Reduction of aromatic compounds using Raney Ni–Al alloy, Al powder in the presence of noble metal catalysts in water

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Dedicated to Prof. George A. Olah Memorial Issue

Abstract

Over the last few years, heterogeneous catalysts have attracted much attention with a view to lowering reaction temperatures and improving the selectivity of many organic syntheses. When designing or optimizing a catalyst, attention is devoted to the nature of the active sites, and how they interact with the reactants, intermediates and products of the catalytic process. It has become clear that the structural and electronic features of an active site are usually affected by the chemical environment in which it operates. Raney Ni–Al alloy and noble metal catalysts such as Ru/C, Rh/C, Pd/C and Pt/C are employed in the selective and complete hydrogenation of various functional groups and aromatic rings in presence of water in a sealed tube. Al powder was found to be capable of reducing a carbonyl group, an alkyne group and the aromatic ring of biphenyl, fluorene, 9,10-dihydroanthracene, polyarenes and N-heterocycles using noble metal catalysts in water under mild reaction conditions.

1. Introduction

Catalysis has played a vital role in the success of the industries of the 20th century and will play an equally important role in the development of new greener industries of the 21st century. The most useful and widely applicable method for the reduction of chemical substances is via catalytic hydrogenation, a process which has found widespread application in organic synthesis as well as industrial processes. In early work, almost all catalytic hydrogenations were accomplished using heterogeneous catalysts. Later, homogeneous catalysts lead to further developments and extended the scope of catalytic hydrogenations to, for example, highly selective transformations. However, still today heterogeneous catalysts continue to offer many advantages over homogeneous catalysts such as the stability of catalyst, ease of separation of products from catalyst, a wide range of feasible reaction conditions and a high catalytic ability for the hydrogenation of hard-to-reduce functional groups including aromatic nuclei and sterically hindered unsaturated systems and for the hydrogenation of carbon-carbon bonds. Herein, some examples that highlight how highly selective hydrogenations have been achieved through heterogeneous catalysts are described, typically being coupled with effective additives, acids and bases, and solvents.

2. Hydrogenation Catalysts

For the hydrogenation, typically heterogeneous transition metal catalysts are employed in the form of metals, oxides, or sulfides that are either unsupported or supported. The physical form of a catalyst suitable for a particular hydrogenation is determined primarily by the type of reactors to be employed, such as fixed-bed, fluidized-bed, or batch. For industrial purposes, unsupported catalysts are seldom employed since supported catalysts have many advantages over unsupported catalysts. One exception to this is Raney-type catalysts, which are effectively employed in industrial hydrogenations in the unsupported state. In general, use of a support allows the active component to have a larger exposed surface area, which is particularly important for those cases where a high temperature is required to activate the active component. At that temperature, it tends to lose its high activity during the activation process, such as in the reduction of nickel oxides with hydrogen, or where the active component is very expensive as is the case with the platinum group metals. Unsupported catalysts have been widely employed in laboratory reactions, especially for hydrogenations using platinum metal. Finely divided platinum metal, often referred to as “blacks,” have been preferred for hydrogenation on a very small scale and have played an important role in the transformation or the determination of the structure of natural products that are available only in small quantities. The effect of an additive or impurity appears to be more sensitive for unsupported blacks than for supported catalysts. This is also in line with the observations that supported catalysts are usually more resistant to poisons than are unsupported catalysts [1]. Noble metal catalysts have also been employed in colloidal forms and are often recognized to be more active and/or selective than the usual metal blacks, although colloidal catalysts may suffer from disadvantages due to their instability and the difficulty in the separation of product from catalyst. It is often argued that the high selectivity of a colloidal catalyst results from its high degree of dispersion. However, the nature of the

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colloidal catalysts may well have been modified during the process with protective colloids or with the substances resulting from the reducing agents.

Supported catalysts may be prepared by a variety of methods, depending on the nature of active components as well as the characteristics of the carriers. An active component may be incorporated with a carrier in various ways, such as by decomposition, impregnation, precipitation, co-precipitation, adsorption or ion-exchange. Both-low and high surface area materials can be employed as carriers.

2. a. Nickel Catalysts

The preparation and activation of unsupported nickel catalysts has been studied by numerous investigators [2]. As originally studied by Sabatier and co-workers [3], nickel oxide free from chlorine or sulfur was obtained by calcinations of nickel nitrate. The temperature at which nickel oxide was reduced by hydrogen greatly affected the activity of the resulting catalyst. There is a considerable temperature difference between the commencement and the completion of the reduction. According to Senderens and Aboulenc [4], reduction commences at about 300 °C but the temperature must be raised to 420 °C for complete reduction, although insufficiently reduced nickel oxides are usually more active than completely reduced ones. On the other hand, Sabatier and Espil observed that the nickel catalyst from nickel oxide reduced at 500 °C and was maintained its ability to hydrogenate the benzene ring over 8 h at temperatures between 500 and 700 °C [5]. Benton and Emmett found that, in contrast to ferric oxide, the reduction of nickel oxide was autocatalytic and that the higher the temperature of preparation, the higher the temperature necessary to obtain a useful rate of reduction, and the less the autocatalytic effect [6]. Although the hydroxide of nickel may be reduced at lower temperatures than nickel oxide [4], the resulting catalyst is not only unduly sensitive but also difficult to control. When applied to phenol, it tends to produce cyclohexane instead of cyclohexanol [7]. Although supported catalysts may require a higher temperature for activation with hydrogen than unsupported ones, they are much more stable and can retain greater activity even at higher temperatures. Thus, reduced nickel is usually employed with a support like kieselguhr for practical purposes.

2. a. (i) Reduced Nickel

Many investigators, in particular, Kelber [8] Armstrong and Hilditch [9] and Gauger and Taylor [10], have recognized that nickel oxide when supported on kieselguhr makes itself a much more active catalyst than when unsupported, although the reduction temperature required for the supported oxide (350–500 °C) is considerably higher than that required for the unsupported oxide (250–300 °C). Gauger and Taylor studied the adsorption capacity of gases on unsupported and supported nickel catalysts prepared by reducing the nickel oxide obtained by calcining nickel nitrate at 300 °C. The adsorptive capacity of hydrogen per gram of nickel was increased almost 10-fold when supported on kieselguhr (10% Ni), although hydrogen reduction for more than one week at 350 °C or 40 min at 500 °C was required for the supported catalysts, compared to 300 °C or rapid reduction at 350 °C for the unsupported oxide. Adkins and co-workers [11–13] studied in detail the conditions for the preparation of an active Ni–kieselguhr catalyst by the precipitation method, which gave a much better catalyst system than those deposited by decomposing nickel nitrate on kieselguhr. Their results led to the following conclusions:

1) nickel sulfate, chloride, acetate or nitrate may be used as the source of nickel, provided that the catalyst is thoroughly washed, although nitrate is preferred because of the ease in obtaining the catalyst free of halide or sulfate (industrially, however, the sulfate is used by far in the largest quantities because it is cheap and the most generally available [14]).

2) for the carbonate catalysts, the addition of the precipitant to the soluble nickel compound on a kieselguhr gives better results than if the reverse order is followed i.e., the addition of the soluble nickel compound on a kieselguhr to the precipitant; and

3) with potassium hydroxide as the precipitant, the resulting catalyst is somewhat inferior to the carbonate catalysts prepared with sodium carbonate or bicarbonate, and ammonium carbonate is in general the most satisfactory precipitant.

