



**HAL**  
open science

# Magnetically Induced Synthesis of Thermally Sensitive Molecules: Catalytic Amination of Aliphatic Alcohols with MNi@Cu (M = Fe, Co) Nanoparticles

Víctor Varela-Izquierdo, Irene Mustieles Marin, Pier-francesco Fazzini, Gabriel Mencia, Simon Guelen, Rabih Rachet, Bruno Chaudret

## ► To cite this version:

Víctor Varela-Izquierdo, Irene Mustieles Marin, Pier-francesco Fazzini, Gabriel Mencia, Simon Guelen, et al.. Magnetically Induced Synthesis of Thermally Sensitive Molecules: Catalytic Amination of Aliphatic Alcohols with MNi@Cu (M = Fe, Co) Nanoparticles. *Angewandte Chemie International Edition*, 2024, 63 (50), pp.e202412421. 10.1002/anie.202412421 . hal-04814666

**HAL Id: hal-04814666**

**<https://hal.science/hal-04814666v1>**

Submitted on 2 Dec 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Magnetically Induced Synthesis of Thermally Sensitive Molecules: Catalytic Amination of Aliphatic Alcohols with MNi@Cu (M = Fe, Co) Nanoparticles

Víctor Varela-Izquierdo,<sup>[a]</sup> Irene Mustieles-Marín,<sup>[a]</sup> Pier-Francesco Fazzini,<sup>[b]</sup> Gabriel Mencía,<sup>[a]</sup> Simon Guelen,<sup>[c]</sup> Rabih Rachet,<sup>[c]</sup> and Bruno Chaudret<sup>\*[a]</sup>

[a] Laboratoire de Physique et Chimie des Nano-Objets, Université de Toulouse, LPCNO, INSA, UPS, CNRS-UMR5215, 135 Avenue de Rangueil, 31077 Toulouse, France E-mail: chaudret@insa-toulouse.fr

[b] CEMES-CNRS, Université de Toulouse, CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France

[c] Specialty Operations France (a member of the Syensqo Group, spin-off of the Specialty activities of Solvay) - Research & Innovation Center of Lyon, Organic Chemistry and Process Development Dpt 85 avenue des Frères Perret - F - 69192 Saint-Fons Cedex - France

Supporting information for this article is given via a link at the end of the document.

**Abstract:** The synthesis of tertiary amines from alcohols (i.e. heptanol, dodecanol, cyclohexanol, benzylalcohol) and secondary amines (Me<sub>2</sub>NH (DMA), <sup>n</sup>Pr<sub>2</sub>NH, <sup>n</sup>Bu<sub>2</sub>NH) has been achieved in one step using trimetallic nanoparticles (NPs) displaying a magnetic core (Co<sub>4</sub>Ni<sub>6</sub> and Fe<sub>3</sub>Ni<sub>7</sub>) and a Cu shell as both catalysts and heating agent in the presence of an alternating magnetic field. This methodology limits the redistribution reactions occurring on amines at high temperature leading to both much higher conversion and selectivity in the absence of solvent than usually observed using conventional heating. Moreover, Co<sub>4</sub>Ni<sub>6</sub>@Cu NPs were found moisture resistant, thereby allowing for performing the reaction with commercial DMA in water (40 % wt) with again high conversion and selectivity.

Alkylated amines are important components of a variety of chemical compounds displaying applications as fungicides, pharmaceuticals, detergents, surfactants, agrochemicals, dyes, pesticides, and herbicides.<sup>i</sup> Thus, the synthesis of tertiary amines is of great importance for the chemical industry.<sup>ii</sup>

Alkylated amines are classically prepared from alkyl halides<sup>iii</sup> or alkyl sulfates<sup>iv</sup> which are toxic and at the origin of large environmental wastes. Therefore, there has been a growing interest in the development of sustainable strategies for synthesizing these compounds.<sup>v</sup> Among them, primary alcohol amination is a non-toxic alternative since water is the only stoichiometric by-product and since the reaction can be carried out in the absence of additional solvent. A metal catalyst is necessary to dehydrate the alcohol and generate *in situ* a more reactive carbonyl group in a borrowing hydrogen (BH) process, which is generally the rate-determining step (RDS).<sup>vi</sup> Regarding homogeneous catalysis, BH reactions have been developed using mainly Ru and Ir catalysts.<sup>vii,viii</sup> Conversely, copper<sup>ix</sup> appears as the best catalyst for heterogeneous amination although nickel<sup>x</sup> and ruthenium can also be employed.<sup>xi</sup> However, this strategy leads to high conversions but limited selectivity. Hence, one problem of alcohol amination is that at the temperature where the reaction occurs, side reactions are possible including amine redistributions.<sup>xii</sup>

