, coordinated-CN), 120.3 (*s*, uncoordinated-CN), 30.7 (*t*, $^1J_{C–P}$ = 15 Hz, CH), 28.2 (*br d*, $^3J_{C–P}$ = 3.3 Hz, CH$_2$), 25.7–25.2 (*m*, CH), 25.7 (*br s*, CH$_2$), 24.95 (*s*, CH$_2$), 23.3 (*br t*, $^1J_{C–P}$ = 20.5 Hz, bridging CH$_2$), 21.45 (*dd*, $^1J_{C–P}$ = 19.5 Hz, $^2J_{C–P}$ = 15.5 Hz, bridging CH$_2$), 20.5 (*d*, $^3J_{C–P}$ = 8.3 Hz, CH$_3$), 20.2 (*d*, $^3J_{C–P}$ = 8 Hz, CH$_3$), 19.7 (*br d*, $^3J_{C–P}$ = 3.4 Hz, CH$_3$), 19.5 (*pseudo d*, $^3J_{C–P}$ = 1.6 Hz, CH$_3$), 17.05 (*s*, CH$_2$). $^{31}$P{$^1$H}: $\delta$ (ppm) 80.5 (*br d*, $^2J_{P–P}$ = 74 Hz), 65.9 (*br d*, $^2J_{P–P}$ = 74 Hz). Addition of less than 2 equiv. of AdN (e.g., 1 equiv, 18 μL, 0.158 mmol) to **1** (0.100 g, 0.156 mmol) in THF solution (5 mL), was found to yield mixtures of **3** and the doubly coordinated species [{(dippe)Ni}$_2${$\eta^2$-, $\eta^2$-*N,C*–(1,4-(CN)$_2$-butane}], **5**. $^{31}$P{$^1$H} NMR: $\delta$ (ppm) 80.1 (*br d*, $^2J_{P–P}$ = 76.6 Hz), 65.5 (*br d*, $^2J_{P–P}$ = 76.6 Hz).

### 2.4. Preparation of [(dippe)Ni{$\eta^2$-N,C–(CH$_2$)$_4$–CONH$_2$}] (4)

To a dark red solution of **1** (0.100 g, 0.156 mmol) in THF (5 mL) were added 2 equiv. of 5-cyanovaleramide (0.0394 g, 0.312 mmol). The mixture reacted immediately resulting in evolution of H$_{2(g)}$ which was vented to the glovebox under constant stirring. The solution gradually turned from a deep red colour to dark yellow. A beige powder was also observed to precipitate as a result of reaction. The solvent was then stripped in a Schlenk line under vacuum. The remaining residue was re-dissolved in methanol and recrystallized by dropwise addition of a 1:1 (v/v) mixture of THF and toluene in the glovebox. The resulting solid was dried under vacuum (*P* < 30 mTorr) for 6 h. Yield: 85% (0.0612 g, 0.132 mmol) of a yellow solid. NMR spectra for **4** in THF-$d_8$, $^1$H: $\delta$ (ppm) 6.85 (*br s*, 1H, NH), 6.3 (*br s*, 1H, NH), 2.8 (*m*, 2H, CH$_2$), 2.37 (*br t*, $^3J$ = 6.6 Hz, 2H, CH$_2$), 2.17 (*br quintet*, $^3J$ = 6.6 Hz, 2H, CH$_2$), 2.1–1.95 (*m*, 4H, CH), 1.73 (*m*, 2H, CH$_2$), 1.7–1.6 (*m*, 4H, CH$_2$), 1.2–1.01 (*m*, 24H, CH$_3$). $^{13}$C{$^1$H}: $\delta$ (ppm) 177.5 (*s*, uncoordinated carbonyl, –C(O)NH$_2$), 169.2 (*br dd*, $J_1$ = $^2J_{C–P-trans}$ = 19.3 Hz, $J_2$ = $^2J_{C–P-cis}$ = 8.3 Hz, coordinated-CN), 38.6 (*br s*, CH$_2$), 37.6 (*br s*, CH$_2$), 34.1 (*br t*, *J* = 14.5 Hz), 31.4 (*br s*, CH$_2$), 28.9–28.1 (*m*, CH), 25.7 (*br t*, $^1J_{C–P}$ = 22.8 Hz, bridging CH$_2$), 23.9 (*br t*, $^1J_{C–P}$ = 17.3 Hz, bridging CH$_2$), 23–22.6 (*m*, CH$_3$), 22.1–21.9 (*m*, CH$_3$). $^{31}$P{$^1$H}: $\delta$ (ppm) 81.2 (*br d*, $^2J_{P–P}$ = 74.5 Hz), 66.6 (*br d*, $^2J_{P–P}$ = 74.5 Hz).

## 2.5. Catalysis assessments

### 2.5.1. Catalytic hydration of AdN at 150 and 180°C, using nickel(0)

Reactor vessels (100 mL) were charged in separate runs with AdN (5 mL, 0.045 mol), water (1.8 mL, 0.10 mol) and **1** (0.012 g, 0.019 mmol; 0.04 mol% of [Ni(0)]) in a glovebox. The vessels were heated to (a) 150°C and (b) 180°C for a period of 24 h, after which time they were allowed to cool down and opened in a fume-hood, at room temperature. Pearl white crude residues were recovered from each of the vessels using hot ethanol washings and purified by column chromatography using neutral alumina. A first fraction of each was eluted from each column using a 1:1 (v/v) mixture of hexanes and acetone resulting in recovery of unreacted AdN in both cases. 5-Cyanovaleramide loads were recovered as the second fractions from each mixture eluting with a 25:75 (v/v) mixture of hexanes and acetone. Solvent was evaporated to dryness in a rotavapor and the remaining white solids, dried in a vacuum line for 4 h. Yield of 5-cyanovaleramide produced at 150°C, after work-up: 9% (0.4828 g, 0.0038 mol) with a TON of 101 and a TOF of 4 cycles/h. Yield of 5-cyanovaleramide produced at 180°C: 25% (1.3609 g, 0.0108 mol) with a TON of 290 and a TOF of 12 cycles/h. m.p. of 5-cyanovaleramide = 67–69°C. Anal. Calcd. (%) for $C_6H_{10}N_2O$: C, 57.12; H, 7.99; N, 22.21. Found: C, 56.32; H, 7.80; N, 21.33. MS-EI⁺: $m/z$ = 127 (0.9%, [M⁺]), 110 (6.25%, {[M⁺]–NH₂}), 77 (15.2%, {[M⁺]–CH₂–CN}), 82 (25%, {[M⁺]–C(O)NH₂}), 72 (6.25%, {[M⁺]–(CH₂)₂–CN}), 59 (100%, {[M⁺]–(CH₂)₃–CN}), 54 (45.5%, {[M⁺]–(CH₂)₂–C(O)NH₂}), 44 (27.7%, {[M⁺]–(CH₂)₄–CN}). FT-IR (KBr disc, cm⁻¹): 3420 (s, asymmetric coupled N–H stretch), 3220 (s, symmetric coupled N–H stretch), 2949 (m, aliphatic C–H stretch), 2249 (s, aliphatic C≡N stretch), 1683–1619 (s, overlap, C=O stretch and N–H bend), 1415 (m, C–N stretch), 632 (m, broad N–H out-of-plane bend). NMR spectra for 5-cyanovaleramide in DMSO-$d_6$, ¹H: δ (ppm) 7.17 (br s, 1H, NH), 6.651 (br s, 1H, NH), 2.36 (t, J = 6.6 Hz, 2H, CH₂), 1.96 (t, J = 6.6 Hz, 2H, CH₂), 1.43 (m, 4H, CH₂). ¹³C{¹H}: δ (ppm) 174.02 (s, carbonyl), 120.62 (s, –CN), 34.17 (s, CH₂), 24.49 (s, CH₂), 24.21 (s, CH₂), 16.05 (s, CH₂).

