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Alumina-supported nickel catalyst for liquid-phase reactions: an expedient and efficient heterogeneous catalyst for hydrogenation reactions

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The preparation of a new nickel(0)/Al_2O_3 catalyst for hydrogenation reactions is described. The nickel(0)/Al_2O_3 catalysts were prepared by impregnation of alumina with a solution of a nickel(II) salt. After drying, the nickel(II) salt was reduced under mild conditions into nickel(0) using *t*-BuONa-activated sodium hydride in tetrahydrofuran at 65 °C. The nickel(0)/Al_2O_3 catalysts obtained were characterized by transmission electron microscopy and energy-dispersive X-ray spectroscopy. The supported catalysts were successfully used in solution-phase hydrogenation of double and triple bonds. Although the activity of the nickel(0)/Al_2O_3 is comparable to non-supported nickel(0) reagents, it has the advantage of being reusable more than ten times with only a slight decrease of reactivity. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: activated sodium hydride; alumina-supported nickel catalyst; nanomaterial; catalytic hydrogenation; alkenes; alkynes

INTRODUCTION

The use of supported catalysts in organic chemistry is currently an area of intensive research. For example, supported nickel catalysts find wide applications in many important industrial processes including hydrogenation of alkenes,[1–4] aromatics[5,6] and nitriles,[7] hydrogenolysis of alkanes,[8,9] reforming of methane with carbon dioxide,[10] hydrodesulfurization,[1–4,11,12] oligomerization of ethene,[13] amination of ethanol,[14] cross-couplings[15–18] and reduction reactions.[19,20] The intrinsic advantages of supported catalysts are that they can be easily removed by simple filtration upon completion of the reaction and that they can be recycled, thereby reducing the costs.[21–24] Among all the systems developed, alumina-supported nickel catalysts have been found to be very promising catalysts in terms of catalytic activity, as well as in terms of recycling. Nickel/Al_2O_3 catalysts are generally prepared by impregnation of an alumina support material by a nickel(II) salt or by co-precipitation from aluminium(III) and nickel(II) solutions followed by calcination and reduction under flowing hydrogen at high temperatures.[25–29] However, such thermal treatments often cause an alteration of the texture of the support and, therefore, a decrease of the catalytic activity.[30–32]

In recent years, our laboratory has developed a nickel(II) reduction methodology based on the use of alkoxide-activated sodium hydride (NaH) and shown it to be very efficient for the generation of highly dispersed and reactive nickel(0) clusters (see Ref. 33 for a recent report). The main advantages of this protocol are that: (a) the nickel(II) reduction can be performed under mild conditions (generally in refluxing THF); (b) the nickel(0) clusters generated are non-pyrophoric and slightly oxidizable; and (c) the alkoxide-stabilized nanometric nickel(0) particles stay active even after prolonged storage.[33] We have subsequently shown that nickel catalysts prepared by this methodology exhibit high hydrogenation catalytic activity versus ethylenic compounds under normal pressure of hydrogen. In addition, these catalysts a very efficient for a great number of synthetic applications, including reductions of aryl halides,[34–36]

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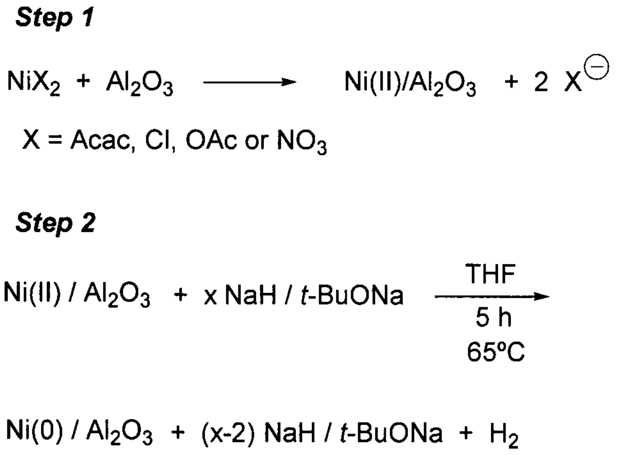
carbon–carbon[37,38] or carbon–nitrogen couplings (see Refs 39–42 for recent reports).

The aim of the present work is to report a new preparation of alumina-supported highly dispersed nickel(0) particles. The catalytic activity of the materials obtained was evaluated in the liquid-phase hydrogenation at atmospheric pressure of double and triple carbon–carbon bonds.