We therefore turned to catalysts heated by magnetic induction. Thus, it has been shown that in such systems, the temperature at the surface of the catalyst is much higher than that of the surrounding solvent which could in principle allow the synthesis of thermally sensitive products.<sup>xiii</sup> Consequently, in recent years, promising results have been obtained due to the extremely localized, fast and highly energy efficient nature of this methodology which avoids heating the whole reactor. Magnetic nanoparticles (Mag-NPs) can produce heat when exposed to an alternating magnetic field (AMF) working at high frequency and can therefore act as both heat source and catalyst.<sup>xiv</sup> Furthermore, an additional catalytic layer can be deposited on Mag-NPs for addressing selected reactions.<sup>13, xv</sup> A few research groups including ours explored the magnetic activation of heterogeneous catalytic reactions in the gas phase.<sup>xvi</sup> Magnetic heating has however also been used in liquid phase reactions such as C–C coupling,<sup>xvii</sup> amide condensation,<sup>xviii</sup> and more recently in hydrogenation<sup>xix</sup> and hydrodeoxygenation reactions.<sup>13, 14b, xx, xxi</sup>

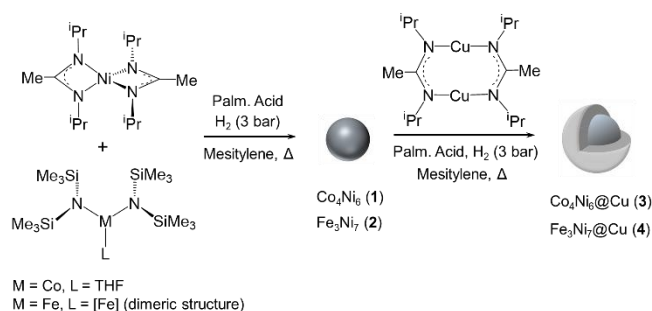
The selective synthesis of N,N-dialkyldodecylamine is an important target for the chemical industry which can be achieved by reaction of dodecylalcohol with secondary amines using a copper catalyst at high temperature (>150°C).<sup>9d</sup> However, Cu NPs have limited thermal stability and are prone to deactivation.<sup>9f,12</sup> Since we have previously found that magnetic induction could be beneficial for anchoring and stabilizing a catalytic metal on the surface of magnetic nanoparticles, this led us to perform alcohol amination under magnetic induction using Mag-NPs combining a magnetic core and a catalytic copper shell.<sup>xxii</sup> Related Mag-NPs, FeC<sub>2.2</sub>@Cu has recently been reported by Lin et al. to catalyse the selective hydrodeoxygenation (HDO) of aromatic aldehydes using magnetic induction heating.<sup>21</sup>

In this work, we have prepared highly active catalysts for alcohol amination using a metal alloy core composed of Co<sub>4</sub>Ni<sub>6</sub><sup>xxiii</sup> (1) or Fe<sub>3</sub>Ni<sub>7</sub> (2)<sup>xxiv</sup> and a Cu layer provided by a reaction of the NPs with an organometallic copper precursor. We show that under magnetic induction these Mag-NPs catalyse efficiently and selectively the synthesis of trialkylamines whereas in a classical procedure where the solution is uniformly heated at comparable temperature they lead to little conversion and a poorer selectivity.

## Results and Discussion

### Synthesis and characterization of the Cu catalyst

Copper-decorated  $\text{Co}_4\text{Ni}_6$  nanoparticles ( $\text{Co}_2\text{Ni}_3@Cu$ , **3**) were synthesized through a two-step organometallic approach (**Scheme 1**). First of all,  $\text{Co}_4\text{Ni}_6$  nanoparticles were prepared by reduction of  $\{\text{Ni}[\text{iPrNC}(\text{CH}_3)\text{N}^i\text{Pr}]\}$  and  $\{\text{Co}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})\}$  in the presence of palmitic acid, following a procedure recently reported in our group.<sup>23</sup> Then,  $\{\text{Cu}_2[\text{iPrNC}(\text{CH}_3)\text{N}^i\text{Pr}]_4\}$  was added to a colloidal suspension of  $\text{Co}_4\text{Ni}_6$  Mag-NPs in mesitylene. The resulting mixture was pressurized with hydrogen (3 bar) and heated first at 80°C for 3 h then at 120 °C for 24 h. The temperature was optimized in order to favour the decomposition of the Cu precursor at the surface of the  $\text{Co}_4\text{Ni}_6$  (heterogeneous nucleation) and to limit the homogeneous nucleation of Cu NPs in solution.