2. a. (ii) Nickel from Nickel Formate

Nickel formate usually occurs as the dihydrate. When it is heated, it first loses water at about 140 °C and then starts to decompose at 210 °C to give a finely divided nickel catalyst with evolution of a gas mixture composed mainly of carbon dioxide, hydrogen and water [14]. The main reaction is expressed in eq.1.1 and some of the nickel formate may be decomposed according to the reaction in eq.1.2 [15–17].

$$Ni(HCOO)_2 \,.\, 2H_2O \longrightarrow Ni + 2CO_2 + H_2 + 2H_2O \qquad (1.1)$$

$$Ni(HCOO)_2 \,.\, 2H_2O \longrightarrow Ni + CO + CO_2 + 3H_2O \qquad (1.2)$$

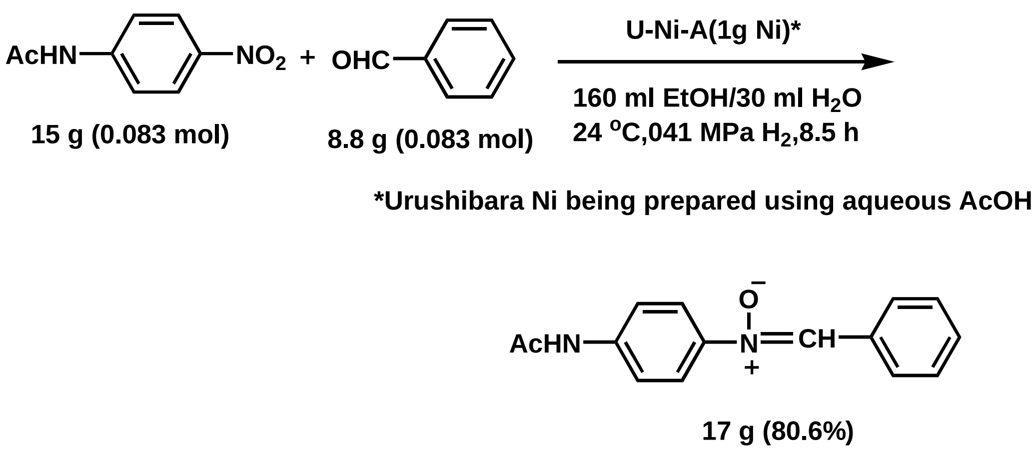
Thus, an active nickel catalyst may be prepared simply by heating the formate in oil at around 240 °C for about 1 h. This method has been employed in the oil-hardening industry for the preparation of a wet-reduced catalyst [18], although the decomposition temperature is too high for normal oil-hardening and the catalyst may not be prepared directly in a hydrogenation tank, particularly for edible purposes. Nickel formate is prepared by the reaction between nickel sulfate and sodium formate [19] or the direct reaction of basic nickel carbonate [20] or nickel hydroxide with formic acid.

2. a. (iii) Raney Nickel

In 1925 and 1927, Raney patented a new method for the preparation of an active catalyst from an alloy of a catalytic metal with a substance that may be dissolved by a solvent and that will not attack the catalytic metal. Firstly, a nickel–silicon alloy was treated with aqueous sodium hydroxide to produce a pyrophoric nickel catalyst. Shortly afterwards (1927), the method was improved by treating a nickel–aluminum alloy with sodium hydroxide solution, which allowed for more facile preparation and the pulverization of the aluminum alloy. Some of the most commonly used compositions of nickel and aluminum in the alloy are 50% Ni–50% Al, 42% Ni–58% Al and 30% Ni–70% Al. The nickel catalyst thus prepared is highly active and is now widely known as Raney Nickel, which is probably the most commonly used nickel catalyst not only for laboratory uses but also for industrial applications [21].

2. a. (iv) Urushibara Nickel

Urushibara nickel catalysts [22] are prepared by activating finely divided nickel deposited on zinc dust from an aqueous nickel salt, by either an alkali or an acid. The uniform deposition of finely divided nickel particles on zinc dust, which is obtained by the rapid addition of a concentrated aqueous solution of nickel chloride to a suspension of zinc dust in water at a temperature near 100 °C with efficient stirring during the addition, leads to a catalyst of high activity. Subsequent activation was accomplished by caustic alkali or an acid such as acetic acid [23,24]. The activation process by alkali or acid is assumed to involve the dissolution of basic zinc chloride, produced on the active nickel surface during reaction of the zinc dust with nickel chloride in water. Evidence for this was obtained from the dissolution of a large quantity of chloride ion by treatment with caustic alkali and by comparison of the X–ray diffraction patterns of nickel–zinc powders before and after treatment [25]. This assumption was later shown to be valid by Jacob *et al.* by means of X–ray photoelectron spectroscopy (XPS), X–ray diffraction, scanning electron microscopy (SEM) combined with X–ray energy dispersion (EDX), and wet chemical analysis [26]. The Urushibara catalyst obtained by activation with a base is abbreviated as U–Ni–B and the catalyst obtained with an acid as U–Ni–A. It should be noted that U–Ni–A contains a much smaller amount of zinc (0.5g/g Ni) than U–Ni–B (5g/g Ni) and is advantageous over U–Ni–B in those hydrogenations where the presence of alkali should be avoided. An interesting application of U–Ni–A is the synthesis of *N*–arylnitroes by hydrogenation of an aromatic nitro compound in the presence of an aldehyde.



(1.3)

2. a. (v) Nickel Boride

Paul *et al.* prepared active nickel catalysts by reducing nickel salts such as nickel chloride or nickel acetate with sodium or potassium borohydride [27]. The products thus obtained are neither magnetic nor pyrophoric and do not dissolve as quickly as Raney Ni in hydrochloric acid or potassium triiodide. They exhibited an activity comparable to or slightly inferior to Raney Ni, as exemplified by the hydrogenation of safrole, furfural and benzonitrile at room temperature and atmospheric pressure. Usually, the catalyst from nickel acetate was slightly more active than that from nickel chloride. In the hydrogenation of safrole, the catalyst exhibited a greater resistance to fatigue than Raney Ni in a series of 29 hydrogenations. The average composition of the catalyst deviated only slightly from a content of 7–8% boron and 84–85% nickel, which corresponds to the formula Ni_2B. Hence, such catalysts have been denoted nickel borides. A more active catalyst was obtained by introduction of an alkali borohydride into the solution of the nickel salt, since the formation of nickel boride was always accompanied by decomposition of the alkali borohydride according to eq. 1.4. The overall reaction is formulated as in eq. 1.5, although the boron content of the products has been reported to vary with the ratio of reactants used in preparation [28–29].

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2 \quad (1.4)$$

$$2Ni(OAc)_2 + 4NaBH_4 + 9H_2O \longrightarrow Ni_2B + 4NaOAc + 3B(OH)_3 + 12.5\ H_2 \quad (1.5)$$

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2. b. Cobalt Catalysts

Cobalt catalysts have been not as widely used as nickel catalysts for the usual hydrogenations, however their effectiveness *versus* nickel catalysts has often been recognized for the hydrogenation of aromatic amines and nitriles to the corresponding primary amines and also in Fischer–Tropsch synthesis [30]. The catalytic activity of reduced cobalt [31–32] and that of a properly prepared Raney Co [33] is even higher than those for the corresponding nickel catalysts in the hydrogenation of benzene. The methods of preparation for cobalt catalysts are very similar to those used for the preparation of nickel catalysts.

2. b. (i) Reduced Cobalt

The temperature required for the reduction of cobalt oxides to the metal appears to be somewhat higher than for the reduction of nickel oxide. Catalysts with a higher catalytic activity are obtained by the reduction of cobalt hydroxide or basic carbonate rather than by reduction of the cobalt oxide obtained by calcination of cobalt nitrate; the comparison was made in the decomposition of formic acid [34]. Winans reported good results when using technical grade cobalt oxide activated by freshly calcined powdered calcium oxide in the hydrogenation of aniline at 280 °C and an initial hydrogen pressure of 10 Mpa [35].