RESULTS AND DISCUSSION

Nickel/Al_2O_3 catalysts were prepared in a two-step procedure: irreversible adsorption of a nickel(II) salt on the support and reduction under mild conditions using *t*-BuONa-activated sodium hydride (NaH) as a reducing agent. In the first step, several nickel(II)/Al_2O_3 samples were prepared by a classical adsorption procedure of various nickel(II) salts (Scheme 1, step 1). To this end, commercially available alumina (α-alumina or, surply, chromatographic alumina) was added at 50 °C to a solution of nickel acetylacetonate ($Ni(acac)_2$) or nickel chloride ($NiCl_2$) in acetone or to nickel acetate ($Ni(OAc)_2$) or nickel nitrate ($Ni(NO_3)_2$) in water and the mixture was stirred for 1 h. The support, initially white, turned gradually light green during this step. After cooling to room temperature, the impregnated alumina was washed with acetone and dichloromethane to remove the unadsorbed nickel(II). The solution was greenish only after the first wash. A low amount of nickel was found in subsequent wash solutions (<0.5% of the initial charge) even after exhaustive washings, indicating that nearly all the nickel(II) salt remaining on the support was strongly adsorbed on the alumina. The samples were next dried at 110 °C under reduced pressure. For a catalyst precursor prepared from 20 g alumina and 18 mmol $Ni(acac)_2$, selected as representative, the nickel content, determined by chemical analysis of the dried sample, was found to be 1.48%. The weight gains of the impregnated alumina were determined as 6.1 wt% for the $Ni(acac)_2$/alumina, 6.0 wt% for the $Ni(OAc)_2$/alumina, 5.8 wt% for the $NiCl_2$/alumina and 4.9 wt% for the $Ni(NO_3)_2$/alumina catalyst precursors. The deviation observed between the percentage of nickel retained on the support compared with the weight gain of alumina clearly indicates an interaction of the nickel(II) counter ion with the support according to the model proposed by Poncelet and coworkers.[43]



Step 1

$$NiX_2 + Al_2O_3 \longrightarrow Ni(II)/Al_2O_3 + 2\,X^{\ominus}$$

X = Acac, Cl, OAc or NO_3

Step 2

$$Ni(II)/Al_2O_3 + x\,NaH/t\text{-}BuONa \xrightarrow[\substack{5\ h\\ 65^{\circ}C}]{THF} Ni(0)/Al_2O_3 + (x-2)\,NaH/t\text{-}BuONa + H_2$$

Scheme 1.

The second step of the process was the reduction of the adsorbed nickel(II) salt with *t*-BuONa-activated NaH (Scheme 1, step 2). For this purpose, the nickel(II)/Al_2O_3 sample was added in one portion to a degreased NaH suspension in tetrahydrofuran (THF) and the mixture was heated at 65 °C. It is noteworthy that an excess of NaH was necessary to ensure neutralization of hydroxylated sites of alumina, as well as for the destruction of traces of water remaining in the support. *tert*-Butanol (two equivalents relative to nickel) was then added dropwise and the mixture was refluxed for a further 5 h. *tert*-Butanol rapidly reacts with NaH to form the corresponding sodium salt, which acts as an activating agent of NaH. The *in situ* generated NaH/*t*-BuONa reducing agent then allows the reduction of impregnated nickel(II) salt. At the end of the preparation, the catalyst was black in colour.

Electron energy loss and electron diffraction studies of the catalysts prepared from $Ni(acac)_2$ and $Ni(OAc)_2$ confirmed first the zero oxidation state of nickel in the supported catalysts. For both catalysts, the amount of nickel(0) coated on the alumina surface, determined by chemical analysis of the dried samples, was found to be 1.77 ± 0.05%.

The particle sizes of the nickel metal in the catalysts prepared from $Ni(acac)_2$ and $Ni(OAc)_2$ were observed by transmission electron microscopy (TEM) as shown in Fig. 1. In both cases, the nickel metal particles were homogeneously dispersed in an even size around 5 nm on the alumina support. It is noteworthy that the size of nickel crystallites produced by our method involving the reduction of a nickel(II) salt with *t*-BuONa-activated NaH was similar to that obtained from reductions with molecular hydrogen at 450 °C for 2 h.[26]

Finally, analysis of the diffraction pattern for both nickel/Al_2O_3 samples showed that the nickel particles were highly ordered and that the microcrystalline units have a hexagonal close-packed (hcp) structure (Fig. 2). This result is in accordance with our previous work on nickel(0) clusters.[33] Indeed, reduction of $Ni(OAc)_2$ or $Ni(acac)_2$ with the *t*-BuONa/NaH system produces nanometric particles of nickel metal (1–2 nm) that originally possess an hcp structure.