**Scheme 1.** Synthesis of Mag-NPs **3** and **4** with a Cu shell.

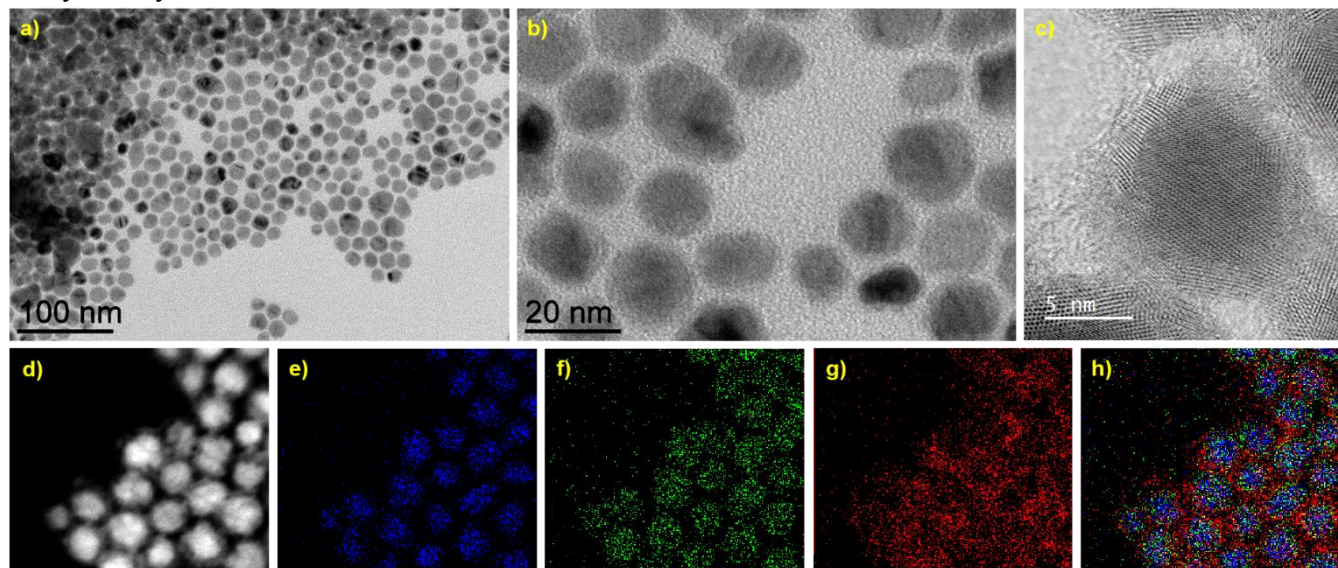
The  $\text{Co}_4\text{Ni}_6@Cu$  Mag-NPs were characterized by transmission electron microscopy (TEM) evidencing the presence of well-dispersed nanoparticles of ca. 18 nm (Figure 1a-b). On average, the copper containing NPs are slightly larger than the starting  $\text{Co}_4\text{Ni}_6$  NPs (ca. 15 nm) ones. Scanning transmission electron microscopy in high angle annular dark field (STEM-HAADF) at high resolution and STEM-HAADF with energy dispersive X-Ray spectroscopy (STEM-HAADF-EDX, Figure 1c-h) demonstrated the presence of an irregular layer of Cu decorating the  $\text{Co}_4\text{Ni}_6$  NPs.

A similar procedure (see ESI) leads to polydisperse  $\text{Fe}_7\text{Ni}_3@Cu$  Mag-NPs (Scheme 1) of 24 nm mean size and displaying an irregular copper shell with a  $\text{Fe}_7\text{Ni}_3$  core (ca. 17 nm) (ESI, Figure S4).

X-Ray diffraction (XRD) analysis of the materials evidenced the presence of *fcc* phases corresponding respectively to the CoNi and FeNi cores as well as the presence in both cases of *fcc* Cu (ESI, Figure S5). The magnetic properties of  $\text{Co}_4\text{Ni}_6@Cu$  and  $\text{Fe}_3\text{Ni}_7@Cu$  were measured using vibrating sample magnetometry (VSM) technique at 5 and 300 K (ESI, Figures S6 and S7). The saturation magnetization ( $M_s$ ) is in both cases close to 100 A. m<sup>2</sup>. kg<sup>-1</sup> for the starting Mag-NPs and reduced to 40-50 A.m<sup>2</sup>.kg<sup>-1</sup> after deposition of copper. At 300 K, the remaining magnetization ( $M_R$ ) of all NPs are found between 0 and 3 mT. The coercive field ( $H_c$ ) values measured at 5 K are respectively 69 and 41 mT for  $\text{Co}_4\text{Ni}_6$  and  $\text{Fe}_3\text{Ni}_7$  and are reduced to 20-30 mT upon copper deposition. (see ESI Table S1).

