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Catalytic syntheses of aromatic amines

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Abstract

The most important manufacturing processes for aniline and other bulk arylamines are based on the continuous catalytic hydrogenation of nitro compounds, employing heterogeneous copper, nickel or platinum-group metals. For more complex amines produced on a smaller scale, homogeneous catalysis with its greater possibilities for chemo- and regioselective hydrogenation is increasingly the method of choice. A newer alternative process of increasing importance for aniline and phenylenediamines is the nucleophilic amination of phenols. The catalytic amination of haloarenes has also been employed commercially. Amination processes also find application in the production of pyridines and pyrroles.

1. Introduction

A survey of catalytic routes to aromatic amines is presented. These include the hydrogenation of nitroarenes and the amination of phenols, haloarenes and others. Also covered are amination routes to pyridines and pyrroles.

Rather than attempting to provide comprehensive coverage of such a broad area, a selection has been made by placing emphasis on aspects that are the subject of recent or current research attention. For other topics, citations to secondary literature such as reviews, monographs and reference works are given where these provide recent overviews. For published work from Japan and other Asian countries, English language publications have generally been relied on.

2. Arylamines

The arylamines include a number of bulk organic chemicals, including aniline itself, diphenylamine and the phenylenediamines. The aniline derivative 4,4′-methylenedianiline, produced by condensation with formaldehyde, and the toluenediamines are intermediates in the manufacture of isocyanates and polyurethanes.

Aromatic amination is conducted on scales ranging from the large-scale, continuous production of the above industrial products to the small-scale batch manufacture and laboratory synthesis of large numbers of substituted derivatives.

For the production of aniline and other bulk arylamines, catalytic hydrogenation of nitroarenes has long displaced the traditional Bechamp reduction employing iron and hydrochloric acid. To a lesser extent, the amination of chlorobenzenes has also been employed, while in recent years catalytic amination of phenols has become an important commercial process. These alternatives are summarized in Scheme 1.

While heterogeneous catalysts are employed in large-scale processes, a growing literature attests to the importance of homogeneous catalysis for smaller scale synthetic applications. For speciality products, aryl nitroso compounds or hydroxylamines may form alternative starting materials.

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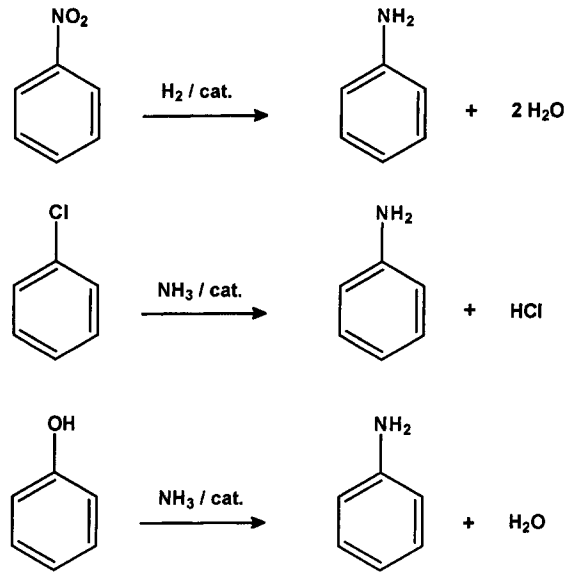


Scheme 1. Industrial routes to aniline.

2.1. *Catalytic hydrogenation of nitroarenes*

Nitroarenes, conventionally produced by nitration with mixed nitric/sulphuric acids, form the starting materials for many arylamine processes. It may be noted that the substitution of an acid zeolite for the sulphuric acid has recently been announced [1].

The nitro group is one of the most easily hydrogenated functional groups and the choice of catalysts is therefore wide. For aniline production, many catalysts offering high activity and selectivity are available and the choice for a particular commercial process will reflect technological considerations of stability/regenerability, mechanical strength, susceptibility to poisons and cost. In an organic synthesis in which several possible products may be obtained by the hydrogenation of a polyfunctional starting material, the selectivity to the desired product is likely to determine the choice of catalyst.

