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Rapid Communication

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In situ supported rhodium catalyst on mesoporous silica for chemoselective hydrogenation of nitriles to primary amines

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Abstract: Heterogeneous rhodium supported on mesoporous silica ($Rh_{insitu}/mesSiO_2$) was easily prepared, in one step, by incorporating rhodium units onto the silica framework during the sol–gel process. $Rh_{insitu}/mesSiO_2$ was revealed to be an excellent active and selective catalyst for the hydrogenation of aromatic, heteroaromatic, aliphatic nitriles, and aliphatic nitriles bearing aromatic or heteroaromatic rings to primary amines, regardless of their steric hindrance. The catalytic system that is efficiently recyclable operates under mild conditions in the presence of ammonia.

Keywords: rhodium-supported catalyst, nitriles, hydrogenation, primary amines, mesoporous silica

1 Introduction

Amines are crucial chemical compounds utilized in the synthesis of a diverse range of organic chemicals that hold significant industrial value [1–4]. Their usage is extensive; for example, they are employed as agrochemicals, pharmaceuticals, prodrugs, anti-corrosives, cosmetics, and dyes [1–5]. The synthesis of amines varies based on the initial organic compound or feedstock, such as biomass [1–4,6]. On an industrial scale, amines are produced through several methods, primarily including amination of alkenes, reductive amination of alcohols and aldehydes, and reduction of nitriles [1]. Although these methods benefit from readily available raw materials, they face several challenges, including high temperature and pressure requirements, catalyst deactivation, and low selectivity due to the formation of numerous side products [1].

Recently, the great interest in molecular hydrogen as a renewable green energy source, has focused attention on the search for suitable systems for its storage. Among the solutions recently proposed are liquid organic hydrogen carriers (LOHCs) such as RCH_2NH_2/RCN couples [7]. Therefore, the development of an environmentally friendly and cheap process to synthesize primary amines from nitriles is important not only from a synthetic viewpoint but also for the fight against global warming [7]. Nowadays, amines are still prepared by using at least stoichiometric amounts of hydride-reducing agents for nitrile reduction [8–11] and for direct reductive amination (DRA) of aldehydes and ketones [3,12,13]. However, these reducing agents, such as $NaBH_4$ and mainly $NaBH_3CN$, and their by-products have the disadvantages of being toxic and potential contaminants for the final products, which hinders their large-scale use and are not acceptable in the concept of green chemistry. Unlike a process based on hydride-reducing agents, catalytic hydrogenation of nitriles to amines is interesting from economical and ecological aspects, and various interesting processes have been developed, especially during the last decade [14–20]. Generally, nitrile reduction generates a mixture of amines (1°, 2°, and 3°) and imine intermediates. It has been demonstrated that chemoselectivity can be influenced by the catalyst, the support, the structure of the nitrile to reduce, and the reaction conditions [14,15,17]. Also, to increase chemoselective formation of primary amines, ammonia is most widely used [14,15]. Additionally, mineral bases [14,15] or *in situ* trapping agents such as acids [14,15,21], CO_2 [22], di-tert-butyl decarbonate [22,23], and acetic anhydride [14,15,22] were also successfully utilized.

In catalytic hydrogenation of nitriles, significant interest is in the formation of primary amines. Most recently, homogeneous hydrogenation processes, notably based on Pincer metal complexes, have gained significant development for

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the highly selective hydrogenation of nitriles to primary amines. However, most of these homogeneous processes need dry solvents that are, in many cases, harmful and are performed under harsh conditions of pressure and temperature, with the obvious problem of recovering the catalysts in their active form and recycling them [14,16,18–20]. In contrast to homogeneous processes, the heterogeneous hydrogenation of nitriles has been extensively studied. However, many processes are still limited by their inadequate selectivity to primary amines, the difficult fabrication of the catalysts, and the drastic conditions used [14,16–19]. However, excellent heterogeneous processes for the selective hydrogenation of nitriles to the desired amines (1°, 2°, or 3°) have been lately reported as a result of the judicious control of various parameters such as the catalyst nature and the support used, as well as the hydrogenation conditions. Thus, various supported catalysts for the chemoselective formation of primary amines in good to excellent yields, under mild conditions have been recently published, specifically [$Co(OAc)_2$/Phen@/α-Al_2O_3]-800 [24], Ru nanoparticles/K-doped Al_2O_3 [25], B_{12}@CeO_2-8 [26], Fe_3C@G-CNT-700 [27], nano-N_3C/Al_2O_3 [28], Ni/$ZnAlO_x$-600 [29], and MC/Ni [30].