### 2.5.2. Catalytic hydration of AdN at 230 and 260°C, using nickel(0)

Reactor vessels were charged in separate runs with AdN (5 mL, 0.045 mol), water (1.8 mL, 0.10 mol) and **1** (0.0057 g, 0.009 mmol; 0.02 mol% of [Ni(0)]) in a glovebox, following the procedure described in Section 2.5.1. Two of the vessels were heated to 230°C for 24 and 36 h and a third one was heated to 260°C overnight (~12 h) after which times heating was stopped and the vessels allowed to cool down to room temperature following the above described procedure. In the case of the vessels heated at 230°C, pearl white residues were recovered from the vessels using hot ethanol washings. An insoluble component present in both vessels after reaction was separated from the alcoholic solutions by filtration, yielding analytically pure adipamide loads which were further washed with ethanol and vacuum dried for 4 h. The remaining alcoholic solutions were evaporated to dryness and the recovered residues purified by column chromatography using neutral alumina. Overall conversion after 24 h at 230°C: 61% with a TON of 2738 and a TOF of 114 cycles/h. Overall conversion after 36 h at 230°C: 78% with a TON of 3203 and a TOF of 89 cycles/h. Yield of 5-cyanovaleramide produced after 24 h at 230°C: 14% (0.7665 g, 0.0061 mol). Yield of 5-cyanovaleramide produced after 36 h at 230°C: 29% (1.6121 g, 0.0128 mol). Yield of adipamide produced after 24 h at 230°C: 47% (3.0096 g, 0.0209 mol). Yield of adipamide produced after 36 h at 230°C: 49% (3.0931 g, 0.0215 mol). m.p. of adipamide = 227–230°C. Anal. Calcd. (%) for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.71; H, 8.02;

N, 19.02. MS-EI⁺: $m/z$ = 144 (1.8%, [M⁺]), 127 (18.75%, {[M⁺]–NH₂}), 110 (8%, {[M⁺]–(NH₂)₂}), 99 (60.7%, {[M⁺]–C(O)NH₂}), 86 (100%, {[M⁺]–CH₂–C(O)NH₂}), 72 (70.5%, {[M⁺]–(CH₂)₂–C(O)NH₂}), 59 (53.6%, {[M⁺]–(CH₂)₃–C(O)NH₂}), 44 (48.2%, –C(O)NH₂). FT-IR (KBr disc, cm⁻¹): 3425 (s, asymmetric coupled N–H stretch), 3223 (m, overlap, symmetric coupled N–H stretch), 2944 (m, aliphatic C–H stretch), 1695 (s, overlap, C=O stretch and N–H bend), 1429 (m, C–N stretch), 669 (m, broad N–H out-of-plane bend). NMR spectra for adipamide in DMSO-$d_6$, ¹H: δ (ppm) 7.23 (br s, 2H, NH), 6.70 (br s, 2H, NH), 2.02 (br t, J = 6.3 Hz, 4H, CH₂), 1.44 (br t, J = 6.3 Hz, 4H, CH₂). ¹³C{¹H}: δ (ppm) 174.22 (s, carbonyl), 34.98 (s, CH₂), 24.89 (s, CH₂). In the case of the system heated at 260°C, 100% conversion of AdN into a carbonaceous residue (2.7404 g) of considerably high carbon content (C, 75.98; H, 5.28; N, 8.78) was obtained, accompanied by extensive formation of ammonia inside the vessel. The product was thermally stable and insoluble. The carbonaceous product was analysed by scanning electron microscopy (SEM). The presence of NH₃(g) was confirmed bubbling the gas from the reactor into concentrated HCl(aq), which resulted in precipitation of ammonium chloride (NH₄Cl). M. p. of NH₄Cl = 340°C (subl.). FT-IR (KBr disc, cm⁻¹): 3283 (s, N–H stretch), 1954 (m, combination band), 1704 (m, combination band), 1433 (s, N–H bend). Powder XRD pattern as compared to a standard, 2θ scale (deg): 3.872, 2.739, 2.235, 1.937, 1.733, 1.582, 1.370, 1.292, 1.226, 1.169, 1.119.

### 2.5.3. Catalytic hydration of SuN using [Ni(0)]

A series of vessels were charged in separate runs with SuN (5 g, 0.06 mol), water (2.2 mL, 0.12 mol) and **1** (0.0039 g, 0.006 mmol; 0.01 mol% of [Ni(0)]) in a glovebox. The vessels were initially heated to 60°C for a period of 1 h, intended to ensure complete melt of SuN and in situ generation of the nickel(0) catalyst **2**. The vessels were then further heated to 120 (24 h), 140 (24 and 72 h), 160 (24 h) and 230°C (0.4 h). No conversion of SuN was found for the system heated at 120°C. The system heated at 140°C for a period of 24 h showed formation of minute amounts of succinamide and succinimide in an estimated 0.4:0.6% relationship, according to ¹H NMR analysis of the crude reaction mixture in CDCl₃ (overall conversion: ~5% with TON = 91, TOF = 4). Formation of carbonaceous residue (0.3091 g) was observed as well. Heating of the vessel for a longer period of time (72 h) at the same temperature (140°C) yielded almost complete conversion into the carbonaceous by-product (6.7242 g), although minute amounts (0.2404 g) of succinamide and succinimide in 0.4:3.4% relationship could be recovered from the upper section of the vessel and analysed by ¹H and ¹³C{¹H} NMR, also in CDCl₃ (overall conversion: 100%). Heating to higher temperatures, 160 or 230°C, yielded in both cases a complete conversion into the carbonaceous by-product. Repeated attempts to extract extra amounts of succinamide or succinimide from these loads using polar organic solvents were all found to fail. NMR spectra for the mixture of succinamide and succinimide obtained after 72 h at 140°C, in CDCl₃, ¹H: δ (ppm) 9.26 (br s, 1H, NH, succinimide), 6.32 (br s, 1H, NH, succinamide), 6.07 (br s, 1H, NH, succinamide), 2.77 (br s, 4H, CH₂, succinimide), 2.74 (br s, 4H, CH₂, succinamide). ¹³C{¹H}: δ (ppm) 179.12 (s, carbonyl, succinimide), 172.26 (s, carbonyl, succinamide), 29.88 (s, CH₂, succinamide), 29.15 (s, CH₂, succinimide).

## 2.6. Co-catalysis assessments using stainless steel vessels

### 2.6.1. BN hydration using PTSA only

Reactor vessels were charged in separate runs with BN (5 mL, 0.05 mol), water (1.25 mL, 0.07 mol) and PTSA (0.095 g, 0.5 mmol; 1.0 mol% of PTSA). The vessels were heated to 160 and 180°C for 24 h. The vessels were opened in a fume hood and their contents removed using acetone washings. These were evaporated using a

rotavapor and the crude residues weighed. Re-dissolution of the crude residue in acetone and filtration through an alumina frit yielded pure benzamide loads. Yield of benzamide produced at 160 °C: 3% (0.1870 g, 0.0015 mol) with a TON of 3 and a TOF of 0.1 cycles/h. Yield of benzamide produced at 180 °C: 11% (0.6197 g, 0.0051 mol) with a TON of 10 and a TOF of 0.4 cycles/h. m.p. of benzamide: 131 °C. Anal. Calcd. for $C_7H_7NO$: C 69.41, H 5.82, N 11.56. Found: C 69.67, H 6.00, N 11.70. NMR spectra for benzamide in CDCl$_3$, $^1$H: $\delta$ (ppm) 7.80 (br d, J = 7.2 Hz, 2H, CH), 7.51 (br t, J = 7.2 Hz, 1H, CH), 7.42 (br t, J = 6.9 Hz, 2H, CH), 6.47 (br s, 1H, NH), 6.32 (br s, 1H, NH). $^{13}$C{$^1$H}: $\delta$ (ppm) 169.89 (s, carbonyl), 133.21 (s, ipso), 132.21 (s, CH), 128.83 (s, CH), 127.55 (s, CH).