The influence of the nickel precursors on the catalytic behaviour of the nickel/Al_2O_3 materials was next estimated in the liquid-phase hydrogenation of styrene into ethylbenzene performed at 25 °C under 1 atm of hydrogen using 1 mol% of nickel. Ethanol (EtOH) was selected as the most appropriate solvent on the basis of previous work on

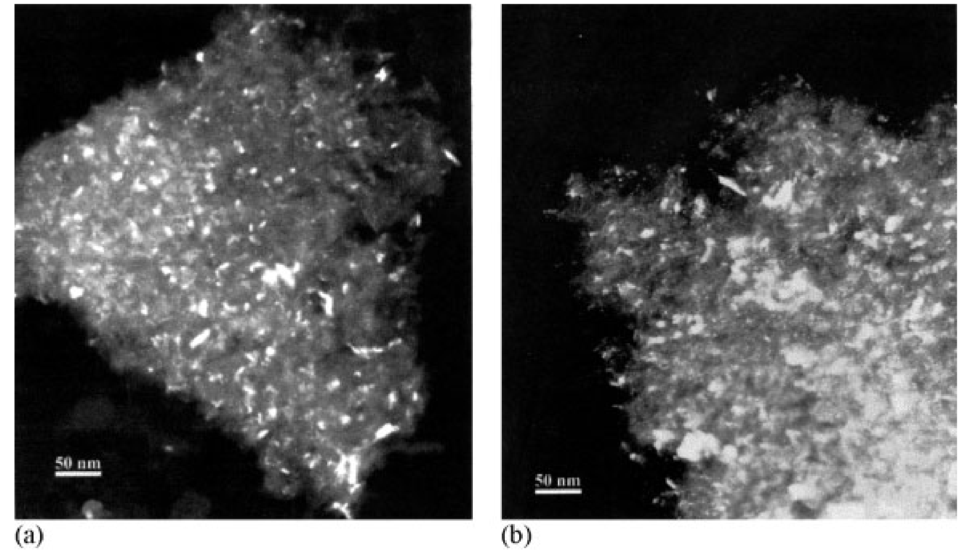


Figure 1. Dark-field TEM micrographs of nickel/Al_2O_3 catalysts after reduction: (a) $Ni(acac)_2$; (b) $Ni(OAc)_2$.

hydrogenations involving nickel(0) clusters.[44,45] The work-up involved only a decantation followed by removal of the reduced hydrocarbon in EtOH with a syringe under a hydrogen or nitrogen atmosphere. The reaction times, conversions of styrene and turnover numbers (TONs) of various prepared supported nickel catalysts are given in Table 1.

We found that alumina-supported nickel catalysts obtained with $Ni(acac)_2$ or $Ni(OAc)_2$ as precursors showed similar activities in the catalytic hydrogenation of styrene into ethylbenzene (entries 1 and 2). Reactions were completed in 2 min and afforded ethylbenzene in quantitative yields. $NiCl_2$ can also be used (100% conversion in 6 min; entry 3), whereas hydrogenation with $Ni(NO_3)_2$ as nickel precursor proceeded in less than 15% yield (entry 4). The order of styrene to ethylbenzene conversion over the catalysts employed is as follows: $Ni(acac)_2 = Ni(OAc)_2 > NiCl_2 \gg Ni(NO_3)_2$. In fact, the reduction of $Ni(NO_3)_2$ was not observed in our reaction conditions. The same trend has already been observed in homogeneous catalysis using our