Rhodium-based catalysts have been widely used for the hydrogenation of different unsaturated groups [31], except for nitrile hydrogenation to amines. To date, the reported homogeneous and heterogeneous catalysts for the formation of tertiary, secondary, and particularly primary amines are very scarce [14–16,18]. For instance, Freifelder studied low-pressure hydrogenation of aliphatic nitriles to primary amines catalyzed by Rh/Al_2O_3 at room temperature and in the presence of ammonia [32]. Excellent results were obtained, especially in the case of nitriles containing tertiary amine or ether moieties. Under their conditions, the catalyst did not show any sign of *N*-benzyl group hydrogenolysis. In the absence of ammonia, secondary amines were formed predominantly. Rh/Al_2O_3 was also investigated by Chatterjee and co-workers for the selective hydrogenation of dinitriles in supercritical carbon dioxide, and they reported that adiponitrile was converted to 6-aminocapronitrile, without the formation of 1,6-hexamethylenediamine [33]. Yoshida et al. reported that rhodium hydride complexes $RhH[P(iPr)_3]_3$ and $Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4$ are excellent homogeneous catalysts for the hydrogenation of aromatic and aliphatic nitriles to the primary amines under ambient conditions, with $RhH[P(iPr)_3]_3$ being more efficient [34]. $RhH[P(iPr)_3]_3$ was further used by Xie et al. for the hydrogenation of phenyl acetonitrile and benzonitrile under CO_2 pressure [22]. While phenylacetonitrile gave excellent yield of primary amine, benzylamine was obtained in moderate yield in the case of benzonitrile. Various aliphatic nitriles have been hydrogenated successfully to primary amines using Rh/C in acetic acid and under flow conditions at 90°C [35]. An excellent transfer hydrogenation of aliphatic and aromatic nitriles has been revealed by using the catalyst Fe_3O_4@nSiO_2–NH_2Rh-Cu@mSiO_2, and formic acid as hydrogen donors under mild conditions [36]. Finally, we reported that $[Rh(COD)Cl]_2$ in aqueous ammonia generated a water-soluble complex, which is a highly selective catalyst for the hydrogenation of aromatic and sterically hindered aliphatic nitriles to primary amines with excellent and moderate yields [37].

Generally, the support exerts a large influence on the catalytic activity and selectivity of heterogeneous catalytic reactions, partly due to its interaction with the incorporated metallic active species. For the heterogeneous hydrogenation of nitriles, diverse supports such as alumina, silica, and carbon have been used to support catalysts like Pd, Rh, Ni, and Co. Highly ordered mesoporous materials such as MCM-41 and HMS are interesting supports, owing to the large surface area and the uniform and large pore size that promote high loading and dispersion of the metal catalysts [38–41]. The processes used to synthesize the supported catalysts also have a great influence on the catalyst performance. Post-grafting and impregnation methods are the usual approaches to prepare supported catalysts, and for the hydrogenation of nitriles, the impregnation approach is predominant. In contrast to the previous approaches, *in situ* synthesis of the supported catalysts is an elegant process that allows its formation in one step, and the leaching of the active metals is minimized or circumvented. It has been demonstrated in many different reactions that the *in situ* catalysts lead to better results than the catalysts prepared by the impregnation method [42–44]. As far as nitrile hydrogenation is concerned, to the best of our knowledge, few mesoporous catalysts have been studied [45–47], and the catalysts prepared by the *in situ* approach are very scarce [44]. Also, we are not aware of any process based on a supported rhodium catalyst, which is described in the same report, for the hydrogenation of aromatic, heteroaromatic, and aliphatic nitriles to primary amines. Herein, we report a convenient method based on an *in situ* supported rhodium catalyst on mesoporous silica for the hydrogenation of aromatic, heteroaromatic, aliphatic nitriles, and aliphatic nitriles substituted with aromatic or heteroaromatic rings.

2 Materials and methods

2.1 Materials and instruments

Nitriles and catalyst precursors were acquired from Sigma-Aldrich Company. NMR spectra were performed on a Bruker AC-200 spectrometer at 200 (^{1}H) and 50 MHz (^{13}C), using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ in most cases as solvent. Surface areas and pore sizes were determined by Brunauer–Emmett–Teller (BET) analysis and by Professor Serge Kaliaguine (Université Laval, Quebec). X-ray diffraction (XRD) analysis was performed by Professor Ralf Brüning (Mount Allison University, New Brunswick).

2.2 *In situ* catalyst and mesoporous silica synthesis

A typical procedure for the preparation of $Rh_{insitu}/mesSiO_2$ and mesoporous silica $mesSiO_2$ is as follows: To a warmed HCl solution (33 mL, 0.03 mol·L^{-1}) containing the desired amount of the catalyst precursor ($RhCl_3·xH_2O$), dodecylamine (13.5 mmol) was added. Then, the mixture was stirred vigorously for a few minutes. At room temperature, a solution of tetraethyl orthosilicate (50 mmol) in 21 mL of EtOH/iPrOH (17 mL/4 mL) was added, and a gel started to form. After 20 min, the resulting gel was allowed to age for 18 h at ambient temperature. The product thus obtained was filtered and then washed thoroughly with water, followed by methanol. The final catalyst was obtained after calcination in air at 600°C for 4 h. The rhodium content was determined by atomic absorption spectroscopy.