### 2.6.2. Catalytic hydration of BN using [Ni(0)] and PTSA at 160 and 180 °C, temperature and reaction time optimization

Vessels were charged in separate runs with BN (5 mL, 0.05 mol), water (1.25 mL, 0.07 mol), **1** (0.0133 g, 0.020 mmol; 0.1 mol% of [Ni(0)]) and PTSA (0.095 g, 0.5 mmol; 1.0 mol% of PTSA). The vessels were heated to a) 160 and 180 °C for 24 h and b) 180 °C for 72 h. Work-up of all reaction mixtures was performed as described above. Yield of benzamide produced at 160 °C, after 24 h: 18% (1.0747 g, 0.0089 mol) with a TON of 215 and a TOF of 9 cycles/h. Yield of benzamide produced at 180 °C, after 24 h: 38% (2.2187 g, 0.0183 mol) with a TON of 442 and a TOF of 18 cycles/h. Yield of pure benzamide produced at 180 °C, after 72 h: 72% (4.2496 g, 0.0351 mol) with a TON of 859 and a TOF of 12 cycles/h.

### 2.6.3. Catalytic hydration of BN using [Ni(0)] and PTSA, at 180 °C, combined catalyst/co-catalyst mol% optimization

Reactor vessels were charged in separate runs with BN (5 mL, 0.05 mol) and water (1.25 mL, 0.07 mol) varying the proportion of **1** and PTSA to values different from the 0.1:1.0 mol% proportion. The quantities and resulting mol percents of each of these experiments is listed in Table 1.

The vessels were heated to 180 °C for 72 h. Yield of benzamide produced using the 0.1:0.1 proportion of {[Ni(0)]:PTSA}: 22% (1.2783 g, 0.0106 mol) of white crystals with a TON of 224 and a TOF of 3 cycles/h. Yield of benzamide produced using the 0.1:0.4 proportion of {[Ni(0)]:PTSA}: 92% (5.4325 g, 0.0448 mol) with a TON of 1078 and a TOF of 15 cycles/h. Yield of benzamide produced using the 0.01:0.04 proportion of {[Ni(0)]:PTSA}: 11% (0.6655 g, 0.0055 mol) with a TON of 1141 and a TOF of 16 cycles/h. Yield of benzamide produced using only 0.4 mol% of [Ni(0)]: 9% (0.5072 g, 0.0042 mol) with a TON of 22 and a TOF of 0.3 cycles/h. Yield of benzamide produced using the 0.4:0.4 proportion of {[Ni(0)]:PTSA}: 26% (1.5090 g, 0.0125 mol) with a TON of 64 and a TOF of 1 cycle/h.

### 2.6.4. Catalytic hydration of AN using [Ni(0)] and PTSA

Reactor vessels were charged in separate runs with AN (5 mL, 0.10 mol), water (1.25 mL, 0.07 mol) using different proportions of **1** and PTSA similarly to the procedure described above for BN (Table 2).

The charged vessels were heated to 180 °C for 72 h. Yield of acetamide produced using only 0.1 mol% of [Ni(0)]: 3% (0.1461 g,

**Table 1**

| 1 | | | PTSA | | |
|---|---|---|---|---|---|
| m (g) | n (mmol) | mol% of [Ni(0)] | m (g) | n (mmol) | mol% of PTSA |
| 0.0139 | 0.022 | 0.1 | 0.0098 | 0.052 | 0.1 |
| 0.0139 | 0.022 | 0.1 | 0.0372 | 0.196 | 0.4 |
| 0.0016 | 0.002 | 0.01 | 0.0038 | 0.020 | 0.04 |
| 0.0624 | 0.097 | 0.4 | – | – | – |
| 0.0624 | 0.097 | 0.4 | 0.0372 | 0.196 | 0.4 |

**Table 2**

| 1 | | | PTSA | | |
|---|---|---|---|---|---|
| m (g) | n (mmol) | mol% of [Ni(0)] | m (g) | n (mmol) | mol% of PTSA |
| 0.0301 | 0.047 | 0.1 | – | – | – |
| 0.0301 | 0.047 | 0.1 | 0.0188 | 0.099 | 0.1 |
| 0.0301 | 0.047 | 0.1 | 0.0723 | 0.380 | 0.4 |
| 0.1250 | 0.194 | 0.4 | – | – | – |
| 0.1250 | 0.194 | 0.4 | 0.0723 | 0.380 | 0.4 |

0.0025 mol) with a TON of 27 and a TOF of 0.4 cycles/h. Yield of acetamide produced using the 0.1:0.1 proportion of {[Ni(0)]:PTSA}: 66% (3.7399 g, 0.0633 mol) with a TON of 673 and a TOF of 9 cycles/h. Yield of acetamide produced using the 0.1:0.4 proportion of {[Ni(0)]:PTSA}: 55% (3.1170 g, 0.0528 mol) with a TON of 561 and a TOF of 8 cycles/h. Yield of acetamide produced using only 0.4 mol% of [Ni(0)]: 12% (0.6801 g, 0.0115 mol) with a TON of 30 and a TOF of 0.4 cycles/h. Yield of acetamide produced using the 0.4:0.4 proportion of {[Ni(0)]:PTSA}: 76% (4.2917 g, 0.0727 mol) with a TON of 186 and a TOF of 3 cycles/h. m.p. of acetamide: 78–80 °C. NMR spectra for acetamide in CDCl$_3$, $^1$H: $\delta$ (ppm) 5.72 (br s, 1H, NH), 5.53 (br s, 1H, NH), 1.95 (s, 3H, CH$_3$). $^{13}$C{$^1$H}: $\delta$ (ppm) 173.7 (s, carbonyl), 22.80 (s, CH$_3$).

### 2.6.5. Catalytic hydration of AdN using [Ni(0)] and PTSA

A vessel was charged with AdN (5 mL, 0.045 mol), water (1.6 mL, 0.09 mol), **1** (0.0279 g, 0.043 mmol; 0.1 mol% of [Ni(0)]) and PTSA (0.0669 g, 0.350 mmol; 0.4 mol% of PTSA), which resulted in the immediate formation of a red solution after mixing. The vessel was heated in a mantle to 230 °C for 24 h. Only adipamide was obtained in this experiment. Yield of adipamide: 60% (3.8331 g, 0.0316 mol) with a TON of 614 and a TOF of 26 cycles/h.

### 2.6.6. Catalytic hydration of SuN using [Ni(0)] and PTSA

A vessel was charged with SuN (5 g, 0.06 mol), water (2.2 mL, 0.12 mol),), **1** (0.0403 g, 0.063 mmol; 0.1 mol% of [Ni(0)]) and PTSA (0.0933 g, 0.490 mmol; 0.4 mol% of PTSA). The vessel was heated to 140 °C for a period of 24 h. Complete conversion of SuN into the carbonaceous solid was observed (6.5317 g), accompanied by extensive formation of NH$_{3(g)}$.

### 2.6.7. Catalytic hydration of BN using $NiCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$/PTSA

Vessels were charged in separate runs with BN (5 mL, 0.05 mol), water (1.25 mL, 0.07 mol) and $NiCl_2 \cdot 6H_2O$ (0.0097 g, 0.041 mmol; 0.1 mol% of [Ni(II)]) both in the absence and in the presence of PTSA (0.0381 g, 0.2 mmol; 0.4 mol% of PTSA). The vessels were heated to 180 °C for 24 h. Yield of benzamide produced using 0.1 mol% of $NiCl_2 \cdot 6H_2O$: 12% (0.6883 g, 0.0057 mol) with a TON of 140 and a TOF of 2 cycles/h. Yield of benzamide produced using the combined 0.1:0.4 mol% of $NiCl_2 \cdot 6H_2O$ and PTSA: 21% (1.2233 g, 0.0101 mol) with a TON of 246 and a TOF of 3 cycles/h.