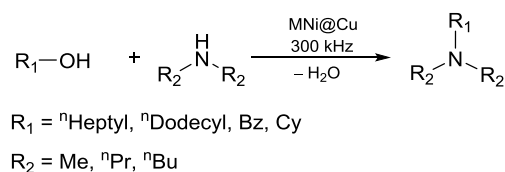
The Specific Absorption Rate (SAR) for Mag-NPs **3** and **4** at 93 kHz was lower than for pure  $\text{Co}_4\text{Ni}_6$  (323 W.g<sup>-1</sup> at 49 mT) or  $\text{Fe}_3\text{Ni}_7$  (600 W.g<sup>-1</sup> at 49 mT), reaching 46 and 47 W.g<sup>-1</sup> respectively at 49 mT (ESI, Figure S8). Upon deposition of non-magnetic materials, the overall heating efficiency decreases for the core-shell NPs as previously reported in our group.<sup>22,xxv</sup>

### Catalytic study



**Figure 1.** a-b) TEM images for  $\text{Co}_4\text{Ni}_6@Cu$  NPs (**3**, Mean size =  $18 \pm 3$  nm). c) HR-STEM micrograph of isolated NPs. The NPs exhibited a polycrystalline structure. d) STEM-HAADF image for  $\text{Co}_4\text{Ni}_6@Cu$ . e-f) Chemical mapping of  $\text{Co}_4\text{Ni}_6@Cu$  showing e) Ni in blue, f) Co in green, g) Cu in red, h) Overlapping Ni + Co + Cu.

The catalytic properties of  $\text{Co}_4\text{Ni}_6@\text{Cu}$  and  $\text{Fe}_3\text{Ni}_7@\text{Cu}$  were investigated for the reaction between terminal and secondary alcohols and secondary amines  $\text{R}_2\text{NH}$  ( $\text{R} = \text{Me}, {}^n\text{Pr}, {}^n\text{Bu}$ ) as substrates to prepare the corresponding tertiary amine using an AMF (Scheme 2).



**Scheme 2.** Alcohol amination reaction with alcohols and secondary amines. M = Co, Fe. Bz = benzyl, Cy = Cyclohexyl.

### Neat reactions with dibutyl- and dipropylamine

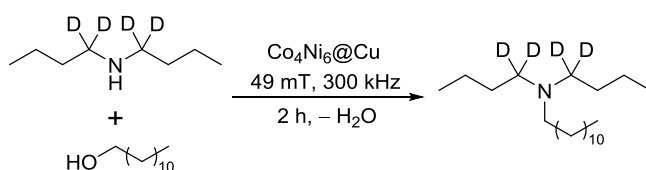
The reactions were first performed using dodecanol (5 mmol), dibutylamine (5 mmol), the catalyst (0 – 6 mol % of Cu), and the internal standard (dodecane, 1 or 5 mmol) in the absence of solvent and under an argon atmosphere. When the magnetic field was applied, the Mag-NPs reorganized to form chains along the magnetic field direction as previously observed.<sup>18c, 24</sup> In addition, some bubbles could be observed in the vicinity of the NPs. To determine the influence of the magnetic field on the catalytic process the reactions were carried out for 2 hours at 39 mT and 49 mT (Table 1, entries 3 and 4 respectively). In this context, the conversion increased at higher field without loss of selectivity. In addition, the temperature on the Fisher-Porter bottle external walls was measured using an IR camera.

Moreover, a drastic increase of conversion from 32% to >99% was obtained when the catalyst loading was tripled from 2 to 6 mol % of Cu at 49 mT (Table 1, entry 6). In this case, the mean temperature (151°C) and the reactor pressure increased through  $\text{H}_2$  formation as analysed by GC-MS. Thus, total conversion was achieved with 79% of selectivity for the desired product N,N-dibutyldodecanamine (DBDA). Two side products (N-butylidodecanamine, and N-butylidodecanamine) were obtained in low yield (8% and 13%, respectively).

In contrast, a poor selectivity was obtained when using  $\text{Co}_4\text{Ni}_6$  as catalyst (Table 1, entry 1) although the mean temperature recorded during the catalysis was 150 °C, similar to that observed with  $\text{Co}_4\text{Ni}_6@\text{Cu}$ . Thus, the reaction provided *inter alia* undecane, resulting from the decarbonylation of dodecanol.