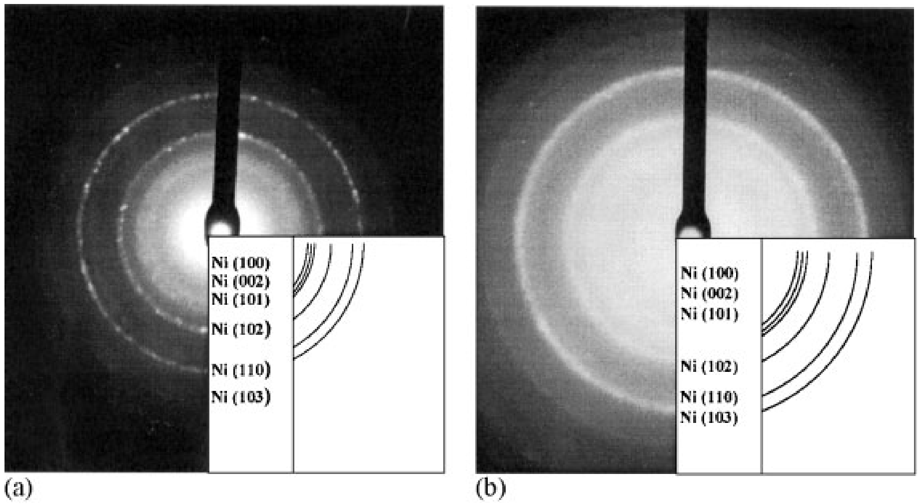
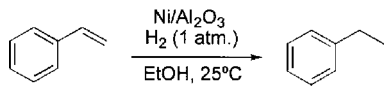


Figure 2. Selected-area electron diffraction pattern of the crystalline nickel particles supported on alumina: (a) $Ni(acac)_2$; (b) $Ni(OAc)_2$.

Table 1. Hydrogenation of styrene using various nickel(0) precursors[a]



Entry	Reaction			
	Ni(0) source	Time (min)[b]	Conversion (%)[b]	TON[c]
1	$Ni(acac)_2$	4	100	1500
2	$Ni(OAc)_2$	4	100	1500
3	$NiCl_2$	6	100	1000
4	$Ni(NO_3)_2$	>10	<15	–

[a] Reactions conditions: 20 mmol styrene, 1 mol% nickel supported on alumina, 15 ml EtOH, 1 atm H_2, 25 °C.

[b] Determined by gas chromatography analysis.

[c] TON in moles of ethylbenzene per mole of nickel after 1 h.

non-supported nickel clusters.[46] The differences in performance displayed by these four nickel(0) precursors may be directly related to the effectiveness of *t*-BuONa-activated NaH in the reduction of the nickel(II) salt into nickel(0).

Hydrogenation of unsatured hydrocarbons with nickel/Al_2O_3 catalysts

Since the catalytic hydrogenation of unsaturated hydrocarbons over nickel catalysts is an important commercial process in the production of fine chemicals and pharmaceuticals,[1–4] hydrogenations of representative alkenes, dienes and alkynes were investigated. All hydrogenations were performed at room temperature and atmospheric pressure using α-alumina-supported nickel(0) catalysts prepared either with $Ni(acac)_2$ or $Ni(OAc)_2$ (nickel coated on the support:1.775%). The results are reported in Table 2.

The nickel/Al_2O_3 is a very active catalyst for the hydrogenation of activated alkenes (entries 1 and 3) and alkynes (entry 11).

High TON (up to 1500 h^{-1} for styrene, entry 1) were reached and reactions were completed in less than 4 min. When the ethylenic group is either not activated or hindered (entries 2 and 10), the activity of the catalyst is decreased. Hydrogenation of non-activated alkenes required 5 mol% of the supported nickel catalyst for total conversion of the substrate. Cyclooctene was transformed in cyclooctane in 89% yield after 232 min using 1 mol% nickel/Al_2O_3, whereas the same reaction was completed in 84 min with 5 mol% of the catalyst (compare entries 4 and 5).

Using dienes as starting materials, mono- or di-hydrogenation products could be obtained selectively. 1,5-cyclooctadiene and 1,3-cyclooctadiene could be reduced to cyclooctene when the hydrogenation was stopped after 8 min just after the uptake of one equivalent of hydrogen (entries 6 and 8). Complete saturation of both double bonds was achieved by extending the reaction time to 90 min (entries 7 and 9).

Partial hydrogenation of alkynes, however, could not be obtained, even by decreasing reaction times and/or by adding quinoline to the reaction medium. For instance, stopping the hydrogenation of diphenylacetylene after 2 min yielded 40% of (*E*)-stilbene, 50% 1,2-diphenylethane and 10% unconverted starting material remained. Using only 1 mol% of the nickel/Al_2O_3 catalyst, diphenylacetylene and oct-1-yne were quantitatively converted into 1,2-diphenylethane and octane in respectively 8 min and 34 min (entries 11 and 12).

Recycling of the catalyst

The potential of the nickel/Al_2O_3 catalyst to be recycled was finally tested by reusing the supported reagent in hydrogenation reactions of styrene (20 mmol styrene, 1 mol% nickel/Al_2O_3, EtOH, 25 °C, 1 atm H_2). After the first hydrogenation, the reaction mixture was decanted and ethylbenzene in EtOH was removed using a syringe. The nickel/Al_2O_3 catalyst was immediately used for the next hydrogenation cycle by reinjecting a solution of styrene in EtOH into the reaction vessel.