The same procedure was used to prepare the mesoporous silica $mesSiO_2$ but without the presence of any catalytic precursor.

Both samples were characterized by small-angle XRD diffraction and BET analysis.

2.3 Supported catalysts prepared by impregnation

A typical procedure for the preparation of $M_{impr}/mesSiO_2$ is as follows: Supported catalysts $M_{impr}/mesSiO_2$ were prepared using the incipient wetness technique by dissolving 0.08 mmol of the organometallic precursor $Pd(OAc)_2$, $RuCl_3$, $Pt(COD)Cl_2$ or $[Rh(COD)Cl]_2$ (0.04 mmol) in MeOH (20 mL) for 10 min. Mesoporous silica ($mesSiO_2$, 1 g) was added, and the mixture was stirred at room temperature for 1 h. The solid was then filtered, washed thoroughly with methanol, and dried at room temperature for 30 min before use.

2.4 Typical procedure for the hydrogenation of nitriles

In a glass liner, $MeOH/NH_3$ (10 mL) and nitrile (2.5 mmol) were introduced successively. Then, a calculated amount of $Rh_{insitu}/mesSiO_2$ in order to adjust rhodium loading (molar ratio of Rh to the nitrile, typically 0.8 mol%) was added. The glass liner was then placed in a 45 mL autoclave and the mixture was stirred at room temperature for 5 min. The autoclave was purged three times with N_2 and then three times with H_2 (50 psi). After the pressure was adjusted to 80 psi of hydrogen, the autoclave was heated at 90°C in an oil bath for the desired reaction time. After the reaction was completed, the autoclave was cooled to room temperature, and the remaining hydrogen was cleared out. Then, the mixture was filtered and washed with diethyl ether or ethyl acetate. The organic filtrate was dried and concentrated; then, $CDCl_3$/TMS was added to the resulting products, followed by ^{1}H NMR and ^{13}C NMR analysis. For the purified samples, SiO_2 column chromatography was used with ethyl acetate and methanol as the eluent.

For the recycling experiments, it is critical that the reactions are executed under the same conditions as those of the initial hydrogenation reaction. This includes utilizing the same amount of benzonitrile and maintaining an identical weight ratio (%w/w) of the catalyst to benzonitrile. Generally, the quantity of catalyst recovered is less than the amount originally employed. Therefore, to ensure an adequate supply of catalysts for the first recycling experiments, recovered catalysts with the same rhodium loading from several benzonitrile hydrogenations were consolidated and calcined at 600°C for 4 h. The solid obtained from this process was then reused in the recycling experiments. This approach was similarly applied to the second round of recycling experiments. It is vital for the recovered catalysts to be calcined to remove any organic residues that may have built up on their surfaces. Without this procedure, the outcomes may be unsatisfactory in terms of both activity and selectivity toward primary amines.

3 Results and discussion

3.1 Characterization of $mesSiO_2$ and Rh_{insitu}/$mesSiO_2$

The results of small-angle XRD analysis of mesoporous silica ($mesSiO_2$) and the catalyst $Rh_{insitu}/mesSiO_2$ are illustrated in Figure 1. Both samples exhibit a diffraction peak at approximately 2θ = 1.8°, indicating the presence of a mesoporous structure [38–41]. The observed broadening of the diffraction peaks, along with their low intensities, implies that the mesopores lack a well-ordered arrangement.

The nitrogen adsorption–desorption isotherms and the associated NLDFT pore size distributions were carried out to investigate the mesoporous structure of the two samples in detail (Figures 2 and 3). The mesoporous architectures of both samples are confirmed by the patterning of type IV isotherms with H1 hysteresis loops [39–41]. As illustrated in Figure 2, $mesSiO_2$ displays a larger hysteresis loop compared to $Rh_{insitu}/mesSiO_2$, likely due to the presence of larger pores in $mesSiO_2$. Figure 3 reveals an average pore size of 50.9 Å for $mesSiO_2$, whereas the predominant signal for $Rh_{insitu}/mesSiO_2$ is centered around 25.8 Å. The calculated surface areas and pore volumes for $mesSiO_2$ and $Rh_{insitu}/mesSiO_2$ are 526 and 505 $m^2 \cdot g^{-1}$, and 1.62 and 0.8 $mL \cdot g^{-1}$, respectively.