2. b. (ii) Raney Cobalt

Raney Co has been less studied compared to Raney Ni catalysts because of its lower activity and higher cost. For these reasons, Raney Co has found limited laboratory or industrial use. Early preparations and uses of Raney Co catalysts were described by the groups of Faucounau [36] Dupont [37] and Signaigo [38]. Faucounau prepared the catalyst by treating 47% Co–Al alloy with an excess of 30% sodium hydroxide below 60 °C until no more hydrogen was evolved (12 h). The resulting catalyst was used at 100 °C and 10MPa H_2 for the hydrogenation of olefinic compounds, aldehydes, ketones and aromatic side chain linkages. At 200 °C, the

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aromatic core could also be reduced. Dupont and Piganiol obtained a catalyst of improved activity for the hydrogenation of limonene and alloocimene, but the activity was still only about 1/400th of that of Raney Ni as compared in the hydrogenation of alloocimene under ordinary conditions. Signai developed a 50% Co–50% Al alloy by adding a concentrated sodium hydroxide solution to a suspension of the alloy in water under boiling conditions, and employed the catalyst for the hydrogenation of dinitriles to diamines in high yield at 10–13 MPa H_2.

2. b. (iii) Cobalt Boride

Cobalt boride catalysts have been shown to be highly active and selective in the hydrogenation of nitriles to primary amines [39,40]. Barnett and coworkers used Co boride (5%) supported on carbon for the hydrogenation of aliphatic nitriles and obtained the highest yields of primary amines among the transition metals and metal borides investigated including by Raney Co [40]. An example is the hydrogenation of propionitrile in isopropyl alcohol over cobalt boride (5% on C) in the presence of a 15:1 molar ratio of ammonia to the nitrile gave propylamine in a high yield of 99%.

$$\underset{\textbf{13.8 g (0.25 mol)}}{CH_3CH_2CN} \xrightarrow[\substack{\textbf{300 ml i-PrOH-NH}_3\ \textbf{(NH}_3\textbf{: nitrile 15:1)} \\ \textbf{70 }^{o}\textbf{C, 0.2 MPa H}_2\textbf{, 26 h}}]{\textbf{1 g Co boride (5\% on C)}} \underset{\textbf{99\%}}{CH_3CH_2CH_2NH_2} \qquad \textbf{(1.6)}$$

2. b. (iv) Urushibara Cobalt

Urushibara Co catalysts can be prepared in exactly the same way as the corresponding Ni catalysts, using cobalt chloride hexahydrate instead of nickel chloride hexahydrate as the starting material. Similarly, as with Raney catalysts, Urushibara Co has been found to be more effective and selective than Urushibara Ni in the hydrogenation of nitriles, affording high yields of primary amines [41, 42].

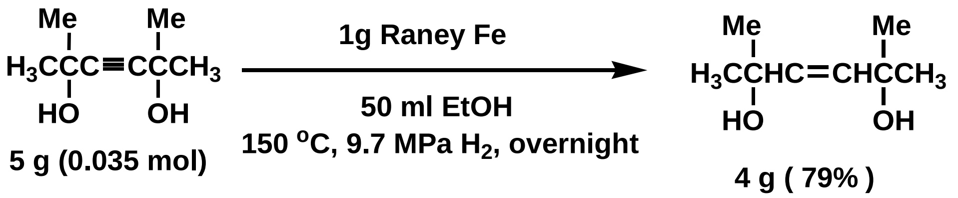
2. c. Copper Catalysts

For hydrogenation catalysts, unsupported reduced copper systems are usually not active and tend to loss activity at high temperatures. Sabatier prepared an active unsupported copper catalyst by slow reduction of black tetracupric hydrate with hydrogen at 200 °C [43]. Sabatier and Senderens originally claimed that benzene could not be hydrogenated over a copper catalyst [44]. However, Pease and Purdum were successful in transforming benzene into cyclohexane at 140 °C over an active copper catalyst, which was obtained by slow reduction of the oxide in hydrogen at an initial temperature of 150 °C and finally heating to 300 °C [45]. According to Ipatieff *et al.*, the hydrogenating activity of reduced copper is very much dependent on the presence of traces of impurities, especially of nickel [46]. Pure copper catalyst prepared from precipitated hydroxide or basic carbonate and containing not less than 0.2% of oxygen catalyzed the hydrogenation of benzene with difficulty at 225 °C and ordinary pressure, but readily hydrogenated benzene at 350 °C and a hydrogen pressure of 15 MPa. On the other hand, a copper catalyst containing 0.1% of nickel oxide readily hydrogenated benzene at 225 °C under normal pressure. Thus, copper catalysts are almost completely inactive towards the hydrogenation of benzene under usual conditions [31, 32]. However, copper catalysts are known to be highly selective, as in the partial hydrogenation of polynuclear aromatic compounds such as anthracene and phenanthrene, and also in the selective hydrogenation of nitrobenzene to aniline without affecting the aromatic nucleus [47–49].

2. d. Iron Catalysts

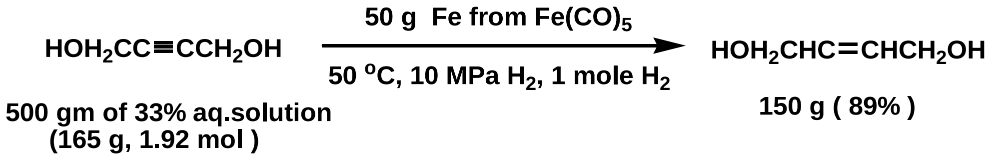
Iron catalysts have found limited use in common hydrogenations, although they play industrially important roles in the ammonia synthesis and the Fischer–Tropsch process. Iron catalysts have been reported to be selective for the hydrogenation of alkynes to alkenes at elevated temperatures and pressures. Raney Fe, which was inert for the hydrogenation of olefins, was effective for the semi-hydrogenation of acetylenes as reported by Paul and Hilly [50]. The absorption of hydrogen ceased spontaneously after the uptake of 1 equiv. Thus, over Raney Fe, hydrogenations of 1-heptyne (135 °C and 5.2 MPa H_2) and 1-octyne (100 °C and 6.2 MPa H_2) afforded the corresponding 1-alkenes in 90 and 85% yields, respectively. Thompson, Jr. and Wyatt also studied the use of Raney Fe for the partial hydrogenation of acetylenes

[51]. Although diphenylacetylene was hydrogenated to dithenylmethane at 100 °C and 6.9 MPa H_2, 2,5-dimethyl-3-hexyne-2,5-diol was hydrogenated nearly quantitatively to the corresponding olefin at 150 °C and 9.7 MPa H_2 (Eq 1.7).



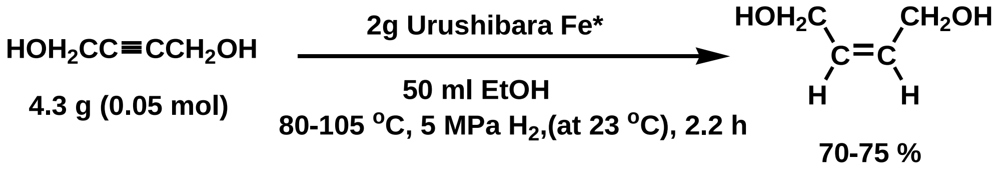
(1.7)

Reppe *et at.* hydrogenated 2-butyne-1,4-diol over an iron catalyst, prepared by the decomposition of pentacarbonyliron in water at 50 °C and 10 MPa H_2 and obtained 2-butene-1,4-diol in 90% yield, by interrupting the reaction at the uptake of hydrogen corresponding to 1equiv. (eq 1.8) [52].