### 2.6.8. Catalytic hydration of BN using [(dippe)NiCl$_2$] and [(dippe)NiCl$_2$]/PTSA

Vessels were charged in separate runs with BN (5 mL, 0.05 mol), water (1.25 mL, 0.07 mol) and [(dippe)NiCl$_2$] (0.0152 g, 0.039 mmol; 0.1 mol% of [Ni(II)]) both in the absence and in the presence of PTSA (0.0381 g, 0.2 mmol; 0.4 mol% of PTSA). The vessels were heated to 180 °C for 24 h. Yield of benzamide produced using 0.1 mol% of [(dippe)NiCl$_2$]: 4% (0.2183 g, 0.0018 mol) with a TON of 46 and a TOF of 1 cycles/h. Yield of benzamide produced using the combined 0.1:0.4 mol% of [(dippe)NiCl$_2$] and PTSA: 34% (2.0117 g, 0.0166 mol) with a TON of 437 and a TOF of 6 cycles/h.

**Table 3**
Distinctive $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR of compounds **2** and **3**.

| Compound | $^{31}P\{^1H\}$ | | $^{13}C\{^1H\}$ | |
|---|---|---|---|---|
| | | | $\eta^2$-Bound-CN | Unbound-CN |
| 2 | 84.4 (*br d*, $^2J_{P–P}$ = 68 Hz) | 70.1 (*br d*, $^2J_{P–P}$ = 68 Hz) | 164.6 (*dd*, $J_1$ = 29 Hz, $J_2$ = 9 Hz) | 119.3 (*s*) |
| 3 | 80.5 (*br d*, $^2J_{P–P}$ = 74 Hz) | 65.9 (*br d*, $^2J_{P–P}$ = 74 Hz) | 165.7 (*dd*, $J_1$ = 25.5 Hz, $J_2$ = 9.5 Hz) | 120.3 (*s*) |

**Table 4**
Hydration of AdN using nickel(0).

| Entry | $T$ (°C) | $t$ (h) | mol% | 5-Cyanovaleramide (%) | Adipamide (%) | Carbonaceous by-products | Conv. (%)[a] | TON[b] | TOF (TON/h) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 150 | 24 | 0.04 | 9 | 0 | No | 9 | 101 | 4 |
| 2 | 180 | 24 | 0.04 | 25 | 0 | No | 25 | 290 | 12 |
| 3 | 230 | 24 | 0.02 | 14 | 47 | No | 61 | 2738 | 114 |
| 4 | 230 | 36 | 0.02 | 29 | 49 | No | 78 | 3203 | 89 |
| 5 | 260 | 12 | 0.02 | 0 | 0 | Yes | 100 | – | – |

[a] All experiments performed at the stoichiometric proportion of substrates (i.e., 26% volume of water).
[b] TON = {[(mol of 5-cyanovaleramide) × (1 $H_2O$)] + [(mol of adipamide) × (2 $H_2O$)]}/[mol of [Ni(0)].

**Table 5**
Hydration of SuN using nickel(0).

| Entry | $T$ (°C) | $t$ (h) | mol% | Succinamide (%) | Succinimide (%) | Carbonaceous by-products | Conv. (%)[a] |
|---|---|---|---|---|---|---|---|
| A | 120 | 24 | 0.01 | 0 | 0 | No | 0 |
| B | 140 | 24 | 0.01 | 0.4 | 0.6 | Yes | ~5 |
| C | 140 | 72 | 0.01 | 0.4 | 3.4 | Yes | 100 |
| D | 160 | 24 | 0.01 | 0 | 0 | Yes | 100 |
| E | 230 | 0.4 | 0.01 | 0 | 0 | Yes | 100 |

[a] All experiments performed at the stoichiometric proportion of substrates (i.e., 31% volume of water).

## 3. Results and discussion

### 3.1. Catalytic hydration of dicyanoalkanes using nickel(0)

The catalytic hydration of dicyanoalkanes was undertaken using stainless steel reactor vessels. Both substrates react readily with [(dippe)NiH]$_2$ (**1**) at room temperature. The use of 2 equiv. of the corresponding dicyanoalkane in THF yielded monocoordinated nickel(0) species of the type [(dippe)Ni{$\eta^2$-*N*,*C*–(CH$_2$)$_n$–CN}] ($n$ = 2, 4; compounds **2** and **3**, Eq. (1)) [8i,k,l].

functions yielded doublet-of-doublets (*dd*) in these spectra, considerably deshielded from the chemical shifts of the –CN functions in the free substrates ($\delta \sim 117$ for free SuN *vs.* $\delta$ 164 in **2**, and $\delta \sim 119$ for free AdN *vs.* $\delta$ 165.7 in **3**). The unbound-CN functions appeared as singlets slightly shifted from those of the free substrates and thus, confirmed the two dicyanoalkanes to coordinate by only end to [(dippe)Ni$^0$].

In terms of their relevance for the hydration reactions we envision the catalytic processed to occur by intermediacy of such compounds in their neat solutions, similarly to what was observed
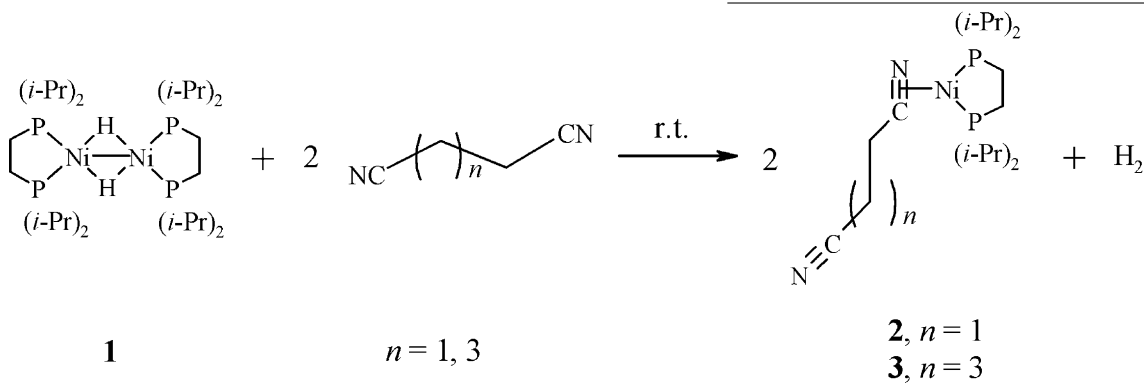


$$\textbf{2}, n = 1$$
$$\textbf{3}, n = 3 \tag{1}$$

Table 3 displays the main distinctive $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR features of the obtained compounds. The presence of asymmetric doublets of 68 and 74 Hz in their corresponding $^{31}P\{^1H\}$ NMR spectra corresponds to chemically un-equivalent phosphorus environments around the nickel atom, the magnitudes of the $^2J$(P,P) coupling constants for these doublets being characteristic of nickel(0) [8f,i,k,l].

The $^{13}C\{^1H\}$ NMR spectrum of each of the compounds showed signals for coordinated and uncoordinated nitrile moieties as expected for monometallic nickel(0) compounds with formula, [(dippe)Ni{$\eta^2$-*N*,*C*–(CH$_2$)$_n$–CN}] ($n$ = 2, 4). The coordinated-CN

for the related nickel(0) compounds, [(dippe)Ni($\eta^2$-*N*,*C*–R)] (R = –Ph,–Me) [8g] or [(dippe)Ni($\eta^2$-*N*,*C*-1,*n*-(CN)$_2$–benzene)] ($n$ = 2, 3, 4) [8f]. Tables 4 and 5 show the results obtained for these systems using compounds **2** and **3** as catalysts.