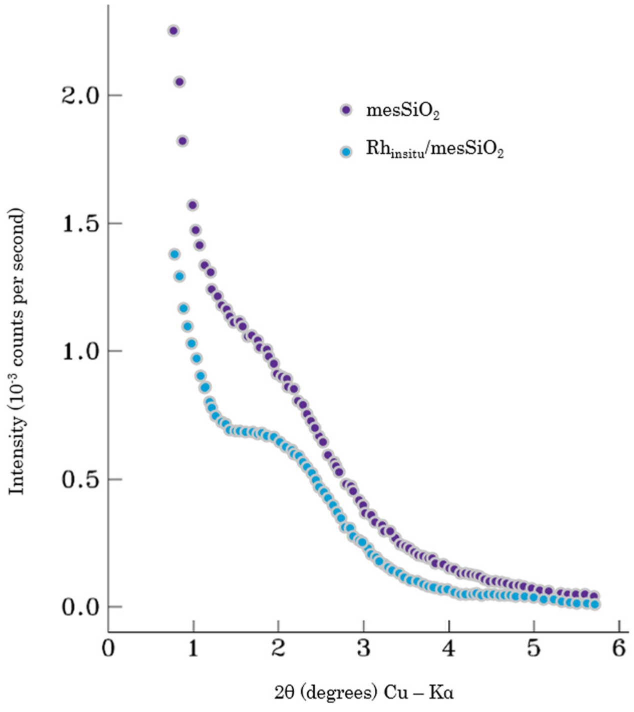


Figure 1: Small-angle XRD patterns of $mesSiO_2$ and $Rh_{insitu}/mesSiO_2$.

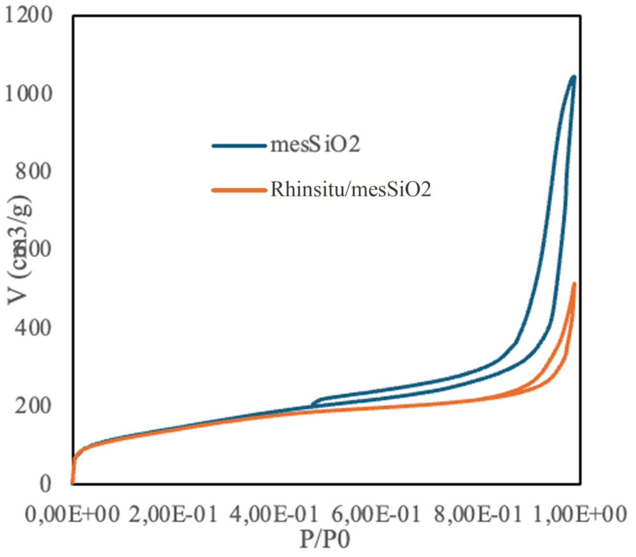


Figure 2: N_2 adsorption–desorption isotherms of $mesSiO_2$ and $Rh_{insitu}/mesSiO_2$.

3.2 Catalytic hydrogenation of nitriles to primary amines

At the inception of our project focused on the reduction of nitriles, we conducted an in-depth investigation into the hydrogenation of benzonitrile, which was selected as the model substrate. This process was examined in organic solvents such as methanol and tetrahydrofuran, as well as in water, all without the inclusion of ammonia. The experiments were carried out at temperatures ranging from 50°C to 100°C and under hydrogen pressures between 50 and 200 psi. We evaluated a variety of homogeneous catalysts, including $Pd(OAc)_2$, $RuCl_3$, $[Rh(COD)Cl]_2$, $[Ir(COD)Cl]_2$, and $Pt(COD)Cl_2$, both individually and in

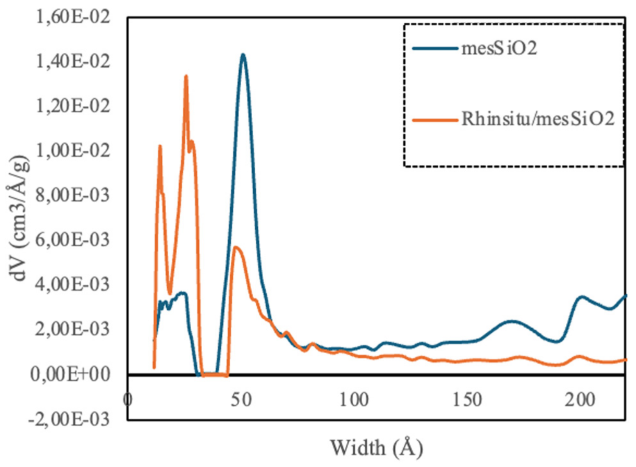


Figure 3: NLDFT pore size distributions of $mesSiO_2$ and $Rh_{insitu}/mesSiO_2$.

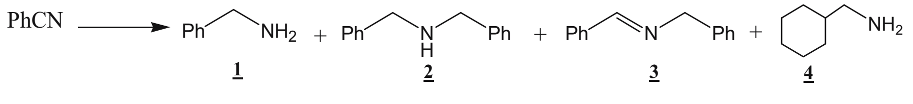
conjunction with ligands such as TPPTS ($P(m\text{-}C_6H_4SO_3Na)_3$) or BQC (2,2′-biquinoline-4,4′-dicarboxylic acid dipotassium salt). Additionally, we tested heterogeneous catalysts like Pd/C, Pd/SiO_2, and Pt/SiO_2. Unfortunately, the selectivity for the primary amine was found to be unsatisfactory. Furthermore, the introduction of ammonium salts such as NH_4Cl or $AcONH_4$ did not yield any significant enhancement in selectivity. These salts are known to improve the selectivity for primary amines in the reductive amination of carbonyl compounds, as ammonium ions can protonate the primary amine, resulting in alkylammonium ions which are less nucleophilic. Consequently, this inhibits the formation of highly alkylated imines and amines [15].