(1.8)

Taira hydrogenated 2-butyne-1,4-diol using Urushibara Fe as the catalyst in ethanol at 80–100 °C and an initial hydrogen pressure of 5–7 MPa until the hydrogen uptake ceased and obtained *cis*-2-butene-1,4-diol in 70-75% yield (eq 1.9) [53].



(1.9)

*** Prepares from the reaction of $FeCl_3$ with Zn dust followed by digestion with aq. AcOH**

2. e. Platinum Group Metal Catalysts

The platinum group metals such as ruthenium, rhodium, palladium, osmium, iridium and platinum have all been used as hydrogenation catalysts. Platinum appears to be the first transition metal that was used as a catalyst for hydrogenation. In as

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early as 1863, Debus found that methylamine was produced by passing hydrogen cyanide vapor, mixed with hydrogen, over platinum black [54]. Among the platinum metals, platinum and palladium have been by far the most widely used catalysts since the earliest stages of catalytic hydrogenation. A characteristic feature of these metals is that they are active under very mild conditions, compared to the base metals, and have conveniently been used in liquid-phase hydrogenation at room temperature and atmospheric or only slightly elevated pressure of hydrogen. Willstatter and Hatt subjected benzene to hydrogenation to give cyclohexane over a platinum black at room temperature and atmospheric pressure in acetic acid or without solvent [55]. Subsequently, a number of aromatic hydrogenations were conducted using platinum catalysts at room temperature and low hydrogen pressure. On the other hand, since the early twentieth century, palladium catalysts have been widely employed for the selective hydrogenation of acetylenic and olefinic compounds under mild conditions. Ruthenium and rhodium received little attention until the mid-1950s, but since then they have been widely used as highly active and selective catalysts for the hydrogenation of various compounds, in particular, for aromatic hydrogenations. Osmium and iridium have found much less use than the other four metals mentioned above, although high selectivity was often recognized as a property of these catalysts in some hydrogenations.

Platinum metal catalysts have been employed either in the form of unsupported fine metal particles, which are usually referred to as blacks, or are used in a supported state on inert porous or nonporous materials. Unsupported catalysts may also be prepared in a colloidal form by liberating the metal in the presence of a suitable protective colloid. Unsupported catalysts still find wide use in laboratory hydrogenations and are preferred particularly for small scale hydrogenations where loss of product should be avoided. On the other hand, supported catalysts have many advantages over unsupported catalysts. Supports permit a greater efficiency in the use of an expensive metal by giving a larger exposed active surface and in some cases may facilitate metal recovery. Further, supported catalysts usually have a greater

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resistance to poisoning and are more stable at elevated temperatures and/or pressures. The activity and/or selectivity of a supported catalyst, however, may rely greatly on the physical and chemical nature of the support used. Most of the platinum metal catalysts supported on carbon or alumina are commercially available.

2. f. Rhenium Catalysts

At the beginning of 1951, Broadbent and coworkers published a paper on the attractive catalytic properties of Rhenium catalysts in hydrogenations [56]. Prior to that, this metal as a hydrogenation catalyst had attracted little attention. The first paper to address this appeared in 1954 [57]. Some characteristic properties of rhenium catalysts are now known, such as their efficiency in the selective hydrogenation of α, β-unsaturated aldehydes to unsaturated alcohols, the hydrogenation of carboxylic acids to alcohols, and the hydrogenation of carboxamides to amines. Rhenium also plays an important role, together with platinum, in a reforming process known as *rheniforming* [58]. Ammonium perrhenate NH_4ReO_4 or rhenium heptoxide Re_2O_7 are the usual convenient starting materials for the preparation of the catalysts.

2. g. The Oxide and Sulfide Catalysts of Transition Metals other than Rhenium

In addition to hydrogenation and hydrogenolysis, transition metal oxides or sulfides are capable of catalyzing various reactions, although usually at relatively high temperatures and pressures. Compared to metallic catalysts, they are resistant to poisons and stable at high temperatures. Industrially, they are often used as mixed oxides or sulfides. For example, the most common catalyst used in the hydro-desulfurization process is a mixture of cobalt and molybdenum oxides supported on γ-alumina, which is sulfide before use??. Nickel-molybdenum and nickel-tungsten oxides are also known as effective catalyst systems for this process [59]. Molybdenum sulfides are active for the hydrogenolysis of aldehydes, ketones, phenols and carboxylic acids affording the corresponding hydrocarbons [60]. They are also effective for the hydrogenolysis of sulfur-containing compounds. The sulfides of the platinum metals have been found to be active at lower temperatures than are required when using the base metal sulfides. They are tolerant of poisons and have proved particularly useful for conducting hydrogenations in the presence of impurities. They can also be used for the hydrogenation of sulfur-containing compounds, and for the selective hydrogenation of halogen-containing aromatic nitro compounds [61].

3. Hydrogenation Reaction Using Water as Solvent

An essential aspect of Green Chemistry is to utilize water not only as a source of hydrogen and/or oxygen but also as an alternative solvent [62]. Water as a solvent for organic reactions has many advantages over organic solvents including amongst others things its cost, safety, simplicity of operation and most importantly its benign environmental nature [63–65]. Recently, the Pd/C-Al-water-facilitated selective reduction of a broad variety of functional groups and Pd/C catalyzed hydrogenolysis of dibenzodioxocin lignin model compounds using silanes and water as a hydrogen source has been reported [66, 67]. Also, water has been used as a stoichiometric H or D atom donor for the tetrahydroxydiboron-mediated palladium-catalyzed transfer hydrogenation and the deuteriation of alkenes and alkynes [68]. In addition, hydrogenations and deuterium labeling has been carried out with Al-based metal alloys under aqueous conditions [69].

3. a. Hydrogenation of Carbonyl Group

An important reaction in synthetic organic chemistry is the transformation of a carbonyl group to a methylene unit. For the reduction of a carbonyl group, various classical types of reduction methods such as alkali metal–mediated reduction in liquid ammonia [70], Lewis acid–promoted metal–hydride reduction [71], Clemmensen reduction [72], and Wolf–Kishner–Huang–type reductions [73, 74] are typically employed. Further methods have been developed such as H_3PO_2–mediated reduction [75], reduction in supercritical *i*-PrOH at high temperatures (350–400 °C) [76], hydrogenation of aromatic ketones catalyzed by sol-gel entrapped combined with Pd–$[Rh(COD)Cl]_2$ under high hydrogen pressure (400 psi) [77], a hydrogenation procedure in a three–phase emulsion [78], and a Pd–catalyzed hydrogenation of ketones at a high temperature (200 °C) under a hydrogen atmosphere of 30 bar [79]. Also sodium dithionite promoted reduction, Pt and Pd catalyzed hydrogenation, Ru-mediated reduction in presence of HCO_2H/Et_3N, electrochemical reduction and yeast-catalyzed reduction [80–84] have been reported. Some of the literature methods have disadvantages such as harsh reaction conditions, whereby high reaction temperatures and/or high pressure are employed, or hazardous reagents are used, and a large amount of reducing agents is usually required.

The selective reduction of ketones and reductive amination of carbonyl compounds has been reported, based on the application of Raney-type Ni–Al alloy in aqueous medium as the hydrogen source as well as solvent [85,86]. Tashiro *et al.* have pioneered the use of various metal-Al alloys (Ni–Al, Co–Al, Cu–Al, Fe–Al) in water for the reduction of aryl ketones to the corresponding alcohols or alkane derivatives. Raney Ni–Al alloy in water was found to be a good reducing agent for the reduction of aromatic ketones and aldehydes to the corresponding cyclohexane derivatives, but a large amount of alloy was required in these studies [87]. Thereafter, the reduction of acetophenones was performed using Raney Ni–Al alloy in water under microwave irradiation. Also reported were the reductive reactions of a series of aromatic ketones with noble metal catalysts such as Rh, Ru, Pd or Pt in the presence of Al powder in water in a sealed tube [88,89]. Recently, the reduction or the oxido-reduction reaction of cinnamaldehyde and its derivatives with Ni–Al alloy and Al powder in water was also reported [90].