According to the results shown in these tables, the hydration process of the two cyanoalkanes is seemingly affected by the chain length. In the case of AdN, its hydration resulted in the gradual and progressive conversion of this substrate into 5–cyanovaleramide (NC–(CH$_2$)$_4$–C(O)NH$_2$) and adipamide (H$_2$NC(O)–(CH$_2$)$_4$–C(O)NH$_2$) as temperature was increased from 150 to 230 °C (entries 1–4, Table 4), whereas hydration of SuN was

achieved at a temperature as low as 140 °C although without selectivity for the diamide. No monoamide was observed either with the latter system and instead, extensive formation of carbonaceous material (C content ∼43%) was systematically observed. Formation of the by-product was accompanied by the evolution of ammonia during catalysis from that temperature (140 °C), whose amount was observed to increase to complete conversion of SuN at higher temperatures (entries B–E, Table 5). Carbonization resulting from AdN hydration was not observed until heating to 260 °C (entry 5, Table 4). In the case of SuN, a minute amount of a mixture of succinamide and succinimide in a 0.4-to-0.6% ratio (∼5% conversion) was recovered from the system heated at 140 °C for 24 h (entry B, Table 5). Prolonged heating for 72 h at the same temperature (entry C, Table 5) did not increase the amount of succinamide and succinimide recovered from the mixture, although the ratio of the latter by-product did increase slightly to give a 0.4-to-3.4% ratio. The rest of the recovered material was carbonaceous suggesting complete conversion of SuN, which was rationalized as a competing process after hydration (vide infra). Contrasting with these observations, a poor 9% conversion into the monoamide intermediate, 5-cyanovaleramide (TON = 101, TOF = 4) was observed at 150 °C while attempting hydration of AdN (entry 1, Table 4). Even more so, formation of adipamide was not observed after heating the catalytic system at 180 °C, for a period of 24 h (entry 2, Table 4) either, unlike

to previously reported cases concerning hydration of mononitriles (BN and AN) [8g] or DCBs [8f], using nickel(0). As such, the results obtained with AdN show the more refractory nature of this system to undergo complete hydration.

Heating to 230 °C was required in order to promote the formation of adipamide, which was separated by solubility from a mixture of 5-cyanovaleramide and adipamide (entries 3 and 4). Heating the mixture for 24 h resulted in a 14:47 ratio of the latter products in 61% conv. whereas 36 h resulted in an increment of the monoamide intermediate only, maintaining the produced diamide percentage constant between the two experiments (29:49% ratio, 78% conv.). Heating to a higher temperature such as 260 °C did not result in improvement of the selectivity towards the diamide product leading instead to a complete conversion of AdN into carbonaceous material (see entry 5 of Table 4).

As rationalized, the results obtained for AdN hydration suggest that the second hydration step involving conversion of 5-cyanovaleramide to adipamide would appear as a more energetically demanding step unlike to the first one going from AdN to 5-cyanovaleramide. The latter however, may not be directly attributed to the energetics associated to the nucleophilic addition of water over the nitrile in the latter intermediate but to the increase in the polarity of the reaction media as it becomes enriched with it. In principle, this suggests that hydrogen bonding interactions
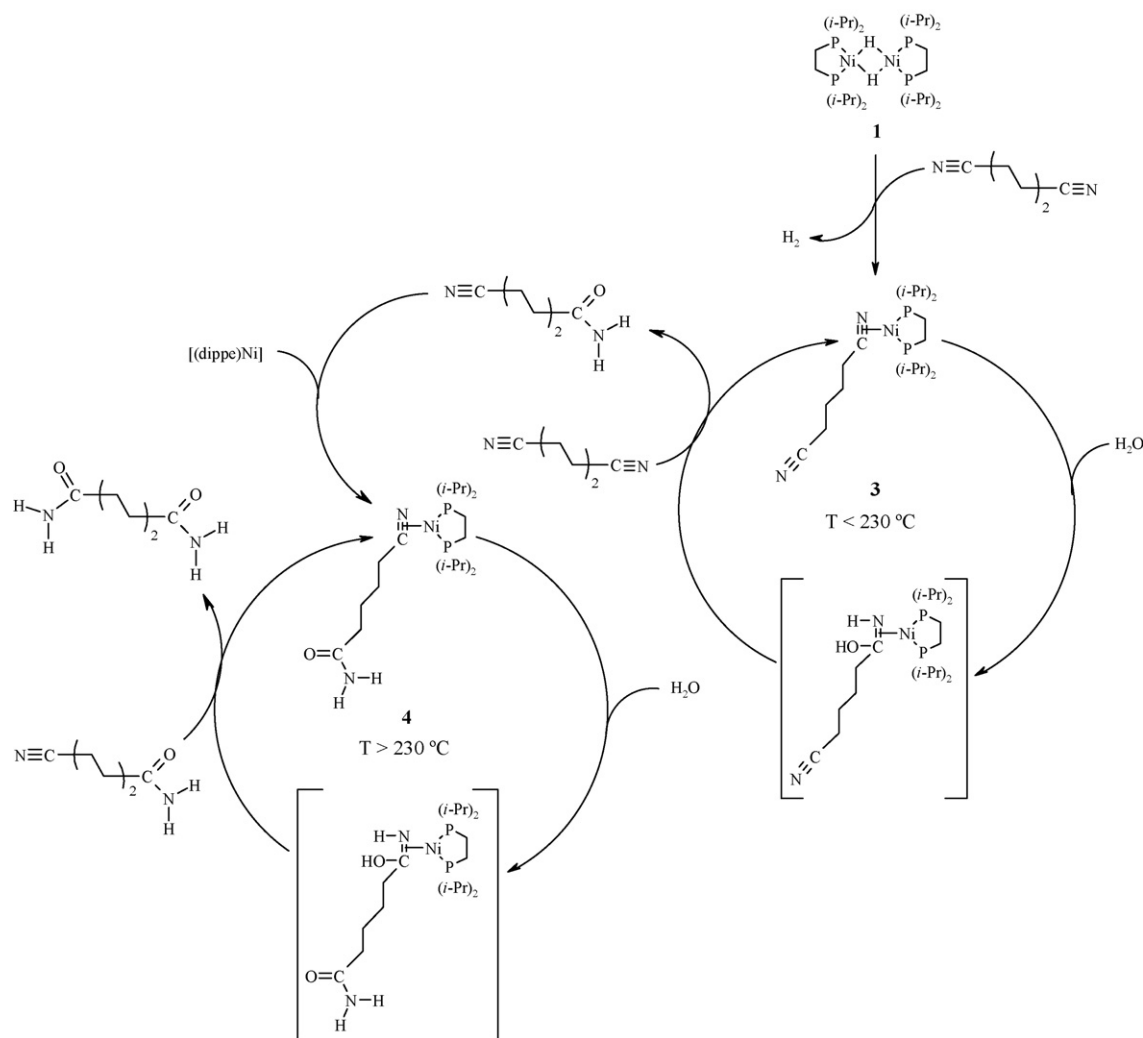