We then performed some reactions in aqueous ammonia, and we were delighted to discover that $[Rh(COD)Cl]_2$ is an excellent recyclable catalyst for the hydrogenation of nitriles to primary amines [37]. The hydrogenation, however, has to be performed under 400 psi of H_2 to minimize the formation of the corresponding amides and alcohols. Consequently, using nonaqueous ammonia, our goal is to discover a good heterogeneous catalyst that operates under mild temperature and H_2 pressure conditions and that leads principally to primary amines.

Primarily, we prepared four different heterogeneous catalysts by the impregnation method, using $Pd(OAc)_2$, $RuCl_3$, $Pt(COD)Cl_2$ and $[Rh(COD)Cl]_2$ as the catalytic precursors, and mesoporous silica ($mesSiO_2$) as the support. The supported catalysts ($M_{impr}/mesSiO_2$) were then tested for the hydrogenation of benzonitrile in $MeOH/NH_3$ at 90°C and H_2 pressure of 80 psi (Table 1). While ruthenium and platinum catalysts gave average conversions, palladium and rhodium catalysts led to the full transformation of benzonitrile with the highest selectivity to benzylamine reached in the case of $Rh_{impr}/mesSiO_2$ (94%, Table 1, entry 4). When benzonitrile was subjected to hydrogenation with extended reaction time, no over-hydrogenation products were observed (Table 1, entry 5). Unfortunately, the analysis of the product mixture with atomic absorption indicated the leaching of the catalyst from the support. Additionally, the recycling of the catalyst $Rh_{impr}/mesSiO_2$ resulted in the production of benzylamine (83%), dibenzylamine (4%), and benzylidenebenzylamine (13%), indicating a notable reduction in selectivity for benzylamine. This decline in selectivity could be attributed to various factors, including a reduction in the rhodium content or the buildup of organic compounds on the catalyst's surface, as it was reused following a basic wash with methanol.

As a consequence, we prepared a new supported catalyst in one step by the *in situ* technique using the same method for the preparation of mesoporous silica, with the exception of the addition of the rhodium precursor during the sol–gel process. The newly prepared catalyst $Rh_{insitu}/mesSiO_2$ was tested for the hydrogenation of benzonitrile under the same conditions. By increasing the rhodium loading from 0.16 to 0.8 mol% (Rh to benzonitrile ratio) and by adjusting the reaction time, the selectivity to benzylamine increased to the detriment of dibenzylamine, and particularly benzylidenebenzylamine (Table 2). With 0.8 mol% loading, excellent results were obtained after 3 h with the selective formation of benzylamine with 92% yield, and the supported catalyst was recycled twice with the same activity and selectivity (Table 2, entries 5–7). For the recycling experiments, the catalysts must be reactivated by heat treatment at 600°C for 4 h before its use (see Section 2.4). By extending the reaction time to 6 h or increasing the rhodium loading to 1.6 mol%, excellent results were obtained with no extensive formation of over-hydrogenation products, mainly cyclohexanemethylamine (Table 2, entries 8–10). Knowing that the reaction in water will lead to other by-products, the hydrogenation

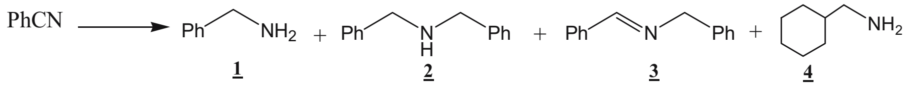
Table 1: Hydrogenation of benzonitrile catalyzed by $M_{impr}/mesSiO_2$ [a]



Run	ML_n	Time (h)	Conversion (%)	1 (%)	2 (%)	3 (%)
1	$Pd(OAc)_2$	24	100	78	20	2
2	$RuCl_3$	24	52	32	4	16
3	$Pt(COD)Cl_2$	24	45	39	4	2
4	$[Rh(COD)Cl]_2$	24	100	94	2	4
5	$[Rh(COD)Cl]_2$	36	100	95	3	2
6[b]	$[Rh(COD)Cl]_2$	36	100	83	4	13

[a] Reaction conditions: benzonitrile (2.5 mmol), H_2 (80 psi), $MeOH/NH_3$ (7 N, 10 mL), 90°C, $M_{impr}/mesSiO_2$ (1 g, 3.2 mol%). [b] First recycling of the catalyst in run 5.