The different chemical species and the reaction mechanisms involving triethylamine in water and other organic solvents possibly affected the dehydrochlorination reactivity or selectivity of chlorophenols over Raney Ni and a facile hydrogenation of ketones catalyzed by Pt/C at ordinary pressure and temperature [91,92]. The chemoselective reduction of various carbonyl compounds to alcohols with ammonia-borane, a non-toxic, environmentally benign and easily handled reagent in neat water was achieved and with quantitative conversion and a high isolated yield [93]. Previously, benzophenone was selected as the model compound for the reduction of the carbonyl group as well as the aromatic rings [94, 95]. Yamato *et al.* have also explored the reduction of benzophenone using Raney Ni–Al alloy and Al powder in the presence of a noble metal catalyst in water at a relatively low temperature in a sealed tube [96].

3. b. Hydrogenation of an Alkyne Group

Addition of hydrogen to aromatic alkynes is another important transformation in synthetic organic chemistry. Catalytic hydrogenations using hydrogen gas or hydride transfer agents are commonly employed for this transformation. Numerous hydrogenation reactions have been reported, for which the active catalysts commonly employed include systems based on metals such as Pd, Rh, Ru, Ni, Pt, Ir, Os, V, Fe, and Nb [97]. There is particular interest in the use of Pd given its excellent performance in the selective hydrogenation of alkynes [98]. Nowadays, isolated single atom Pd sites in intermetallic nanostructures are used for the high catalytic selectivity in the semi-hydrogenation of alkynes and light mediated preparation of palladium nanoparticles as catalysts for alkyne *cis*-semi-hydrogenation [99,100]. It was found that *N*,*N*-dimethylformamide (DMF) can act as a hydride source in the nickel-catalyzed asymmetric hydrogenation of α,β-unsaturated esters [101]. Also a Hantzsch amido dihydropyridine has been reported as a transfer hydrogenation reagent for α, β-unsaturated ketones, while pyridine derivatives were reduced via a borane-catalyzed transfer hydrogenation reaction with ammonia-borane [102,103]. Recently, the use of a copper catalyst as a monophasic catalytic system and silica-supported copper nanoparticles has been reported for the selective semi-reduction of alkynes [104,105]. In another study, a non-classical Co-H_2 system was used to assess the effect of hydrogen spin on isomerization and E-selectivity in an alkyne semi-hydrogenation reaction [106]. Unfortunately, some industrial reduction processes face a challenging problem involving separation of reduced products from unreacted feed gaseous starting materials. To that end, rationally tuned micropores within enantiopure metal-organic frameworks (MOFs) have been explored for the highly selective separation of acetylene and ethylene, as well as tuning the gate opening pressure of metal-organic frameworks for the selective separation of hydrocarbons [107,108]. Moreover, microporous metal-organic frameworks with dual functionalities are suitable for the highly efficient removal of acetylene from ethylene/acetylene mixtures. In addition, a microporous metal-organic framework for the highly selective separation of acetylene, ethylene and ethane from methane at room temperature has been reported [109,110]. Very recently, disilaruthena- and ferracyclic complexes containing isocyanide ligands were used as effective catalysts for the hydrogenation of unfunctionalized sterically hindered alkenes. [111] Moreover, chemoselective hydrogenation has been reported for a supported organoplatinum (IV) catalyst on Zn (II)-modified silica [112].

Over a century ago, Paul Sabatier developed nickel-catalyzed hydrogenations, which have become one of the most commonly applied procedures for organic synthesis [113,114]. Hydrogen is an explosive gas and its production via steam reforming is a highly energy-intensive (700–1000 ^{o}C) process and it also causes considerable emission of carbon dioxide, a well-known greenhouse gas [115]. Thus, the current method for the production of hydrogen cannot be considered to be environmentally-friendly. Therefore, the overall environmental impact of catalytic hydrogenation cannot be considered negligible.

3. c. Hydrogenation of Aromatic Rings

The reduction of aromatic rings is a useful and important technique for obtaining a variety of cyclohexane derivatives. Because of resonance stabilization of the aromatic ring, aromatic hydrocarbons are rarely hydrogenated at room temperature over base metals and Pd catalysts [116]. However, using Ni and Co catalysts at elevated temperatures and pressures most aromatic hydrocarbons can be hydrogenated without any difficulty [117–119]. Moreover, Ru in particular performs better than Rh and Pd in the case of the hydrogenation of benzene and its derivatives at considerable rates even at room temperature [120–122]. Methods reported for the conversion of arenes into cyclohexane derivatives involve two types of reactions: One is the reduction with a greater than stoichiometric amount of reducing agents, such as $LiAlH_4$, borane derivatives [123–126] or dissolving metals (Birch reduction) [127,128]. These reagents are moisture-sensitive and the reaction should be conducted under anhydrous, strongly reducing and basic conditions. These reaction conditions cannot be tolerated by some functional groups, such as esters and ketones. Moreover, a large amount of metal waste is produced under these reaction conditions. Another type is hydrogenation with a transition-metal catalyst, which is a simple, convenient and sustainable method [129,130]. Recently, Raney Ni–Al has been found to be very efficient in the reduction of various aromatic compounds as well as for dechlorination of mono- and dichlorobiphenyls to the corresponding cyclohexane derivatives. The above reaction occurs in the absence of any organic solvents under milder reaction conditions along with dilute KOH or NaOH solutions in order to accelerate the reduction systems [131–134].

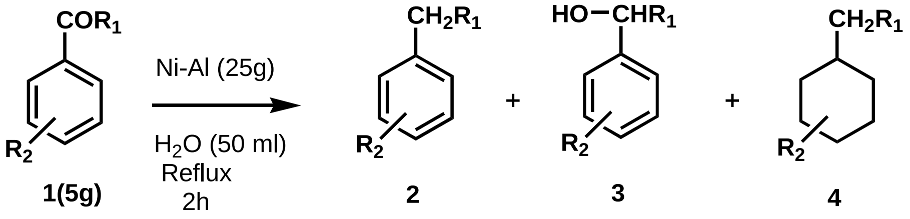
3. d. Hydrogenation of *N*-Heterocycles

Recently, the selective reduction of ketones was reported based on Ni–Al alloy coupled with a high hydrostatic pressure in an aqueous medium. [135] The selective reduction of unprotected indoles as well as quinolines in water using Ni–Al alloy has also been reported [136]. Tashiro *et al.* carried out the reduction of quinoline with Raney Ni–Al alloy in acetic acid aqueous solution [137]. More recently, the application of a heterogeneous catalyst in combination with microwave irradiation has been employed as an environmentally benign tool for some contemporary organic syntheses [138,139]. The first general catalytic approach to effecting transfer hydrogenation (TH) of unactivated alkenes using ethanol as the hydrogen source has been developed by Zheng *et al.* Here, a new NCP-type pincer iridium complex (^{BQ}-NC^{O}P)IrHCl containing a rigid benzoquinoline backbone has been developed and used for an efficient, mild TH of unactivated C–C multiple bonds with ethanol, forming ethyl acetate as the sole byproduct. A wide variety of alkenes such as multi-substituted alkyl alkenes, aryl alkenes, heteroatom-substituted alkenes, O- or *N*-containing heteroarenes and internal alkynes are suitable substrates [140].