Scheme 1. Tentative mechanism for the catalytic hydration of AdN through consecutive cycles.
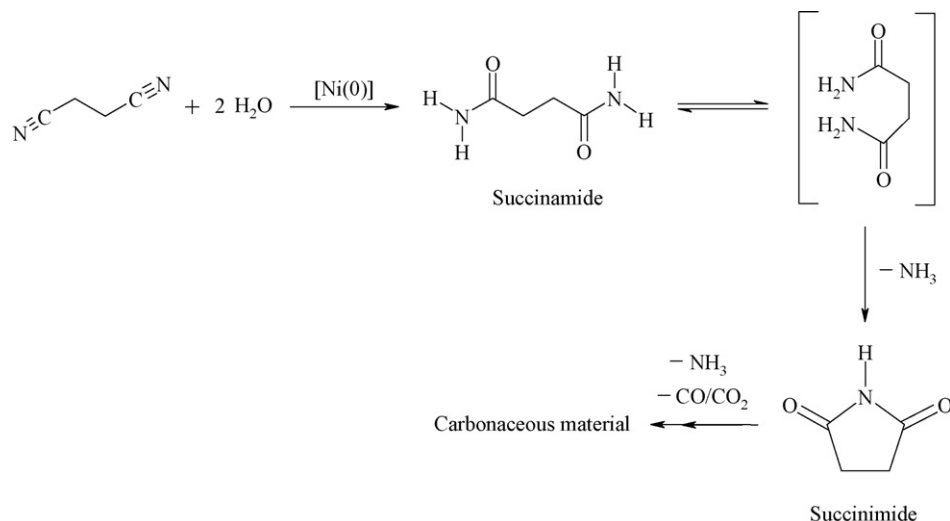
**Scheme 2.** Thermal degradation route proposed for succinamide ($T \geq 140\,°C$).

between unreacted water and the amido ends in the melt mixture could affect the kinetics of the process by changing the mass transfer constants making it look as a slower rate step. As a whole, these results point to a catalytic process that may occur through consecutive catalytic cycles, the second cycle of which is more favourably undergone at the higher temperature limit of $230\,°C$ (see Scheme 1).

The first cycle in Scheme 1 predicts the formation of 5-cyanovaleramide from AdN by a concerted *N,N*-dihydro-*C*-oxobiaddition of water to the *side-on* coordinated nitrile end of the dicyanoalkane in compound **3** (see Refs. [8g,f]) whereas the second cycle involves coordination of free 5-cyanovaleramide to a [(dippe)Ni$^0$] producing the nitrile-bound intermediate [(dippe)Ni($\eta^2$-*N,C*–(CH$_2$)$_4$–CONH$_2$)] (**4**). Nucleophilic addition of water to nitrile end in this compound ultimately leads to the formation of adipamide, which is accompanied by the regeneration of the catalyst.

An independent preparation of **4** was undertaken in the attempt of validating the latter proposal, using the nickel(I) dimer **1**. This was reacted with 5-cyanovaleramide in THF-*d$_8$* solution, which resulted in an immediate color change from deep red to yellow at room temperature. The formation of compound **4** was confirmed by NMR. Eq. (2) illustrates the reaction that takes place.

amido protons in the unbound-C(O)NH$_2$ moiety appeared as singlets centered in $\delta = 6.85$ and 6.3.

In the case of SuN, it is possible that a similar process to the one proposed in Scheme 1 for AdN may also take place, producing 3-cyanopropanamide from a first cycle and succinamide from a second one. These processes are expected to occur however, at considerably lower temperatures from the ones required to promote hydration of AdN according to data in Tables 4 and 5 and thus, it is likely that the apparently lower energy demand for the SuN system to undergo the same process is affected by its shorter chain length. The readiness by which the diamide product undergoes cyclization is apparently an important issue for this system, rapidly degrading the product mixture while increasing the rate of hydration as well. The latter is reflected in the fact that no selectivity towards the monoamide (3-cyanopropanamide) was observed and was only very poorly expressed in the traces of succinamide and the cyclized by-product succinimide that could be recovered from the bulk carbonaceous by-product. Moreover, the relative ratio of succinamide was depleted over time while heating the mixture for 72 h as opposed to 24 h (entries B and C of Table 5) and thus, a conclusion concerning cyclization as a key step for the product degradation can be drawn. If so, the facility by which the competing degradation



(2)
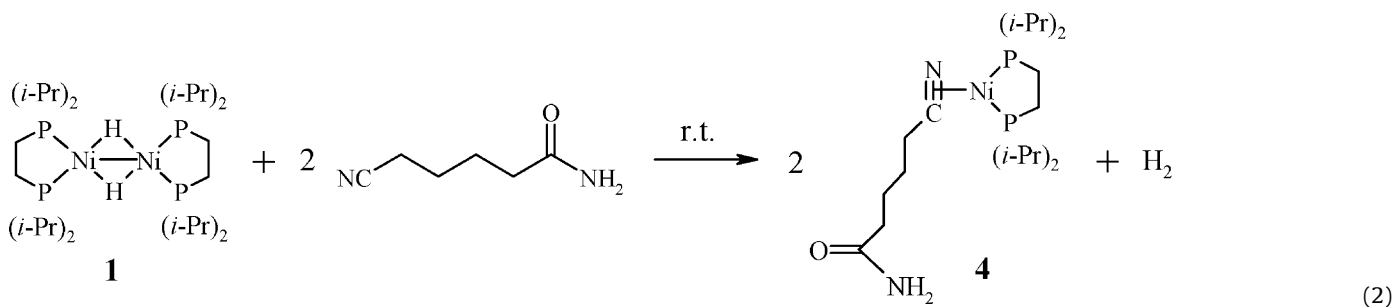
Compound **4** displayed two broad asymmetric doublets at 81.2 and 66.6 ppm in the $^{31}$P{$^1$H} NMR spectrum, with $^2J$(P,P) of 74.5 Hz, as expected for a nickel(0) compound. In the $^{13}$C{$^1$H} NMR spectrum, the same exhibited a broad *dd* at 169.2 ppm ($J_1 = {}^2J_{C-P\text{-}trans} = 19.3$ Hz, $J_2 = {}^2J_{C-P\text{-}cis} = 8.3$ Hz) which was attributed to the $\eta^2$-coordinated nitrile end, whereas the carbonyl moiety yielded a sharp singlet at $\delta = 177.5$, only slightly deshielded from the corresponding chemical shift of the free substrate ($\delta = 176.7$). The $^1$H NMR spectrum led to the same conclusion, as the un-equivalent