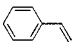
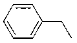
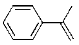
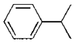
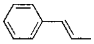
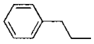
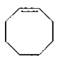
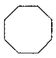
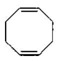
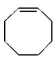
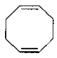
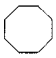
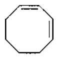
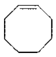
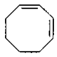
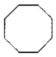
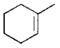
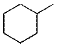
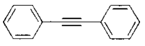
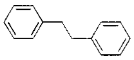
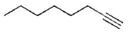
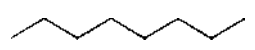
The catalytic activity of the supported nickel was measured after each hydrogenation. Figure 3 reports the evolution of TON after each hydrogenation cycle. Starting from TON = 1500 h^{-1}, the TON slowly decreased as a function of hydrogen cycle to reach its minimum after ten cycles (TON = 847 h^{-1}). However, after ten cycles, the catalyst remained active and gave complete conversion of styrene into ethylbenzene, as indicated by gas chromatography analysis. TEM indicated that nickel nanoparticles stay strongly bound to alumina and only traces of nickel could be detected in the liquid phase after hydrogenation. The slow deactivation of the nickel/Al_2O_3 catalyst may be due to a partial oxidation of nickel(0) particles by molecular oxygen remaining in EtOH or styrene.

Finally, the activity of the nickel/Al_2O_3 catalyst in hydrogenation reactions is only slightly inferior to those of non-supported heterogeneous nickel(0) clusters generated by reduction of $Ni(OAc)_2$ with *t*-BuONa-activated NaH. For example, used at 1 mol% nickel(0) relative to styrene, the activity of the conventional non-supported nickel(0) catalyst is TON = 1560 h^{-1}. Under the same reaction conditions, the activity of the Ni/Al_2O_3 is TON = 1500 h^{-1}. The supported catalyst, however, has the advantage of being reusable more than ten times in hydrogenation reactions with only a slight decrease of reactivity.

CONCLUSION

In summary, a novel supported nickel/Al_2O_3 catalyst was prepared under mild conditions by reduction of alumina-impregnated nickel(II) salts with *t*-BuONa-activated NaH in

Table 2. Hydrogenation of alkenes, dienes and alkynes using alumina-supported nickel catalyst[a]

Entry	Starting material	Ni (mol%)	Reaction time (min)[b]	Product	Conversion (%)[b,c]	TON[d]
1		1	4		100	1500
2		1	46		100	130
3		1	6		100	1000
4		1	232		89	26
5		5	84		100	14
6		5	8		100	150
7		5	90		100	13
8		5	8		100	150
9		5	90		100	13
10		5	250		97	5
11		1	8		100	750
12		1	34		100	176

[a] Reactions conditions: all hydrogenations were carried out using 20 mmol starting material, 1 or 5 mol% nickel supported on alumina, 15 mL EtOH, 1 atm H_2, 25 °C.

[b] Determined by gas chromatography analysis.

[c] Average of two runs.

[d] TON in moles of product per mole of nickel after 1 h.

THF. TEM and energy-dispersive X-ray spectra showed that the nickel(0) particles were highly ordered and that the microcrystalline units originally have an hcp structure. The supported nickel particles were active in the liquid-phase hydrogenation of alkenes and alkynes. In the case of dienes, the nickel/Al_2O_3 catalyst can be employed for mono- or di-hydrogenations, depending on the amount of hydrogen used and the reaction time. The heterogeneous nickel/Al_2O_3 catalyst can finally be recycled at least ten times with only a slight loss in performance.

EXPERIMENTAL

Materials and instrumentation

All manipulations were carried out under an atmosphere of nitrogen. THF was distilled from benzophenone–sodium

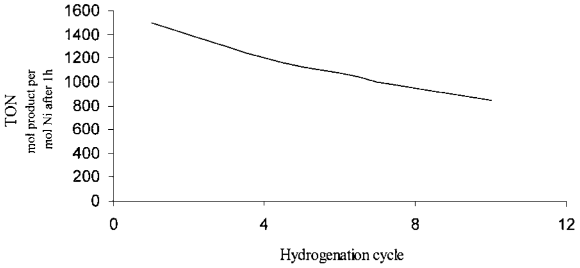


Figure 3. Evolution of the TON with the number of hydrogenation cycles.