Table 2: Hydrogenation of benzonitrile catalyzed by $Rh_{insitu}/mesSiO_2$[a]



Run	Rh Mol%	Time (h)	Conversion (%)	1 (%)	2 (%)	3 (%)	4 (%)
1	0.16	5	77	37	12	28	0
2	0.16	21	100	88	12	0	0
3	0.32	18	100	91	9	0	0
4	0.8	1	98	77	4	17	0
5	0.8	3	100	92	5	0	3
6[b]	0.8	3	100	93	6	1	0
7[c]	0.8	3	100	92	4	4	0
8	0.8	6	100	92	5	0	3
9	0.8	12	100	95	4	0	1
10	1.6	3	100	96	4	0	0
11[d]	0.8	12	100	69	1	6	0

[a] Reaction conditions: benzonitrile (2.5 mmol), $Rh_{insitu}/mesSiO_2$, H_2 (80 psi), $MeOH/NH_3$ (7 N, 10 mL), and 90°C. [b] First recycling of the catalyst in run 5. [c] Second recycling of the catalyst in run 5. [d] Reaction performed with aqueous ammonia instead of $MeOH/NH_3$. The following products were also obtained: benzamide (18%) and benzyl alcohol (6%).

of benzonitrile was still tested by replacing CH_3OH/NH_3 with aqueous ammonia. Not surprisingly, a complex mixture was obtained with benzylamine as the majority product (69%), followed by benzamide (18%), benzylidenebenzylamine (6%), benzyl alcohol (6%), and dibenzylamine (1%) (Table 2, entry 11).

In Table 3, we present most of the reported homogeneous and heterogeneous rhodium catalysts for the reduction of benzonitrile to benzylamine. As can be seen, $Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4$ [34] and Rh-PVP [48,49] were inactive for the formation of benzylamine, while very low yields were obtained in many cases, for instance, Rh/MCM-41, Rh/C, and Rh/Al_2O_3 in $scCO_2$ [45] and Rh/C in CH_2Cl_2/H_2O in the presence of NaH_2PO_4 [50]. Moderate yields were reached by $RhH[P(iPr)_3]_3$ with a slight improvement under CO_2 pressure [22,34] and by 5% $Rh/\gamma\text{-}Al_2O_3$ in CH_2Cl_2/H_2O in the presence of NaH_2PO_4 [50]. With the addition of ammonia, Rh@S-1 led to a good yield of benzylamine [44], and excellent yield was gained with $[Rh(COD)Cl]_2$, as we reported in aqueous ammonia [37]. Finally, a 98% yield was obtained with $Fe_3O_4@nSiO_2–NH_2–RhCu@mSiO_2$, but formic acid was used as the hydrogen donor [36]. Thus, our present results showed the superiority of our catalytic system $Rh_{insitu}/mesSiO_2$ to the reported catalysts for the

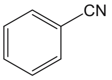
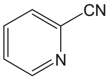
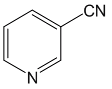
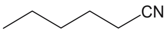
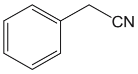
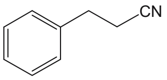
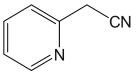
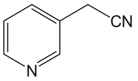
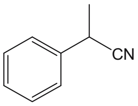
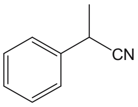
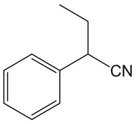
Table 3: Reduction of benzonitrile to benzylamine catalyzed by reported rhodium catalysts

Catalyst	Solvent	Temperature (°C)	H_2 (atm)	Yield (%)	Reference
$Rh_{insitu}/mesSiO_2$	$MeOH/NH_3$	90	5.44	96	This work
$Rh_2H_2(\mu\text{-}N_2)\{P(cyclohexyl)_3\}_4$	THF	20	1	0	[34]
Rh-PVP	MeOH	25	0.99	0	[48]
Rh-PVP	MeOH	30	2.96	0	[49]
Rh/MCM-41	$scCO_2$	50	19.74	1.3	[45]
5% Rh/C	$scCO_2$	50	19.74	7.2	[45]
5% Rh/Al_2O_3	$scCO_2$	50	19.74	4.7	[45]
5%Rh/C	$CH_2Cl_2/H_2O/NaH_2PO_4$	30	5.92	23	[50]
$RhH[P(iPr)_3]_3$	THF	20	1	45	[34]
$RhH[P(iPr)_3]_3$	$THF/scCO_2$	23-25	4.93	61	[22]
5%$Rh/\gamma\text{-}Al_2O_3$	$CH_2Cl_2/H_2O/NaH_2PO_4$	30	5.92	52	[50]
Rh@S-1	$MeOH/NH_3$	80	9.87	68	[44]
$[Rh(COD)Cl]_2$	NH_4OH	100	27.22	90	[37]
$Fe_3O_4@nSiO_2–NH_2\text{-}RhCu@mSiO_2$	$HCOOH–NEt_3$	40	—	98	[36]

hydrogenation of benzonitrile in terms of activity and selectivity to benzylamine.