4. Hydrogenation Using Various Heterogeneous Catalysts

4. a. Raney Ni–Al Alloy

The reduction of a carbonyl group has been carried out using commercially available heterogeneous catalysts in water for the development of an environmentally benign methodology. The functional group that can undergo reduction has been assessed in terms of applicability, yields and chemoselectivity. The reduction of acetophenone has been conducted using various heterogeneous catalysts such as Ni–Al, Co–Al, Cu–Al, Fe–Al in refluxing water for 2h in a sealed tube. Among them, Raney Ni–Al alloy in water was found to be a good reducing agent for the reduction of aromatic ketones and aldehydes to the corresponding cyclohexane derivatives, but a large amount of alloy was employed in these studies [87].



1a : $R_1 = CH_3$, $R_2 = H$;1b : $R_1 = CH_2CH_3$, $R_2 = H$

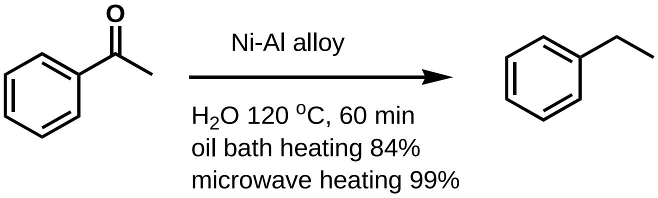
1c : $R_1 = CH_2CH_2CH_3$, $R_2 = H$;1d : $R_1 = CH(CH_3)_2$, $R_2 = H$

1e : $R_1 = CH_3$, $R_2 = 4\text{-}CH_3$;1f : $R_1 = CH_3$, $R_2 = 3\text{-}CH_3$

1g : $R_1 = CH_3$, $R_2 = 2\text{-}CH_3$;1h : $R_1 = C_6H_5$, $R_2 = H$

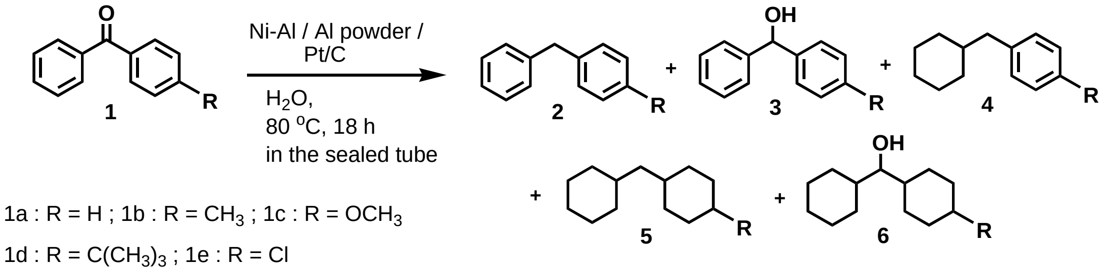
Scheme 1. Reduction of acetophenone using Raney Ni–Al alloy in H_2O [87].

The current decade has seen a tremendous increase in microwave-assisted chemistry. Microwave irradiation drastically accelerates the reaction rate and occasionally enhances the selectivity. To achieve more environmentally benign chemical processes, microwave irradiation is considered as a powerful tool in the field of Green Chemistry. Tashiro *et al.* have introduced microwaves in the reduction of acetophenones with a Raney Ni–Al alloy in water and demonstrated a convenient reduction system. They also reported that the reaction proceeds very rapidly and can be used for deuteration.



Scheme 2. Microwave assisted reduction of acetophenone using Raney Ni–Al alloy in H_2O [88].

Thereafter, benzophenones have been easily reduced to the corresponding hydrocarbon derivatives using Raney Ni–Al alloy in a dilute alkaline aqueous solution without the need for any organic solvents [95]. This method was also used for the reduction of alkylbenzils and alkoxybenzils under similar reaction conditions [134]. Moreover, Yamato *et al.* have developed a new method for the reduction of benzophenone using Raney Ni–Al alloy and Al powder in presence of a noble metal catalyst in water without using any alkaline solution at a relatively low temperature in a sealed tube [96]. The effect of the reaction temperature, reaction time, amount of Ni–Al alloy and the optimum volume of water for the reduction of benzophenone, as shown in fig.1, was investigated. It was observed that Raney Ni–Al alloy in water at 60 °C for 3 h is effective for the reduction of carbonyl groups to methylene moieties in high yields. Pt/C turns out to be the most effective catalyst in the presence of Raney Ni–Al alloy and Al powder at 80 °C for 18 h for the reduction of aromatic rings. A plausible reaction mechanism for benzophenone reduction as presented in fig. 2 was reported.



Scheme 3. Reduction of benzophenones using Raney Ni–Al alloy, Al powder and Pt/C in H_2O [96].

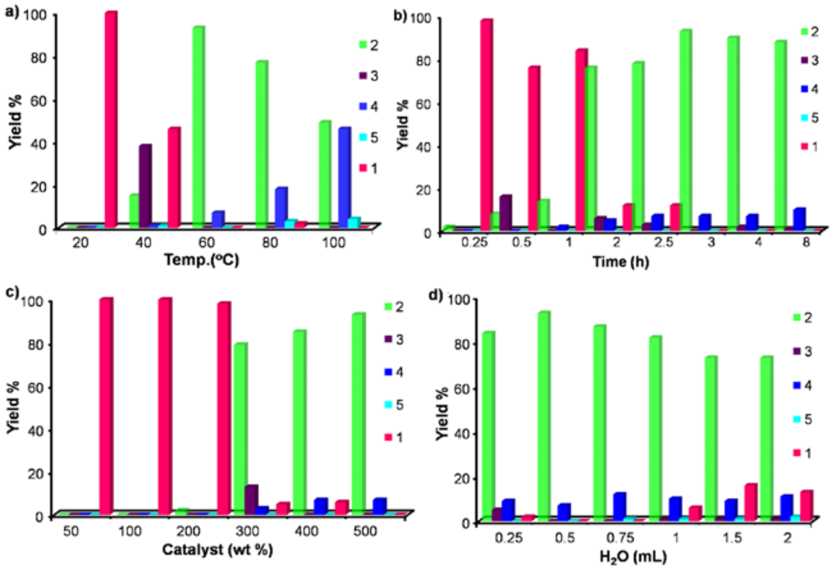


Fig. 1 Reduction of benzophenone using Raney Ni–Al alloy; (a) Temperature effect; (b) Time effect; (c) Catalyst effect; (d) H_2O effect.

Plausible reaction mechanism for benzophenone

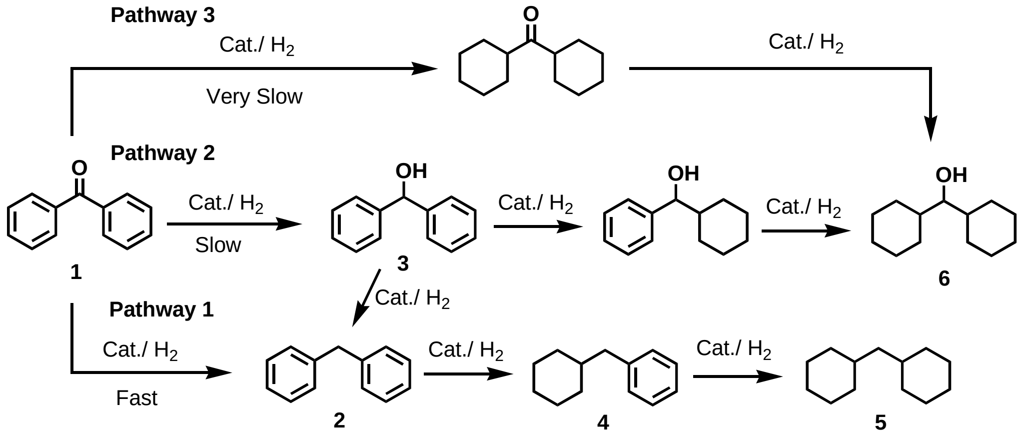
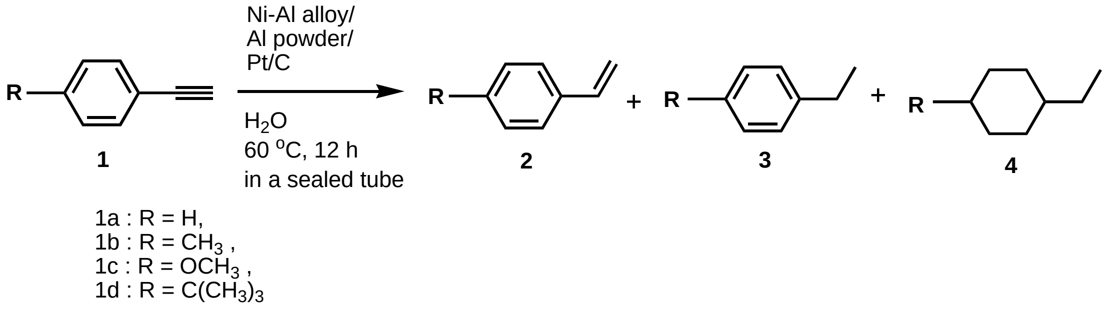