In contrast, when using  $\text{Co}_4\text{Ni}_6@\text{Cu}$  and the same catalyst loading but under conventional heating at 115, 140 and 160 °C (Table 1, entries 7-9), poor yields and selectivities were obtained therefore demonstrating the interest of the magnetic induction technique.

Furthermore, in order to confirm the formation of DBDA (MS  $m/z$  calc. for  $\text{C}_{42}\text{H}_{43}\text{N}$  [ $M$ ]<sup>+</sup> 297.3395, found: 297.4411) and to dismiss the occurrence of any artefact, the reaction was performed with the dibutylamine- $d_4$ , deuterated mainly in  $\alpha$ -position in a 67% of yield (Scheme 3). The dibutylamine was deuterated by reaction with  $\text{D}_2$  (4 bars) in the presence of a Ru catalyst according to a procedure developed in our group<sup>xxvi</sup> and characterized by GC-MS and NMR (see SI, Figure S10). The reaction with dodecanol was analysed with the same GC-MS method and at the same retention time N,N-dibutyldodecanamine- $d_4$  was observed (MS  $m/z$  calc. for  $\text{C}_{42}\text{H}_{39}\text{D}_4\text{N}$  [ $M$ ]<sup>+</sup> 301.3395, found: 301.3883). This demonstrates that it is a simple reaction following the mechanism proposed.



**Scheme 3.** Alcohol amination reaction with dibutylamine- $d_4$ .

Similarly,  $\text{Fe}_3\text{Ni}_7@\text{Cu}$  Mag-NPs (**4**) were tested for this reaction (Table 1, entry 10). The magnetic field applied had to be increased up to 65 mT due to the lack of observation of bubbling in the vicinity of the NPs. The mean temperature recorded with the IR camera on the Fisher Porter external wall was 115 °C. Although lower yields were obtained the catalyst was found highly selective, and no side-products resulting from redistribution reactions were formed. As a result, after 8 hours reaction 43 % of conversion was obtained with total selectivity to DBDA (Table 1, entry 11).

**Table 1.** Catalytic experiments with dodecanol and dibutylamine.

Entry	Catalyst (M mol %)	Cu mol %	Mag. Field (mT)	Time (h)	Temp. <sup>a</sup> (°C)	Conv. (%)	Selec. (%)
-------	-----------------------	-------------	--------------------	-------------	----------------------------	--------------	---------------

1	<b>1</b> (4.3)	0	39	2	150	>99	60
2	<b>2</b> (4.3)	0	39	2	128	<1	-
3	<b>3</b> (4.3)	2.3	39	2	96	21	98
4	<b>3</b> (4.3)	2.3	49	2	107	32	97
5	<b>3</b> (4.3)	2.3	49	8	96	72	80
6	<b>3</b> (12.9)	6.8	49	3	151	>99	79
7 <sup>b</sup>	<b>3</b> (12.9)	6.8	-	3	115	<1	-
8 <sup>c</sup>	<b>3</b> (12.9)	6.8	-	3	140	<1	-
9 <sup>d</sup>	<b>3</b> (12.9)	6.8	-	3	160	34	82
10	<b>4</b> (4.3)	2.3	65	2	115	7	>99
11	<b>4</b> (4.3)	2.3	65	8	95	43	>99

Reaction conditions: 5 mmol of dodecanol/ dibutylamineamine, 1 mmol of dodecane (227  $\mu$ L, internal standard), neat, argon atmosphere, 300 kHz coil. [a] For magnetic induction heating: determined with IR camera on the Fisher-Porter external wall. [b] Conventional heating at 115  $^{\circ}$ C. [c] Conventional heating at 140  $^{\circ}$ C. [d] Conventional heating at 175  $^{\circ}$ C. Conversion (%) calculated with the remaining mmol of dodecanol. Selectivity was estimated with the relative areas of the obtained amines in the FID (GC-MS).

When dibutylamine was replaced by dipropylamine, using  $\text{Co}_4\text{Ni}_6@$ Cu NPs (**3**) as catalyst, the same conversion and selectivity towards the corresponding tertiary amine was obtained at the same reaction time and field applied (Table 2, Entry 1). Moreover, when dodecanol was substituted by heptanol in the same reaction conditions, up to 35% conversion at 39 mT led to 81% of selectivity to N,N-dibutylheptanamine (Table 2, Entry 2). Interestingly, the reaction also proved successful when benzylalcohol and dibutylamine were used, reaching 30% and 63% conversion at 39 and 49 mT, respectively (Table 2, Entries 3 and 4). Furthermore, stoichiometric reactions with cyclohexanol and dibutylamine also produced dibutylcyclohexanamine (Table 2, Entry 5). It is worth noting that the corresponding aldehyde and ketone were observed in the reaction mixture highlighting the oxidising role of the catalyst. However, no conversion was observed in the reaction with 2-dodecanol with the maximum power of the inductor (65 mT). Nevertheless, these results indicate that the amination process may be extended to other alcohols and/or secondary amines.