adduct and stored over sodium wires. *tert*-Butyl alcohol (*t*-BuOH; Aldrich) was distilled from sodium. Acetone was dried over calcium chloride and distilled over potassium permanganate. EtOH was distilled over magnesium. NaH (65% in mineral oil, Fluka) was used after three washings with 20 ml of THF under nitrogen atmosphere. Ni(OAc)$_2$, NiCl$_2$ and Ni(NO$_3$)$_2$ were dried under vacuum (20 mmHg) at 110 °C for 12 h before use. The water content after drying was lower than 0.5 mol%. Anhydrous Ni(acac)$_2$ was used as received.

The commercially available supports were α-alumina (density: 2.22 g cm^{-3}; particle size: 75–250 μm) and a mixture of amorphous and crystallized alumina (density: 0.85 g cm^{-3}; particle size: 50–200 μm). These supports were dried at 110 °C under vacuum (20 mmHg) for 24 h before use.

The progress of hydrogenation reactions was monitored using a Shimadzu GC-17 capillary gas chromatograph fitted with an 'Optima 5' column (22 m × 0.25 mm, ID 0.25 μm). All quantifications of reaction constituents were achieved by gas chromatography using a known quantity of decane as internal reference standard.

Characterization of nickel nanoparticles

Characterization of supported nickel particles was performed using TEM. The TEM specimens were prepared by placing a drop of the catalyst in suspension in THF onto a carbon film supported on a copper grid and were studied using a Philips CM20 with LaB$_6$ cathode operating at 200 kV.

Preparation of the nickel(II)/Al$_2$O$_3$ catalyst precursors

The impregnation technique was used for the production of the supported nickel catalysts. The supported nickel(II)/Al$_2$O$_3$ catalysts were prepared by adding 20 g alumina to a vigorously stirred solution of the nickel(II) salt (18 mmol) in 50 ml deoxygenated solvent (acetone for Ni(acac)$_2$ and NiCl$_2$, water for Ni(OAc)$_2$ and Ni(NO$_3$)$_2$) heated at 50 °C. The solutions were stirred at 50 °C for 1 h and the solvent was evaporated in a rotary evaporator till dryness. The nickel(II)/Al$_2$O$_3$ catalyst precursors thus obtained were finally washed with degassed acetone (2 × 50 ml) and dichloromethane (2 × 50 ml) to remove the non-impregnated nickel and dried at 110 °C under 20 mmHg for 12 h before storage in a dessicator.

Preparation of the nickel(0)/Al$_2$O$_3$ catalysts

A 50 ml Schlenk tube was loaded with degreased NaH (58 mmol) and 15 ml THF. The impregnated nickel(II)/Al$_2$O$_3$ sample (2 mmol nickel(II) on Al$_2$O$_3$) was added under stirring at room temperature and the resulting mixture was heated at 65 °C. A solution of *t*-BuOH (4 mmol) in 5 ml THF was then added dropwise and the mixture was further stirred at 65 °C for 5 h. The suspension, which was initially green, changed gradually to black. After the reduction step, the catalysts were always handled under air-free conditions. After cooling to room temperature, to establish homogeneous sampling for all experiments, the stirred nickel(0)/Al$_2$O$_3$ catalysts suspended in THF were transferred with a syringe into the hydrogenation vessel.

Hydrogenation reactions using the nickel(0)/Al$_2$O$_3$ catalysts

The hydrogenation reactions were conducted in a 50 ml two-necked round-bottomed flask.[44,45] The substrate (20 mmol) was dissolved in 15 ml degassed EtOH and the solution was introduced into the reactor. After two flushings with hydrogen, hydrogenation was started under atmospheric pressure at room temperature by adding the nickel(0)/Al$_2$O$_3$ catalyst (0.2 mmol or 1 mmol respectively for hydrogenations performed with 1 mol% or 5 mol% catalyst; see Table 2) suspended in THF. The reaction mixture was magnetically stirred at 1000 rpm. The amount of hydrogen consumed during the reaction was determined by measuring the volume variations. After completion, the mixture was decanted. The reduced hydrocarbon in EtOH was removed using a syringe and the products were analysed by gas chromatography by comparison with authentic samples. Conversion was defined by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Starting material consumed (mmol)}}{\text{Starting material charged (mmol)}} \times 100$$

The nickel(0)/Al$_2$O$_3$ catalyst could be used immediately for the next hydrogenation cycle.

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