route affect catalysis is indeed dictated by the chain length of the dicyanoalkane or its resulting diamide, which in the case of SuN leads to the more stable 5-membered intermediate, succinimide. In the case of AdN hydration, the cyclization of adipamide is expected to lead to a less stable 7-membered ring (adipimide) and thus, a higher energy degradation route ($T \geq 230\,°C$) is proposed. It is worth to note that the stability gained by cyclization in the case of succinamide overcomes the rate limitations that may have been attributed to hydrogen bonding during the second cat-
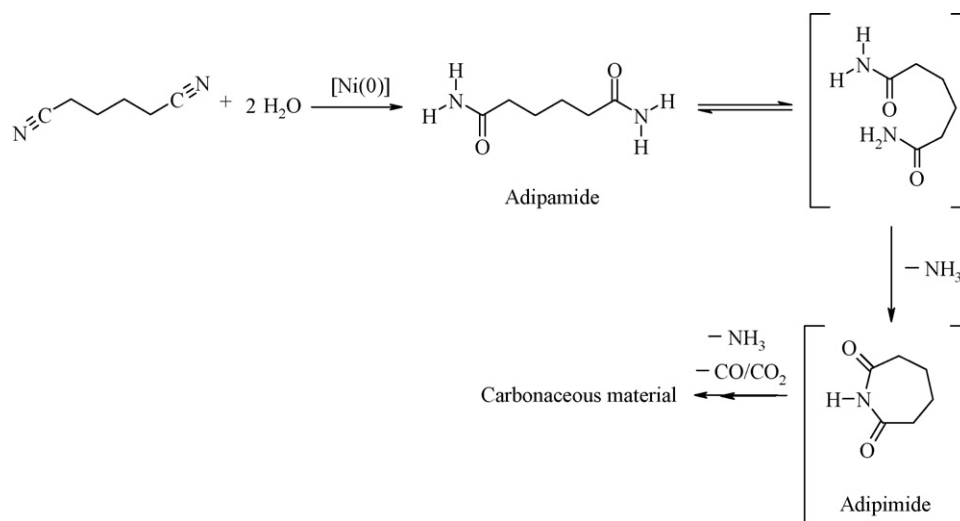
**Scheme 3.** Thermal degradation route proposed for adipamide ($T \geq 230\,^\circ C$).
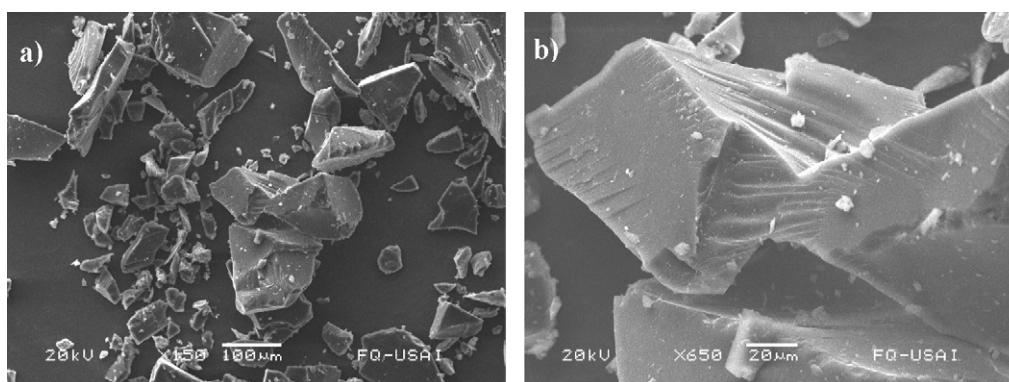


**Fig. 1.** SEM images obtained from the carbonaceous by-product obtained from the AdN hydration process at (a) 100 μm and (b) 20 μm.

alytic cycle if that were to occur as proposed for AdN hydration. The stabilization gained would be expected to be quite large as no 3-cyanopropanamide was recovered in any experiment involving SuN hydration as opposed to formation of 5-cyanovaleramide in the case of AdN and complete degradation of the succinamide was observed even at 140 °C.

In either case, cyclizations of the diamides are clearly envisaged as the key steps leading to product decomposition similarly to what has been reported for polyamide degradation routes [17,18]. Schemes 2 and 3 illustrate these conclusions.

The carbonaceous by-product obtained from AdN experiments was analysed by scanning electron microscopy (SEM). Selected micrographs are shown in Figs. 1 and 2.

### 3.2. Hydration of mono- and dinitriles using nickel(0) and PTSA

The use of p-toluenesulfonic acid (PTSA) as a potential co-catalyst for the hydration of nitriles was proposed under the hypothesis that the use of a Brønsted acid in solution could lead to protonation of the coordinated nitriles in nickel(0) compounds of the type [(dippe)Ni($\eta^2$-N,C–R)]  (R = –Ph,–Me,–(CH$_2$)$_2$–CN,–(CH$_2$)$_4$–CN) [19]. The hypothesis at hand presumed that as a result of such reaction the formation of cationic intermediates with formula [(dippe)Ni($\eta^2$-N(H),C–R)]$^+$[OPhMe]$^-$ with greater electrophilic character could take place, therefore making the nucleophilic addition of water to the protonated nitrile

moiety more favourable. PTSA was selected as the Brønsted acid for these experiments, envisioned as a robust and inexpensive solid whose base was expected to be stable at the high temperature required for catalysis. An illustrated representation of the working hypothesis for the use of PTSA as a co-catalyst for the nitrile hydration reaction is presented in Scheme 4. Tables 6–8 summarize our findings when using the [Ni(0)]:PTSA system.

As is shown in these tables, the use of the combined catalyst/co-catalyst system {[Ni(0)]:PTSA} maximized the catalytic activity with all the substrates. In the case of BN, the use of a 0.1:0.4 mol% of {[Ni(0)]:PTSA} yielded 92% conversion of this substrate into benzamide (TON = 1078, TOF = 15; entry 8) as opposed to the sole use of 0.1 mol% of [Ni(0)], which had permitted a maximum conversion of 19% (TON = 153, TOF = 2; entry 4) [8g]. The same conclusion was drawn for AN hydration for which the use of the same catalyst/co-catalyst ratio permitted to increase the conversion of this substrate from 3 o 55% (entries A and B).

As encountered, the catalytic hydrations were seemingly affected by the [Ni(0)]-to-PTSA ratio present in the mixture. The best results obtained for BN hydration was achieved while using either a 0.1:1.0 or a 0.1:0.4 mol% ratios of {[Ni(0)]:PTSA} (entries 7–8 of Table 6) whereas in the case of AN the use of 0.1:0.1 (66% conv., entry C) or 0.1:0.4 mol% ratio of {[Ni(0)]:PTSA} (55% conv. entry B) both gave good results, in fact better than any of the previous ones in which only [Ni(0)] had been used (see Ref. [8g]). In

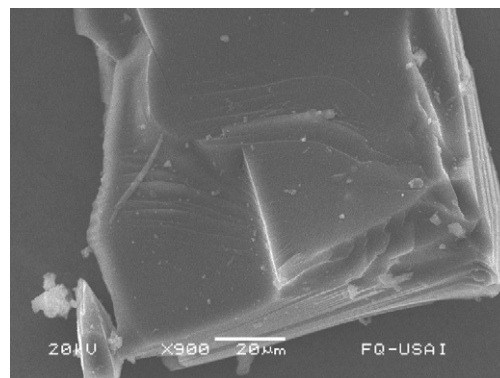**Scheme 4.** Proposal for the hydration of nitriles using nickel(0) and PTSA.
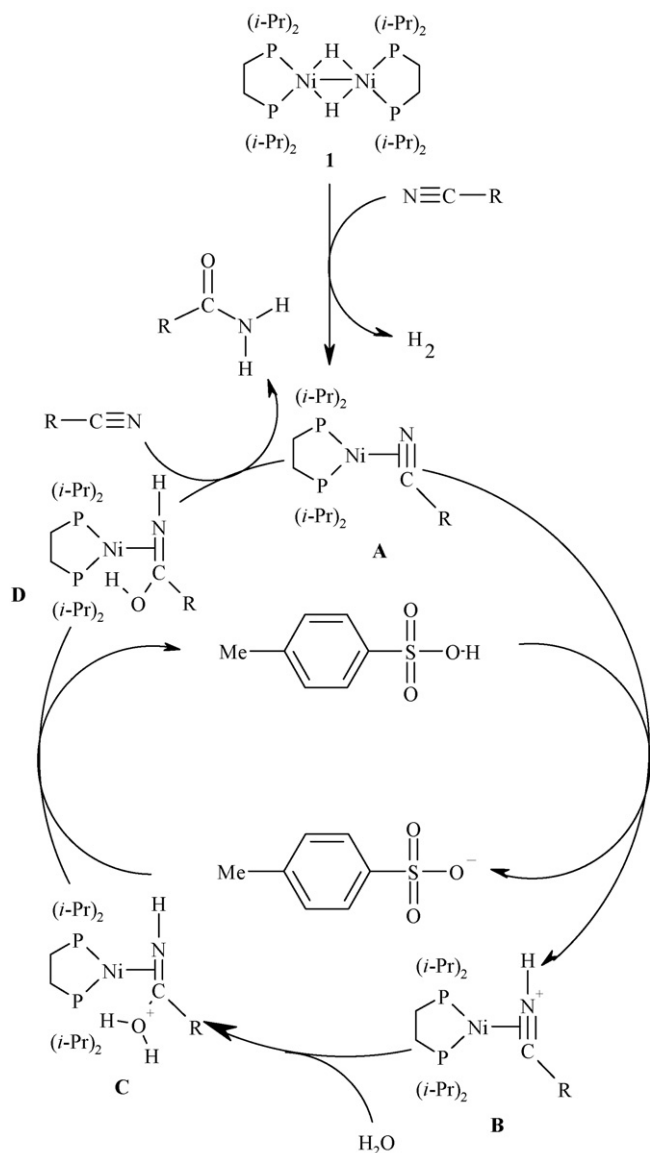