**Table 2.** Catalytic experiments with various alcohols and amines

Entry	Alcohol	Amine	Mag. Field (mT)	Temp. <sup>a</sup> ( $^{\circ}$ C)	Conv. (%)	Selec. (%)
1	dodecanol	<sup>n</sup> Pr <sub>2</sub> NH	39	105	25	>99
2	heptanol	<sup>n</sup> Bu <sub>2</sub> NH	39	103	35	81
3	Benzylalcohol	<sup>n</sup> Bu <sub>2</sub> NH	39	107	30	85
4	Benzylalcohol	<sup>n</sup> Bu <sub>2</sub> NH	49	115	63	61
5	Cyclohexanol	<sup>n</sup> Bu <sub>2</sub> NH	49	109	56	45
6	2-dodecanol	<sup>n</sup> Bu <sub>2</sub> NH	65	-	<1	-

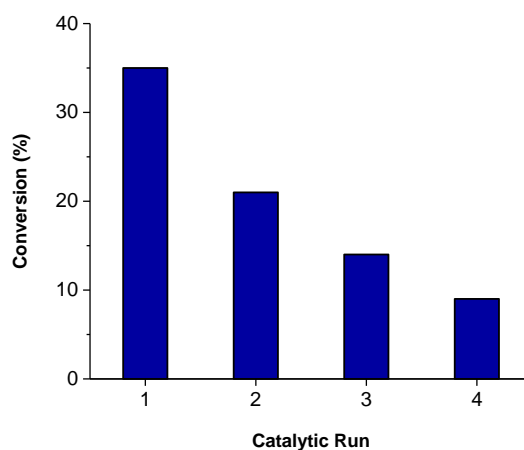
Reaction conditions: 5 mmol of alcohol/ amine, 1 mmol of dodecane (227  $\mu$ L, internal standard),  $\text{Co}_4\text{Ni}_6@$ Cu (**3**, 15 mg, 2.3 mol % Cu), neat, argon atmosphere, 2 h, 300 kHz coil. [a] Temperature determined with IR camera on the Fisher-Porter external wall. Conversion (%) calculated with the remaining mmol of dodecanol. Selectivity was estimated with the relative areas of the obtained amines in the FID (GC-MS).

In order to understand the role of the various reaction was first carried out under a hydrogen atmosphere. Typically, the reactor was loaded with 3 bars of H<sub>2</sub> leading to less conversion but similar selectivity to DBDA after 2 h reaction with 2 mol % Cu of **3**. This result was expected as the first step of the proposed mechanism is the dehydrogenation of alcohol into an aldehyde.

Then, dodecanal and dibutylamine were mixed in a round bottom flask in absence of catalyst leading selectively to N,N-dibutyldodecenamine at room temperature (ESI, Figure S26).

Reusability tests were performed with Co<sub>4</sub>Ni<sub>6</sub>@Cu using reaction conditions that afford almost quantitative selectivity to the desired product. A notable constant loss of conversion was observed for every run (about 40% decrease in activity, Figure 3). However, the selectivity was maintained above 98% (ESI, Table S4). TEM analysis of the particles has also been recorded after the fourth catalytic cycle. The images show partial agglomeration of the NPs which keep a mean size near 18 nm. Furthermore, no significant changes of the peaks position and linewidth were observed in the XRD analyses. (ESI, Figure S32).

To improve the recyclability of the catalyst, Co<sub>4</sub>Ni<sub>6</sub>@Cu nanoparticles were supported on either Al<sub>2</sub>O<sub>3</sub> or mesoporous carbon (C<sub>mes</sub>). However, the Co<sub>4</sub>Ni<sub>6</sub>@Cu/Al<sub>2</sub>O<sub>3</sub> catalyst did not exhibit good catalytic activity despite increasing the power of the coil up to 60 mT. Only a 17% conversion rate with total selectivity to DBDA was obtained. Regrettably, this catalyst became totally deactivated after the first catalytic run. In contrast, Co<sub>4</sub>Ni<sub>6</sub>@Cu/C<sub>mes</sub> demonstrated a better catalytic activity (up to 29% conversion) at 60 mT but with a lower selectivity (65%). Subsequently, the catalytic activity decreased in the following runs (24%, 14%, and 3%) with total selectivity to DBDA.