Fig. 2 Proposed reaction pathways for the reduction of benzophenone.

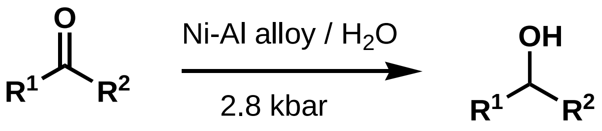
Based on the GC–MS results, it can be assumed that the pathway **1** is a faster way compared to other reaction pathways (**2** and **3**). It may be concluded that the approach of benzophenone towards the catalyst surface is much more favorable to give the desired product in a high yield.

Yamato *et al.* have also established that Raney Ni–Al alloy coupled with Al powder is a good reducing agent for the reduction of an alkyne group to the ethyl radical in high yield. On the other hand, the addition of Pt/C to the mixture of Raney Ni–Al and Al powder was found to be the best catalytic system for the reduction of the aromatic ring at 60 ^oC for 12 h which generates sufficient nascent hydrogen [141].



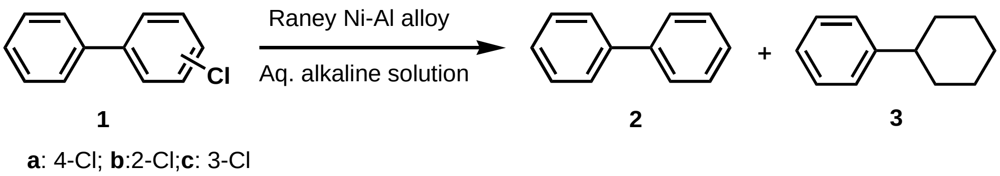
Scheme 4. Reduction of substituted phenylacetylenes (1a-1d) using Raney Ni–Al, Al powder and Pt/C in H_2O [141].

Török *et al*. developed a method for the selective reduction of ketones based on the combination of Raney Ni–Al alloy and high hydrostatic pressure (HHP, 2.8 kbar) in an aqueous medium. The reaction of the Raney Ni–Al alloy with water provides *in situ* hydrogen generation as well as high pressure to ensure the hydrogen generated remains in the solution to allow reduction of carbonyl group [135].



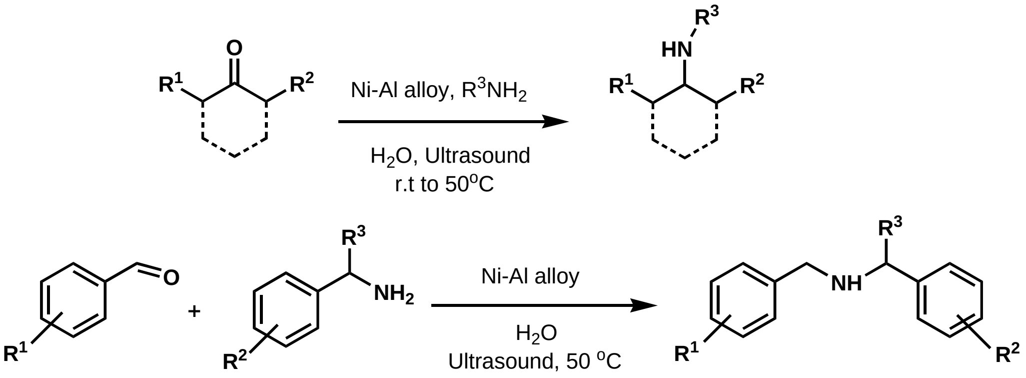
Scheme 5. Reduction of acyclic, cyclic and aryl ketones to their corresponding secondary alcohols with Raney Ni–Al alloy in H_2O under high hydrostatic pressure [135].

Nowadays, much attention has been devoted to the development of methods involving safe, convenient reagents and solvents to minimize waste formation leading to environmentally sustainable process. Polychlorobiphenyls (PCBs) which have once been widely used as an insulator in transformers are found to be hazardous with a high lifespan remaining in the environment for decades. To reduce the environmental hazard due to the above persistent chlorinated organic compounds, Raney Ni–Al alloy in dilute alkaline solution without organic solvents has been found to be an effective agent for dechlorination. This procedure is characterized by ease and quickness of the reaction as well as simple manipulation and mildness of the reaction conditions [131,132].



Scheme 6. Dechlorination of substituted chlorobiphenyls

Primary amines are important building blocks whereas the secondary benzylated benzylamines and anilines are biologically active compounds of pharmaceutical importance. Reductive amination is a well-known process for the preparation of primary and secondary amines. The abovementioned reduction system has also been employed for reductive amination as a green transformation under mild and environmentally benign conditions [86]. This is illustrated below [Scheme 7].



Scheme 7. Selective reductive amination of ketones and aldehydes by Ni–Al alloy in water [86]

Retro-reductive aminations followed by direct transformations of amines to ketones with Pd/C in water under microwave irradiation have been reported by Tashiro *et al.* [142, 143], and this is shown in fig 3.

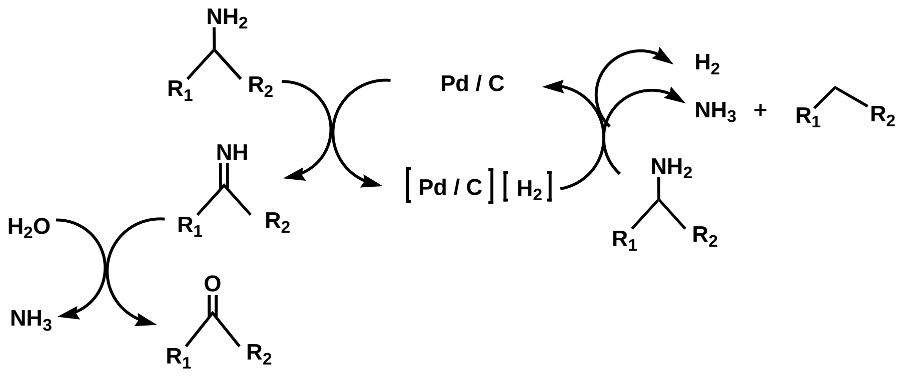
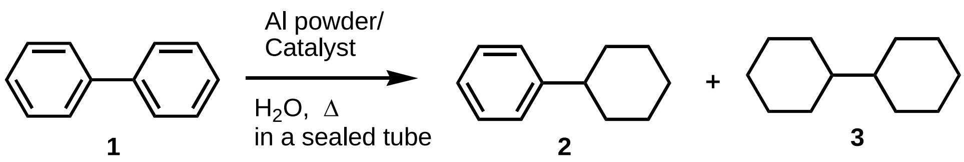


Fig 3. Plausible reaction mechanism for retro-reductive aminations catalyzed by Pd/C in water under microwave irradiation [142].