2.1.1. *Heterogeneous catalysis*

Useful summaries of the catalysts and processes employed in commercial production of aniline and other bulk arylamines are provided in standard reference works [2] (a,b) [3,4] (a). An important consideration in designing a process for the hydrogenation of a nitro compound is the high exothermicity of the reaction (approx. 550 kJ/mol in the liquid phase), requiring attention to heat removal. Another is the fact that some catalysts may be poisoned by nitro compounds, indicating the use of a reactor in which the concentration of starting material is minimized, such as a continuous stirred-tank reactor (CSTR) operated at high conversion [3].

For the production of aniline, numerous processes are in commercial operation; catalysts include supported copper, cobalt, palladium and nickel. The latter two may require the addition of inhibitors to prevent ring hydrogenation as a consequence of their higher activity. Vapour-phase processes employ either fixed-bed or fluid-bed reactors; copper on silica is typically employed as catalyst [2] (b). Vapour-phase processing is also employed for other volatile products, such as the toluidines and xylidines. Instead of hydrogen, natural gas may be used for nitrobenzene hydrogenation, as demonstrated by Bayer workers employing methane/water and copper chromite catalyst [5].

Aniline is also manufactured by liquid-phase processes. The same catalysts may be employed as for vapour-phase processing, with nickel in either supported or Raney form. Recent patents to Mitsui Toatsu claim the use of a palladium catalyst, inhibited with zinc salts, in a CSTR in which the heat of reaction is removed by continuously distilling off the aniline product and water [6,7]. For less volatile products, only liquid-phase processing is appropriate. An example is the production of 1-naphthylamine by hydrogenation of 1-nitronaphthalene using a nickel catalyst [2] (c).

Solvents employed for liquid-phase hydrogenation include lower alcohols, *N*-methylpyrrolidone and liquid ammonia [2] (a). Water may be employed in suitable cases, though the low solubility of hydrogen may cause difficulty, as described for the nickel-catalysed hydrogenation of nitronaphthalenesulphonic acids [8].

In addition to the traditional supported-metal catalysts and Raney metals, catalysts prepared by the chemical anchoring of metal complexes to support materials are described, although their application remains limited to laboratory work. Examples include a silylaminepalladium(II) complex attached to montmorillonite clay [9] and macroporous organometallic polymers containing palladium [10]. Palladium supported on a borohydride exchange resin is claimed to

be active under mild conditions and to hydrogenate the nitro group selectively in the presence of other reducible substituents [11]. Numerous examples of nitro compound hydrogenation by anchored Group VIII metal complexes on organic polymers and on silica and other oxides are collected in the recent monograph of Chaloner et al. [12].

For certain synthetic purposes, nitroso compounds, rather than nitroarenes, form the starting materials for amine preparation. Since these are intermediates in the hydrogenation of nitroarenes, catalysts employed for the latter, such as palladium, are suitable [13].

2.1.1.1. Halo and diamino derivatives Numerous aniline derivatives are also prepared by the hydrogenation of the corresponding nitro compounds. These include alkyl-, acyl-, hydroxy-, alkoxy-, nitro- and haloanilines [3]. When the substituent group is also reducible, catalyst selection may present interesting challenges. An example is provided by the hydrogenation of 2,4-dinitroaniline, in which the 4-nitro group is selectively hydrogenated over Pt/C in acidic solution [14,15], while rhodium in the presence of ammonia is selective for the 2-nitro group [16] (see Scheme 2).

Numerous other examples of chemo- and regioselectivity are collected in a recent survey [17].

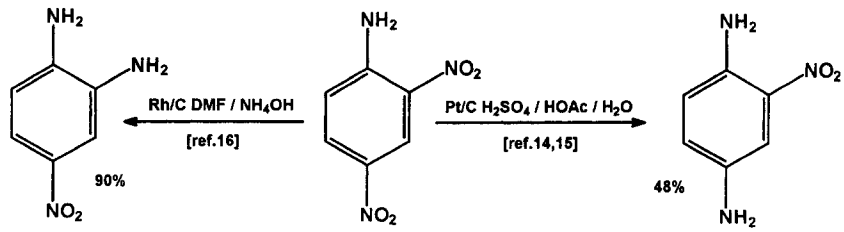
Diamines, such as the commercially important 2,4- and 2,6-diaminotoluenes and the phenylenediamines, are produced by the hydrogenation of dinitro compounds. For the diaminotoluenes, numerous processes involving palladium and nickel catalysts in CSTR or fixed-bed reactors are known [3]. The activity of palladium is enhanced by various metallic promotors. Recently, the promoting effect of iron alloyed with palladium has been studied [18]; it is proposed that the iron improves the dispersion of the metal phase and also facilitates the transfer of hydrogen to the adsorbed dinitrotoluene.