**Fig. 2.** SEM image of the carbonaceous material showing a laminar graphite-like residue (20 μm scale).

the case of AdN, 60% conv. with complete selectivity to adipamide was achieved at the same mol ratio of {[Ni(0)]:PTSA}, also showing a significant improvement in catalytic activity (entry I of Table 8). In the case of SuN, the use of the combined {[Ni(0)]:PTSA} system resulted in complete conversion of the substrate to the carbonaceous by-product after 24 h heating at 140 °C (entry II). In this case, the result shows that although a relatively greater reactivity may be gained as a result of the use of the co-catalyst, the lack of selectivity to the diamide product continued to be a major issue.

### 3.3. Hydration of BN using nickel(II) compounds

Additional to the previous reactivity studies, experiments using the nickel(II) compounds $NiCl_2 \cdot 6H_2O$ and $[(dippe)NiCl_2]$ as catalyst precursors for the hydration of BN were conducted both in the absence and presence of PTSA. The experiments were performed on the basis of the large amount of existing literature that suggests that the nitrile hydration reaction is more favourably undergone when metals in high oxidation states are used [2]. Table 9 summarizes our findings.

The results show that neither $NiCl_2 \cdot 6H_2O$ nor $[(dippe)NiCl_2])$ promote a significant conversion of BN to benzamide at 180 °C when using 0.1 mol% loadings of these compounds (entries A and C). Also, conversions are smaller than the one obtained when using [Ni(0)] at the same catalyst loading (entry 4, Table 6) and remain low even in the presence of PTSA (entries B and D). From these however, the

**Table 6**
Catalytic hydration of BN using nickel(0) and PTSA.

| No. | $T$ (°C) | $T$ (h) | [Ni(0)] (mol%) | PTSA (mol%) | Conv. (%)[a] | TON[b] | TOF (TON/h) |
|---|---|---|---|---|---|---|---|
| 1 | 180 | 24 | – | – | 0 | – | – |
| 2 | 160 | 24 | – | 1.0 | 3 | 3 | 0.1 |
| 3 | 180 | 24 | – | 1.0 | 11 | 10 | 0.4 |
| 4* | 180 | 72 | 0.1 | – | 19 | 153 | 2 |
| 5 | 160 | 24 | 0.1 | 1.0 | 18 | 215 | 9 |
| 6 | 180 | 24 | 0.1 | 1.0 | 38 | 442 | 18 |
| 7 | 180 | 72 | 0.1 | 1.0 | 72 | 859 | 12 |
| 8 | 180 | 72 | 0.1 | 0.4 | 92 | 1078 | 15 |
| 9 | 180 | 72 | 0.1 | 0.1 | 22 | 224 | 3 |
| 10 | 180 | 72 | 0.4 | – | 9 | 22 | 0.3 |
| 11 | 180 | 72 | 0.4 | 0.4 | 26 | 64 | 1 |
| 12* | 180 | 72 | 0.01 | – | 13 | 1350 | 19 |
| 13 | 180 | 72 | 0.01 | 0.04 | 11 | 1141 | 16 |

[a] All experiments performed at the stoichiometric proportion of substrates (i.e., 20% volume of water.).

[b] TON = [(mol of benzamide) × (1 $H_2O$)]/[mol of [Ni(0)].

* From Ref. [8g].

**Table 7**
Catalytic hydration of AN using nickel(0) and PTSA.

| No. | $T(^\circ C)$ | $t$ (h) | [Ni(0)] (mol%) | PTSA (mol%) | Conv. (%)[a] | TON[b] | TOF (TON/h) |
|---|---|---|---|---|---|---|---|
| A | 180 | 72 | 0.1 | – | 3 | 27 | 0.4 |
| B | 180 | 72 | 0.1 | 0.4 | 55 | 561 | 8 |
| C | 180 | 72 | 0.1 | 0.1 | 66 | 673 | 9 |
| D | 180 | 72 | 0.4 | – | 12 | 30 | 0.4 |
| E | 180 | 72 | 0.4 | 0.4 | 76 | 186 | 3 |

[a] All experiments performed at the stoichiometric proportion of substrates (i.e., 20% volume of water).
[b] TON = [(mol of acetamide) × (1 $H_2O$)]/[mol of [Ni(0)].

**Table 8**
Catalytic hydration of AdN (entry I) and SuN (entry II) using nickel(0) and PTSA.

| No. | $T(^\circ C)$ | $t$ (h) | [Ni(0)] (mol%) | PTSA (mol%) | Water vol. (%) | Conv. (%) | TON | TOF (TON/h) |
|---|---|---|---|---|---|---|---|---|
| I | 230 | 24 | 0.1 | 0.4 | 24 | 60[a] | 614[c] | 26 |
| II | 140 | 24 | 0.1 | 0.4 | 31 | 100[b] | – | – |

[a] Only adipamide was obtained.
[b] Only carbonaceous materials were obtained.
[c] TON = [(mol of adipamide) × (2 $H_2O$)]/[mol of [Ni(0)].

**Table 9**
Catalytic hydration of BN using nickel(II) compounds.

| No. | Catalyst system | $T(^\circ C)$ | $t$ (h) | [Ni(II)] (mol%) | PTSA (mol%) | Conv. (%)[a] | TON[b] | TOF (TON/h) |
|---|---|---|---|---|---|---|---|---|
| A | NiCl$_2$·6H$_2$O | 180 | 72 | 0.1 | – | 12 | 140 | 2 |
| B | NiCl$_2$·6H$_2$O/PTSA | 180 | 72 | 0.1 | 0.4 | 21 | 246 | 3 |
| C | [(dippe)NiCl$_2$] | 180 | 72 | 0.1 | – | 4 | 46 | 1 |
| D | [(dippe)NiCl$_2$]/PTSA | 180 | 72 | 0.1 | 0.4 | 34 | 437 | 6 |

[a] All experiments performed at the at the stoichiometric proportion of substrates (i.e., 20% volume of water.).
[b] TON = [(mol of benzamide) × (1 $H_2O$)]/[mol of [Ni(0)].

one using [(dippe)NiCl$_2$] in the presence of PTSA showed the higher values (entry D, Table 9) and as such, it points out the importance that the auxiliary ligand, dippe, has in catalysis.

## 4. Conclusions

The catalytic hydration of adipo and succinonitrile using [Ni(0)] catalysts was achieved under heating. The selectivity for the process was dependent on the length of the carbon chain and was severely affected by a competitive degradation route that led to both carbonization of the product and loss of ammonia. The degradation of the diamides was greatly favoured in the case of succinonitrile and was probably promoted by in situ cyclization of produced succinamide to form succinimide. The use of *p*-toluenesulfonic acid as co-catalyst for the hydration reaction of benzo, aceto and adiponitrile was also attempted in this work. The results showed its use to be beneficial for the purpose of increasing catalytic activity and conversion of these substrates whose amides were obtained in complete selectivity. Catalysis was maximized when using nickel(0) catalysts as opposed to nickel(II) compounds, thus showing the importance that the low oxidation state of the metal has in these catalytic systems.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.10.025.

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