**Figure 3.** Recycling experiments of model reaction. Evolution of the catalyst activity in four catalytic runs with Mag-NPs **3**. Reaction conditions: 5 mmol of dodecanol/ dibutylamine, 1 mmol of dodecane (227  $\mu$ L, internal standard), Co<sub>4</sub>Ni<sub>6</sub>@Cu (**3**, 15 mg, 2.3 mol % Cu), neat, argon atmosphere, 2 h, 49 mT (300 kHz coil).

### Reactions in solution with DMA

Due to the unavailability of pure DMA, the reactions with dimethylamine were carried out with the corresponding solutions in water or THF. Alcohol amination reaction with DMA in water (40 wt%) and under magnetic heating was studied using Co<sub>4</sub>Ni<sub>6</sub>@Cu (**3**) under the conditions previously described. After 2 hours reaction at 49 mT with 6 mol % of Cu, 39 % conversion with total selectivity to N,N-dimethyldodecanamine (DMDA) was observed (Table 3, entry 1). A mean temperature of 110 °C was recorded with the IR camera due to the presence of a high water content in the reaction medium, which results in a lowering of the average temperature of the reaction. Thus, total conversion was reached after 8 hours (Table 3, entry 2). It is noteworthy that the pressure increased during the reaction due to the release of the amino reagent into the gas phase.

**Table 3.** Catalytic runs with DMA

Entry	Solvent	Cu mol %	Mag. Field (mT)	Time (h)	Temp. <sup>a</sup> (°C)	Conv. (%)	Selec. (%)
1	H <sub>2</sub> O	6.8	49	2	110	39	>99
2	H <sub>2</sub> O	6.8	49	8	95	>99	87
3 <sup>b</sup>	H <sub>2</sub> O	4.6	39	12	108	92	92

4	THF	6.8	49	2	120	33	>99
5	THF	6.8	49	8	120	82	95
6 <sup>c</sup>	THF	6.8	49	8	112	27	>99
7 <sup>d</sup>	THF	6.8	49	8	120	96	97

Reaction conditions: 5 mmol of dodecanol/ DMA (40 wt % in water or 2.5 M in THF), 1 mmol of dodecane (227  $\mu$ L, internal standard), argon atmosphere, Co<sub>4</sub>Ni<sub>6</sub>@Cu (**3**, 45 mg, 6.8 mol % Cu), 300 kHz coil. [a] For magnetic induction heating: determined with IR camera on the Fisher-Porter external wall. [b] Entry 3: Co<sub>4</sub>Ni<sub>6</sub>@Cu (**3**) (30 mg, 4.6 mol % Cu). [c] Reaction with an excess of amine (alcohol: amine, 1:1.5). [d] Reaction with excess of alcohol (alcohol: amine, 1.5:1). Conversion (%) calculated with the remaining mmol of dodecanol. Selectivity calculated with mmol of N,N-dimethyldodecanamine formed.

In order to increase the selectivity of the reaction, the catalyst loading was decreased to 4.6 mol % of Cu (30 mg of **3**), leading after 12 hours to 92 % conversion and 92 % selectivity (Table 3, entry 3). Additionally, attempts to scale up the reaction to 15 mmol under the above conditions led to 86% conversion and 82% selectivity.

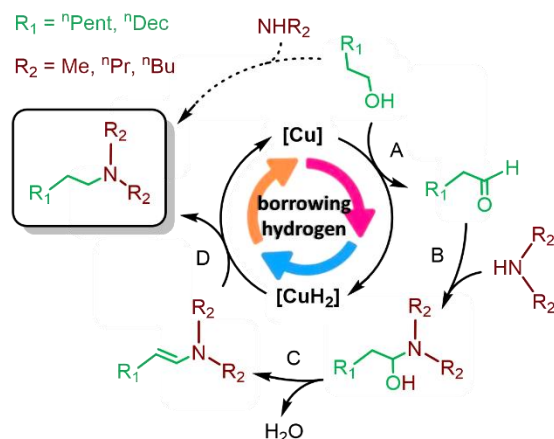
The appearance of the catalyst at the end of the catalysis is completely different due to the water contact. Mag-NPs seem more agglomerated preventing the full recovery of the catalyst (ESI, Figure S33). Nevertheless we could recycle the recovered catalyst and found an even conversion than initially observed but some decrease in selectivity (76% instead of 82%). More work would be necessary to stabilize the catalyst for further recycling.