Choice of solvent is also important: for the hydrogenation of dinitrotoluenes with Raney nickel, the use of tetrahydrofuran is claimed to improve the product selectivity by eliminating by-products formed from the alcohol solvents commonly employed [19].

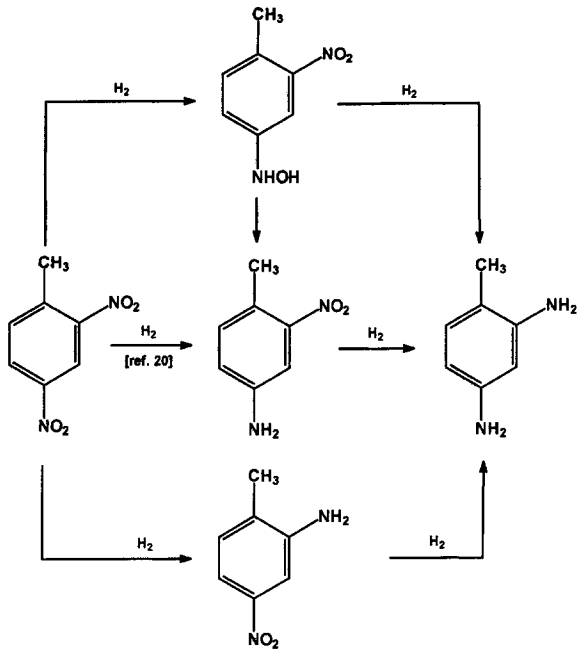
Extensive studies to elucidate the mechanism and reaction kinetics of the hydrogenation of 2,4-dinitrotoluene (2,4-DNT), the most important isomer for toluene diisocyanate production, have recently been conducted [20–22]. The catalyst employed was 5% Pd/C. The multistep reaction sequence resembles the Haber mechanism for the hydrogenation of nitrobenzene. Janssen et al. identified two parallel reaction pathways, proceeding via the two aminonitrotoluenes, as shown in Scheme 3.

The hydrogenation of the *para*-nitro group of 2,4-DNT proceeds via a hydroxylamine intermediate, stable enough for 4-hydroxylamino-2-nitrotoluene to be isolable from the reaction mixture at partial conversion. Neri et al., working under different conditions (atmospheric pressure), showed that the hydrogenation product of this intermediate, 4-amino-2-nitrotoluene, is also directly formed from 2,4-DNT in a third parallel pathway [20].

The same catalysts employed for the dinitrotoluenes are used to hydrogenate 1,3-dinitrobenzene in the production of *m*-phenylenediamine. The *o*- and *p*-isomers are obtained by the hydrogenation, over a palladium catalyst, of the corresponding nitroanilines, which are themselves produced by the amination of the chloronitrobenzenes [2] (d). Margitfalvi et al. have reported the preparation of *o*-phenylenediamine from 4-chloro-2-nitroaniline, employing a Pd catalyst for simultaneous nitro-group hydrogenation and Cl



Scheme 2. Regioselective hydrogenation of a single nitro group in a dinitro compound.



Scheme 3. Mechanism of 2,4-dinitrotoluene hydrogenation over 5% Pd/C, according to Neri et al. [20] and Janssen et al. [21,22].

removal. The stabilized, ionic Pd catalyst was prepared by a surface-anchoring reaction involving lithiation of the surface [23]. A patent to Máthe et al. discloses the use of high-dispersion Pd/C for the catalysis of this reaction on the pilot-plant scale [24].