4. b. Al Powder and Noble Metal Catalysts

In 2006, Tashiro *et al.* carried out the reduction of alkylbenzenes with Rh/C, Ru/C, Pd/C, Pt/C and Al powder in water under refluxing conditions in sealed tubes using sonication which afforded the corresponding cyclohexane derivatives in good yields. The same group also conducted the reduction of polyarenes including biphenyl, naphthalene, acenapthalene and anthracene. It was observed that the reduction of naphthalene led to a mixture of *cis*- and *trans*-decalines with variable ratios under the reaction conditions employed. The reaction was carried out at 130 ^{o}C and a large amount of catalyst was employed. These substrates were also studied with deuterium oxide under the same reaction conditions [144]. Subsequently, Yamato *et al.* carried out the reduction of aromatic compounds such as biphenyl, fluorene and 9,10-dihydroanthracene under mild reaction conditions in presence of noble metal catalysts such as Pd/C, Rh/C, Pt/C or Ru/C with Al powder in sealed tube without any organic solvent at a low temperature. Partial aromatic ring reduction was found with Pd/C and Al powder at 60 °C for 24 h whilst complete reduction of both aromatic rings takes place with Al powder in presence of Pt/C at 80 °C for 12 h [145].



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Scheme 8. Reduction of biphenyl (1) using Al powder and noble metal catalyst in H_2O.

Recently, Yamato *et al.* developed a method for the reduction of diphenylacetylenes to the corresponding diphenylethanes in water in excellent yield using Al powder and Pd/C at 60 °C for 3 h in a sealed tube. The complete reduction of both aromatic rings required 80 °C for 15 h with Al powder in the presence of Pt/C and the following reaction pathways have been suggested [146].

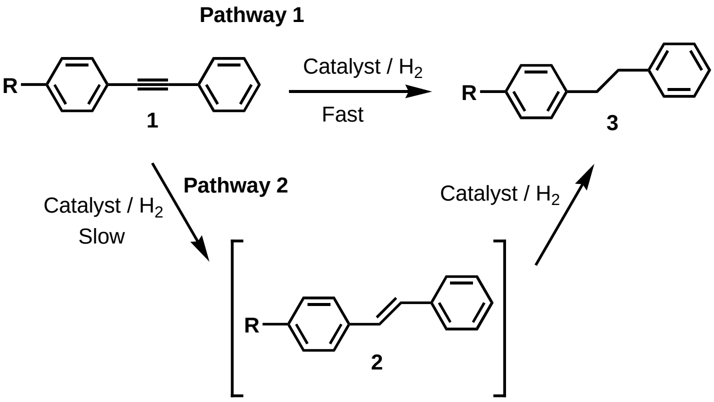

Fig. 4 Proposed reaction pathways for the reduction of diphenylacetylenes.

Reduction of aniline can be carried out with noble metal catalysts in the presence of Al powder in water to the corresponding cyclohexane derivatives. These catalysts not only reduce the aniline but also produce the secondary amine and bicyclohexylamine [147]. The reaction was carried out at high temperature and a large amount of catalyst was used. Recently, Török *et al*. developed a new method for the reduction of various functional groups and aromatic rings as well reductive amination using the above mentioned catalyst under mild reaction conditions. The proposed reaction mechanism for the formation of dicyclohexyl amine from cyclohexanone oxime with 5% Pd/C –Al powder/H_2O system is shown in fig.5 [66].

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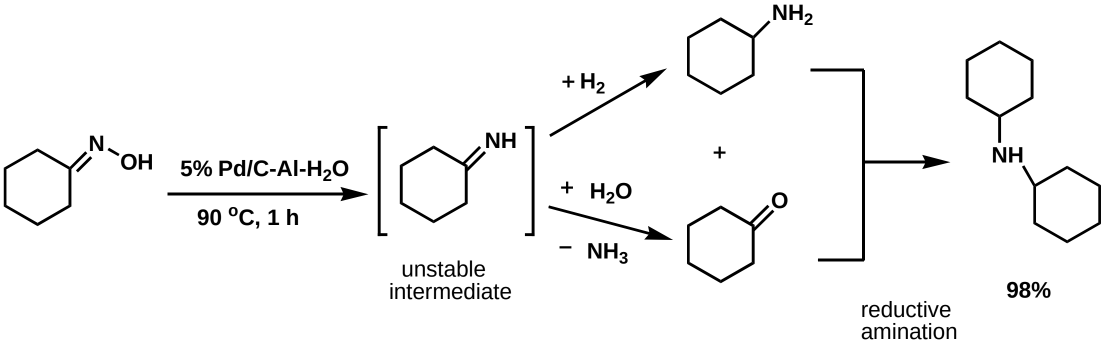
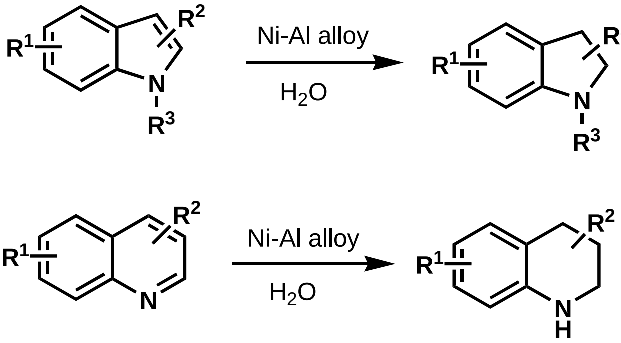


Fig. 5 proposed reaction mechanism for the formation of dicyclohexyl amine from cyclohexanone oxime.

This group also illustrated a simple method for the selective reduction of variety of substituted indoles and quinolines to indolines and tetrahydroquinolines using Raney Ni–Al alloy in water [136]. Tashiro *et al.* also carried out the reduction of quinoline but they also used acetic acid with water [137].



Scheme 8. Selective reduction of indoles and quinolines in water by a Ni–Al alloy [136].

Tashiro *et al.* developed a convenient method for the reduction of imines using zinc powder. They performed the reductive coupling of aromatic imines by the use of zinc powder and additives such as NH_4Cl and 1-tyrosine in water without any organic solvents under mild conditions to give the corresponding vicinal diamines in good yields. Similarly, cross coupling of *N*-benzylideneaniline and benzaldehyde proceeds in aqueous media to afford the corresponding 2-aminoalcohol [148,149]. On the other hand, highly meso-diastereoselective pinacol coupling of aromatic aldehydes mediated by aluminium powder/copper sulphate in water under reflux conditions is known [150].

5. Conclusion

Current reduction methods using heterogeneous catalysts for the reduction of various functional groups as well as aromatic rings in water under mild reaction conditions are discussed herein. Raney Ni–Al alloy in water is an effective reducing agent for the selective reduction of functional groups under various reaction conditions. In addition, microwave irradiation also accelerates the reaction process. Furthermore, heterocyclic aromatic rings can also be reduced using this catalytic system. On the other hand, noble metal catalysts together with Al powder in water can reduce aromatic rings. Furthermore, reductive amination can take place when using noble metal catalyst in water. Moreover, copper sulfate with Al powder in water can play an important role in the case of the pinacol coupling reaction and the reductive coupling of aromatic imines when performed by Zn powder with additives in water. The reaction occurs under mild reaction conditions using water as the hydrogen source which is a cheap and environmentally friendly solvent. Finally, all the techniques are considered green, which provides another very important protocol for the reduction of aromatic compounds.

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