With the important results obtained in the case of benzonitrile, the limits and the hydrogenating power of $Rh_{insitu}/mesSiO_2$ were examined with other nitriles (Table 4). Although 2-cyanopyridine is a very difficult compound to selectively hydrogenate into primary amine, an interesting yield of 65% is achieved in our case (Table 4, entry 2). For comparison, we present in Table 5 many reported catalysts for the hydrogenation of 2-cyanopyridine. For example, $B12@CeO_2$-8 in $iPrOH/NH_4OH$ [26], 10% Pd/C [51], and 10% $Pd(OH)_x/C$ in $iPrOH/Et_3N$ [51] were inactive even under drastic temperature and pressure conditions (Table 5, entries 2–4). Under the same conditions, other catalysts, such as Pt/C and Ru/C, are poorly selective despite the total conversion of 2-cyanopyridine (Table 5, entries 5 and 6). Good results were reached, however, with 10% Pd/C but in the presence of sulfuric acid (57%) [52] and with Co-N-C@MgO-700 (70%) [51] by using high catalyst loading and high temperature and pressure of H_2. Also, only a 51% yield was obtained by a hydrogen transfer process based on 5–10% Pd/C catalyst and HCO_2H/Et_3N at room temperature (Table 5, entry 10) [53]. Finally, the only best result so far was reported for the Ni-NPs@SiO_2-500 catalyst (83%). However, high hydrogen pressure is needed (Table 5, entry 11) [54]. $Rh_{insitu}/mesSiO_2$ catalyst was also proven to be highly effective for the selective hydrogenation of 3-cyanoyridine to 3-(aminomethyl)pyridine with full conversion and 93% selectivity (Table 4, entry 3). In the cases of hexanenitrile, phenylacetonitrile, and 3-phenylpropionitrile, equally

Table 4: Hydrogenation of different nitriles catalyzed by $Rh_{insitu}/mesSiO_2$[a]

Run	Nitrile	Rh Mol%	Time (h)	Conversion (%)	Selectivity to 1° amine (%)
1		0.8	3	100	92
2[b]		0.8	6	100	65
3		0.8	6	100	93
4		0.8	6	100	91
5		0.8	3	100	92
6		0.8	6	100	94
7		1.6	24	100	94
8		1.6	24	100	93
9		1.6	24	89	100
10[c]		1.6	24	96	100
11		1.6	24	100	>99

[a]Reaction conditions: nitrile (2.5 mmol), $Rh_{insitu}/mesSiO_2$, H_2 (80 psi), $MeOH/NH_3$ (7 N, 10 mL), 90°C. [b]Isolated yield. Other unknown products were formed, including ring reduction and very small amount of secondary amine. [c]H_2 pressure is 200 psi.

Table 5: Reduction of 2-cyanopyridine catalyzed by reported catalysts

Run	Catalyst	Solvent	Temperature (°C)	H_2 (atm)	Conversion (%)	Selectivity (%)	Reference
1	Rh_{insitu}/mesSiO_2	$MeOH/NH_3$	90	5.44	100	65	This work
2	B_{12}@CeO_2-8	iPrOH/NH_4OH	140	49.35	0	0	[26]
3	10% Pd/C	iPrOH/Et_3N	130	39.48	>99	<1	[51]
4	10% $Pd(OH)_x$/C	iPrOH/Et_3N	130	39.48	>99	<1	[51]
5	10% Pt/C	iPrOH/Et_3N	130	39.48	>99	31	[51]
6	5% Ru/C	iPrOH/Et_3N	130	39.48	>99	49	[51]
7	10% Pd/C	$CH_2Cl_2/H_2O/H_2SO_4$	30	5.92	100	57	[52]
8	Co-N-C@MgO-700	iPrOH/NH_4OH	80	19.74	26	22	[51]
9[a]	Co-N-C@MgO-700	iPrOH/NH_4OH	130	39.48	>99	70	[51]
10	5–10% Pd/C	HCO_2H/Et_3N	rt	—	—	51[b]	[53]
11	Ni-NPs@SiO_2-500	$MeOH/NH_3$	80	34.54	—	83[b]	[54]

[a] The amount of the catalyst is tripled compared to run 8. [b] Percentage (%) represents the reported yield.

excellent results were obtained with full conversions of the starting nitriles and selectivities of 91–94% (Table 4, entries 4–6). The efficiency of our hydrogenation catalytic system was further assessed in the case of 2-pyridylacetonitrile and 3-pyridyacetonitrile that were fully converted to the corresponding primary amines with the respective selectivities of 94 and 93% using 1.6 mol% Rh loading (Table 4, entries 7 and 8). These two compounds have been rarely studied, and the reported yields were obtained under harsh conditions:

2-Pyridylacetonitrile:

- $[Rh(COD)Cl]_2$, NH_4OH, H_2 (400 psi), 100°C: 54% [37].
- Ni-NPs@SiO_2-500, $MeOH/NH_3$, H_2 (508 psi), 80°C: 85% [54].