Where a halogen-containing product is the goal, dehalogenation becomes a side reaction needing to be suppressed. For sensitive materials such as 4-bromonitrobenzene, lower temperatures and/or pressures are used and catalysts employed are typically palladium inhibited with sulphur, lead or bismuth, or Raney nickel with thiocyanate [2] (a). Phosphorus compounds are applied in the hydrogenation of 3-chloronitrobenzene over Pd/C [25]. Recent examples of inhibitors employed with Pt/C catalyst include the use of formamidine salts to achieve yields of 94–97% in the hydrogenation of 1-chloro-2,4-dinitrobenzene [26,27], and of iron oxide and an amine for hydrogenating 3,4-dichloronitrobenzene [28]. Other systems claimed to hydrogenate nitro (and nitroso) compounds selectively, without hydrogenolysis of halo substituents also present, are tungsten carbide [29] and sulphided nickel and molybdenum hydrotreating catalysts [30].

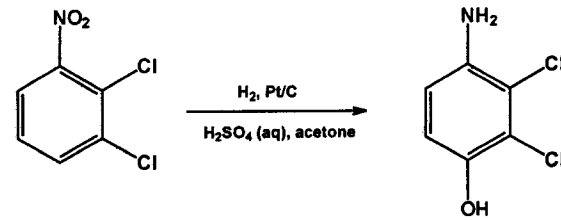
2.1.2. *Bamberger rearrangement*

Phenylhydroxylamines undergo the acid-catalysed Bamberger rearrangement to *p*-aminophenols. Since the hydrogenation of a nitroarene proceeds via a phenylhydroxylamine intermediate, a nitro compound may, under suitable conditions, be hydrogenated to yield an aminophenol rather than the amine product. This elegant variation is employed in the production of several crop-protection chemicals and pharmaceutical intermediates.

For the preparation of 4-aminophenol from nitrobenzene, sulphuric acid is typically employed, with Pt/C as the catalyst giving the lowest production of aniline by-product. Further suppression of aniline results from inhibition of the catalyst with sulphur compounds [31]; 4-aminophenol selectivities from nitrobenzene were 85% in the presence of 2-thiophenecarboxylic acid, compared with 74% without sulphur modifier. It is claimed that pretreating the sulphuric acid with hydrogen peroxide also leads to a selectivity improvement [32]. Alternative acid systems such as trifluoromethanesulphonic acid in acetic acid [33] and phosphinic acid (with Pd/C catalyst) [34] are also described. Improvements in reaction rate and yield are claimed from operating under phase-transfer conditions [35,36]. The fungicide intermediate, 2,3-dichloro-4-aminophenol may be produced, in 75–80% yield, from 2,3-dichloronitrobenzene employing Pt/C catalyst and sulphuric acid in aqueous acetone [8] (see Scheme 4).

Tungsten carbide is also suitable for use under Bamberger conditions, the hydrogenation of nitrobenzene in sulphuric acid giving 4-aminophenol in 58% selectivity at 99% conversion, compared with hydrogenation without acid which gave 95% aniline at complete conversion [29].

The use of methanolic sulphuric acid yields *p*-anisidines from nitrobenzenes, instead of 4-aminophe-



Scheme 4. Hydrogenation with Bamberger rearrangement of 2,3-dichloronitrobenzene [8].

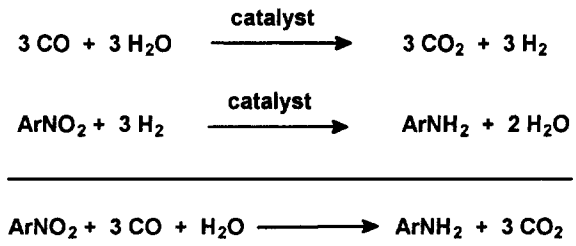
nol [37]. This forms the basis of a process for *p*-anisidine, commercialized by Mitsui Toatsu [38].

2.1.3. *Homogeneous catalysis in nitroarene hydrogenation*

As in the case of heterogeneous catalysis, the choice of homogeneous catalysts capable of hydrogenating nitro compounds with high activity and selectivity is very wide. Although homogeneous catalysts are unlikely to displace heterogeneous for continuous production, the greater opportunities for selectivity tuning, and the often mild operating conditions, make homogeneous catalysis attractive for small-scale and synthetic applications involving multifunctional starting materials.