In a similar context, alcohol amination reaction was further investigated with DMA in THF under the optimized catalytic conditions. Initially, the reaction was studied after 2 hours at 49 mT with 6 mol % of Cu obtaining 33 % of conversion respectively and total selectivity to N,N-dimethyldodecanamine (Table 3, entry 4). Consequently, 82 % of conversion were obtained after 8 hours with 95 % selectivity for DMDA (Table 3, entry 5). Thus, although less conversion was observable than performing the reaction with DMA in water (40 % wt.), a higher selectivity was obtained. Surprisingly, almost full conversion after 8 hours reaction at 49 mT led to 97% of selectivity when an excess of alcohol is employed (Table 3, entry 7). It is important to note that during the reaction, the solution took a light blueish colour due to NPs leaching, which is not observed in water or in the absence of solvent.

Finally, although several by-products can be obtained in this reaction,<sup>12a, xxvii</sup> only N-alkyldodecanamine and N-alkyldidodecanamine were observed under our catalytic conditions in a low yield. Thus, the selectivity of the reaction mainly depends upon the activity of the catalysts in the disproportionation reaction of the dialkylamine (see ESI). Transalkylation reactions of secondary and tertiary amines under thermal and induction heating have been studied in order to explore their potential role in the loss of selectivity of the amination reactions (ESI, Tables S8-S11). The conclusion is that the redistribution remains limited whether under thermal or induction heating and that therefore it occurs at the dehydrogenation step.

### Proposed Mechanism

Regarding the main reaction, a plausible catalytic cycle may begin with the oxidation of the alcohol to the aldehyde mediated by Cu catalytic activity (Scheme 1, step A). The second step is a non-catalytic reaction with the secondary amine to give the hydroxylamine adduct (step B) followed by a dehydration reaction to obtain the enamine (step C). The process is closed by a hydrogenation reaction of the enamine and the regeneration of the Cu catalyst (step D) in a borrowing hydrogen catalytic cycle. This catalytic process entails a self-supplying system for active hydrogen as previously reported by Kimura et al. with a NiCu co-catalyst. In contrast, a mechanism involving an iminium cation as intermediate may be present in the reaction with benzyl alcohol due to the inability of this system to access to the enamine adduct.<sup>xxviii</sup>



**Scheme 2.** Plausible borrowing hydrogen mechanism for the alcohol amination with secondary amines in presence of a Cu self-supplying catalytic system.

## Conclusion

Herein we report two new multifunctional catalytic systems composed of  $\text{Co}_4\text{Ni}_6$  or  $\text{Fe}_3\text{Ni}_7$  cores decorated with a Cu shell. The resulting  $\text{Co}_4\text{Ni}_6@\text{Cu}$  (**3**) material was found highly active and selective for the alcohol amination reaction of fatty alcohols (heptanol, dodecanol) with secondary amines ( ${}^n\text{Pr}_2\text{NH}$ ,  ${}^n\text{Bu}_2\text{NH}$ ) to prepare tertiary amines. The reaction occurs in mild conditions without desiccant, hydrogen pressure or solvent when heated by magnetic induction. Moreover, alcohol amination with DMA can be carried out in the presence of water under magnetic induction leading to remarkable conversions and selectivities. No leaching of the metallic species was detected. In contrast, low conversions and decreased selectivities were obtained in control tests using conventional heating at different temperatures. These results highlight the benefits of magnetically induced catalysis when working with thermally sensitive molecules or intermediates. In this sense, the magnetic core of the Mag-NPs contributes to over-heat the system when an AMF is applied while the surrounding medium remains in mild conditions. On the other hand, the active sites on the shell play the catalytic role. These results provide a perspective for the development of magnetic catalytic systems capable of promoting challenging transformations of thermally sensitive molecules under mild conditions using magnetic induction heating.

## AUTHOR INFORMATION

### Corresponding Author

Bruno Chaudret – Laboratoire de Physique et Chimie des Nano-Objets, Université de Toulouse, LPCNO, INSA, UPS, CNRS- UMR5215, 135 Avenue de Rangueil, 31077 Toulouse, France; Email: [chaudret@insa-toulouse.fr](mailto:chaudret@insa-toulouse.fr)

## Supporting Information

Additional electronic supporting information (ESI) can be found in a separate document.

## Acknowledgements

*The authors gratefully acknowledge SYENSQO for financial support for this work. The authors thank to Alain Moreau and Baptiste Martin (LCC, Toulouse) for the ICP and EPR measurements, respectively and Francis Chouzenoux (LPCNO, Toulouse) for the TGA experiments.*

**Keywords:** induction heating • magnetic nanoparticles • copper • alcohol • amine • DMA



---