3-Pyridylacetonitrile:

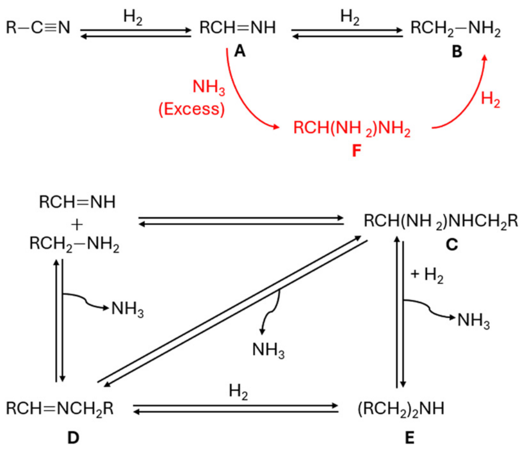
- $[Rh(COD)Cl]_2$, NH_4OH, H_2 (400 psi), 100°C: 67% [37].
- B_{12}@CeO_2-8, iPrOH/NH_4OH, H_2 (435 psi), 120°C: 98% [26].

Sterically hindered nitriles, 2-phenylpropionitrile and 2-phenylbutyronitrile, have also been rarely reported, and the processes used were with high temperatures and high hydrogen pressure [37,54–56]. Fe/Fe-O@SiO_2 was shown to catalyze the hydrogenation of 2-phenylpropionitrile to primary amine with 93% yield. However, the reaction has to be performed at 120°C under 725 psi of H_2 in the presence of ammonia [55]. Concerning 2-phenylbutyronitrile, moderate to excellent yields were obtained, and once again, high hydrogen pressure with a temperature ranging from 80°C to 120°C was used:

- $[Rh(COD)Cl]_2$, NH_4OH, H_2 (400 psi), 100°C: 50% [37].
- Ni-NPs@SiO_2-500, $MeOH/NH_3$, H_2 (508 psi), 80°C: 82% [54].
- Fe/Fe-O@SiO_2, iPrOH/NH_3, H_2 (725 psi), 120°C: 90% [55].
- Cobalt-terephthalic acid MOF@C-800, Toluene/NH_3, H_2 (363 psi), 120°C, 88% [56].

Rh_{insitu}/mesSiO_2 catalyst for both cases led to excellent results as 2-phenylpropylamine and 2-phenylbutylamine were selectively obtained with 96 and >99% yields, respectively, from 2-phenylpropionitrile and 2-phenylbutyronitrile (Table 4, entries 10 and 11). These results indicated that our catalytic system is compatible with sterically hindered nitriles.

Scheme 1 outlines the proposed hydrogenation mechanism for generating primary amines [15,46,57–59] and clarifies the effect of the NH_3 additive. Initially, the starting nitrile leads to the formation of the primary amine $RCH_2–NH_2$ (**B**) through two consecutive hydrogenation reactions, with aldimine (**A**) acting as an intermediate. The reaction between the primary amine and aldimine yields 1-amino-dialkylamine $RCH(NH_2)NHCH_2R$ (**C**), which can release ammonia to yield dialkylimine $RCH{=}NCH_2R$ (**D**). This dialkylimine can subsequently undergo hydrogenation to produce the



Scheme 1: Plausible mechanism for the formation of primary amines.

secondary amine $(RCH_2)_2NH$ (**E**). Alternatively, it can also arise directly from **C** following hydrogenolysis and the liberation of ammonia.

The presence of excess ammonia serves to inhibit the formation reactions of **D** and **E**, thereby favoring the production of primary amine **B**. It was suggested that ammonia interacts with **A** to yield *gem*-diamine **F**, which subsequently transforms into **B** through hydrogenolysis [15]. The protection of primary imine **A** as *gem*-diamine **F** decreases its availability for the addition reaction with primary amine **B**. This results in a deceleration of secondary amine **E** formation due to the inhibition of the **C** and **D** formation reactions [15]. Additionally, it has been observed that dialkylimine **D** reacts with ammonia to generate primary amine **B** and aldimine **A**. This transamination equilibrium shift consequently diminishes the formation of **D** and **E** [15].

4 Conclusions

The hydrogenation of nitriles to amines by homogeneous or heterogeneous rhodium-based catalysts is very rare. $Rh_{insitu}/mesSiO_2$, prepared in a single step by the sol–gel process, has been shown to be an excellent catalyst for the synthesis of primary amines from nitriles in the presence of ammonia, and the catalyst is recyclable without loss of activity or catalytic selectivity. Although rare rhodium-based reports have been published, the diversity of nitriles examined in the same report is limited, particularly with the absence of heteroaromatic nitriles and nitriles that contain heteroaromatic groups. Under moderate conditions of temperature (90°C) and hydrogen pressure (80 psi), $Rh_{insitu}/mesSiO_2$ allowed the selective hydrogenation of aromatic, heteroaromatic, aliphatic, and aliphatic nitriles containing phenyl or heteroaryl groups. It was also shown to be compatible with bulky nitriles such as 2-phenylbutyronitrile.

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Conflict of interest: Authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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