The range of variables influencing selectivity in homogeneous catalysis includes the metal, the ligand, the solvent, and reaction conditions such as temperature and pressure. As in the case of heterogeneous catalysis, Group VIII metals, particularly iron, cobalt, ruthenium, rhodium and palladium are frequently employed for the hydrogenation of nitro compounds [12,39]. In a recent example, dinuclear ruthenium complexes $[RuL(CO)_2Cl]_2$, where L=a nitrogen ligand such as 2-phenylpyridine, were shown to be effective catalysts for the selective hydrogenation of a variety of nitroarenes [40]. No hydrogenolysis of Cl took place in the case of *o*-chloronitrotoluene substrate. The actual catalytic species was proposed to be the solvent adduct of the monomeric complex into which the dimer dissociates.

2.1.3.1. Hydrogenation using water gas The combination of the homogeneous water–gas shift reaction (WGSR) and nitro group hydrogenation (see Scheme 5) provides an alternative technique for arylamine preparation [12,39,41]. The catalysts are typically carbonyl complexes of iron, ruthenium and rhodium, employed in strongly basic solutions in order to facilitate nucleophilic attack on the coordinated CO. Both homogeneous and phase-transfer systems are employed. Advantages of this method include the use of environmentally benign, water-based solvents. Also, for substituted arylamines, new synthetic possibilities arise from the fact that the intermediate monohydride complexes, formed via the reaction of a CO ligand, may differ, in their reactivity to other reducible



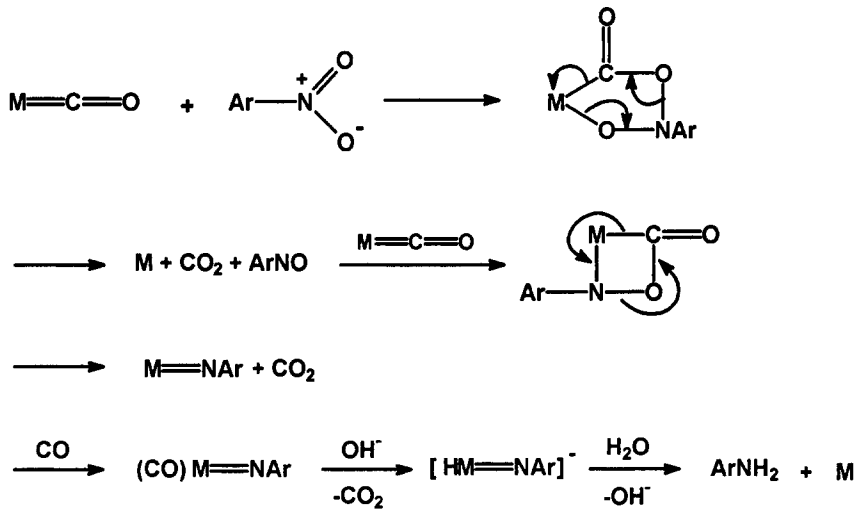
Scheme 5. Combined WGSR and nitroarene hydrogenation.

groups in the nitroarene substrate, from the dihydrides formed from the same precursor complexes with dihydrogen.

In an extensive series of publications, Nomura et al. have developed active and highly selective catalysts for the hydrogenation of nitroarenes, based on rhodium and ruthenium carbonyls such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(CO)_2(acac)$ and $Ru_3(CO)_{12}$ [42]. Ligands employed include mono- and bidentate phosphines [43] and amines [44]. The catalysts are active under ambient conditions and are capable of hydrogenating 1-nitroanthraquinone to 1-aminoanthraquinone with high selectivity [45].

Catalysts based on $Ru_3(CO)_{12}$ with ligands such as triethylamine are found not only to be inactive for other reducible substituents such as cyano and carbonyl in the nitroarene substrates, but also not to hydrogenate substrates such as benzonitrile, phenylacetylene and acetophenone [44]. Such exclusive nitro group selectivity, together with the fact that no free hydrogen from the WGSR is detected at the end of these reactions, has led Nomura to propose a new type of reaction mechanism [45]: an intramolecular hydrogen transfer between a metal nitrene, formed via a cyclic adduct of metal carbonyl species and nitroarene, and hydride (see Scheme 6). The same may hold for the catalyst $Rh_4(CO)_{12}$ with 9,10-diaminophenanthrene [46].

Skupińska et al. showed that the catalyst system $PdCl_2/Fe_2O_3/FeCl_3$/pyridine, employed for the reductive carbonylation of nitro compounds to isocyanates and urethanes, rapidly gives an almost quantitative yield of aniline from nitrobenzene in the presence of water [47]. With the activity further enhanced by iodine employed as promoter, the less active 2,4-DNT similarly gave 2,4-diaminotoluene in high yield.



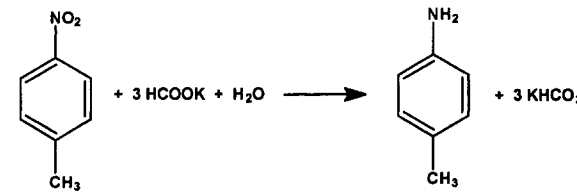
Scheme 6. Proposed mechanism of nitrobenzene reduction with CO/H_2O and $Ru_3(CO)_{12}/NEt_3$ catalyst [45].

Another system for the carbonylative reduction of nitrobenzene in aqueous alkaline solutions has been described by Macho et al. [48,49]. The catalysts are sulphur compounds such as COS and H_2S and the selectivity to the arylamine product is improved by the addition of vanadium(V) compounds.

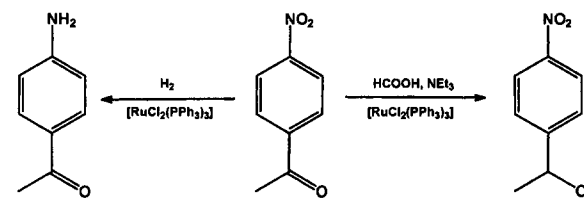
2.1.4. *Transfer hydrogenation*

While hydrogen is invariably employed in bulk processing, transfer hydrogenation offers an alternative when pressure equipment and hydrogen handling facilities are unavailable. Lower aliphatic alcohols and formates are typically employed as hydrogen-transfer agents [12,50] (see Scheme 7).

Transfer hydrogenation with homogeneous catalysts furnishes a further valuable synthetic method for the selective hydrogenation of nitroarenes having other reducible substituents, since the chemoselectivity obtained with a given catalyst may differ, depending on whether direct or transfer hydrogenation is employed. Watanabe et al. have shown, for example, that $RuCl_2(PPh_3)_3$ with HCOOH as hydrogen donor gives the corresponding aniline derivatives from nitrobenzenes with methyl, methoxy and chloro substituents; 2-methylaniline, for example, was obtained in 96% selectivity at 99% conversion [51]. However, with 4-nitroacetophenone, direct hydrogenation is required to obtain 4-aminoacetophenone as product,



Scheme 7. Transfer hydrogenation with formate [50].



Scheme 8. Chemoselectivity in hydrogenation of 4-nitroacetophenone with $[RuCl_2(PPh_3)_3]$ [51].

since transfer hydrogenation with HCOOH selectively reduces the carbonyl group (see Scheme 8). Ruthenium has also been employed by Ben Taleb and Jenner, who showed that $Ru_3(CO)_{12}$ promoted by tertiary amines was effective for the transfer hydrogenation of nitroarenes using methyl formate as donor [52].

The use of hydrazine as reductant may be favoured when it is desired to stop the reaction at an inter-

mediate stage. Yun et al. demonstrated that the hydrogenation of nitrobenzene, with hydrazine monohydrate and a nickel/zinc catalyst, could either be halted at the azobenzene stage or continued to aniline, depending on whether nickel nitrate or chloride were used as catalyst precursor [53]. Boothroyd and Kerr employed *N,N*-dimethylhydrazine and $FeCl_3$ catalyst to give anilines in high yields from nitroarenes such as 4-nitrophenol [54].

Transfer hydrogenation with heterogeneous catalysts is also employed. Conventional hydrogenation catalysts such as nickel or palladium are applicable, but the use of magnesium oxide with alcohol transfer agents is claimed by Kijenski et al. [55]. Hydrazine may also be used as reductant [2] (a); in a recent application Hoechst workers obtained 3-chloroaniline in 96% yield from 3-chloronitrobenzene using hydrazine and Pd/C catalyst [56].

Wiener et al. investigated the transfer hydrogenation of nitroarenes with Pd/C catalyst and formate salt donors. A mechanism involving the successive adsorption of nitroarene, formate anion and water on a single catalytic site was proposed [50]. The use of 4-vinylcyclohexene as donor, with Pd/C catalyst, has recently been reported [57].

Cervilla et al. have demonstrated an interesting example of transfer hydrogenation employing a molybdenum catalyst as model for a nitroreductase enzyme. The dioxomolybdenum (VI) complex is intercalated within a hydrotalcite-like layered double hydroxide to give an active catalytic system for the reduction of nitrobenzene to aniline using thiophenol as hydrogen-transfer agent [58].

2.2. *Nucleophilic amination reactions*

Nucleophilic amination of substituted benzenes is an important reaction for the production of both aniline and its derivatives. Although a range of starting materials can be employed [2] (a), only phenols and chlorobenzene have been employed in large-scale production processes. The use of aniline or its derivatives instead of ammonia provides a route to diphenylamines.

2.2.1. *Phenols and phenolic ethers*

The catalytic amination of phenol (see Scheme 1) is the newest of the several commercial processes for the bulk production of aniline [3] and is operated in Japan (Mitsui Petrochemical) and the USA (Aristech). A lively account of the impact of this process on the established aniline market is given by Szmant [59] (a). From *m*-cresol, *m*-toluidine is produced by an analogous process [4] (a). A comparison of the aniline process economics with the traditional nitrobenzene hydrogenation route was provided by Gans [60]. One of the significant economic advantages of this process is claimed to be the outstanding catalyst stability.

Mechanistically, it is the tautomeric ketone form of phenol which can be considered as susceptible to nucleophilic attack by ammonia. This will be enhanced by coordination of the oxygen to a Lewis acid such as Al(III).

The original Halcon/Scientific-Design aniline-from-phenol process employed a proprietary solid-acid catalyst, based on silica–alumina [2] (b). By-products in the process include di- and triphenylamines and carbazole.

The substitution of ammonia by aniline forms the basis of a process to diphenylamine [3]. The phenol-to-aniline process can also be modified to produce diphenylamine by recycling aniline to the reactor inlet [61].

In addition to silica–alumina, alternative oxide catalysts have been proposed, based on magnesium, boron and titanium oxides, with co-catalysts including cerium, vanadium and tungsten [4] (a). Niobium oxide is claimed in a patent to Tosoh Corp. [62]. Other catalysts include fluorided alumina [63] and silica, impregnated with aluminium hydride and calcined [64].

Alumina as catalyst has been proposed to reduce problems of selectivity and stability loss associated with more strongly Lewis-acidic systems. The use of a γ-alumina with a highly specific pore-size distribution of 3–9 nm is claimed to improve stability [65], while alumina from calcined bayerite is claimed to reduce isomerization in the production of aniline derivatives [66].

Acid zeolites (crystalline aluminosilicates having precisely defined pore diameters) such as HZSM-5 [67,68] have also been claimed for the amination of phenols. The use of ZSM-5 suppresses the heavy by-products obtained (see above) with amorphous catalysts, owing to its specific pore size (0.55 nm). However, at high contact times, 2-methylpyridine is

formed from aniline in a consecutive reaction [69]; alkylanilines also undergo this reaction [70]. Zeolite-beta (BEA) is also active for phenol amination and its use is claimed to give very low diphenylamine formation [71].

Warawdekar and Rajadhyaksha investigated the amination of phenol and anisole over NaY and NaHY zeolites and NaY exchanged with calcium, chromium and copper [72]. For phenol amination the highest activity was found for the most acidic catalysts, NaHY and CuNaY. A mechanism involving the participation of both cations and protons was proposed.

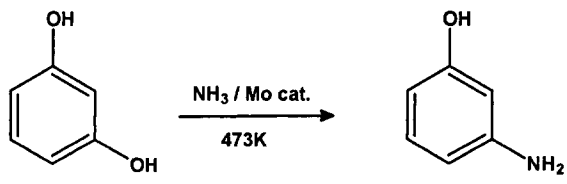
2.2.2. *Dihydroxybenzenes*

The amination of phenols has been extended to dihydroxybenzenes, now available from the modified Hock process from diisopropylbenzenes, thus providing an alternative to the traditional multistep routes to phenylenediamines via nitro compounds. Much of the activity in this area is in Japan, where this process is employed in the manufacture of the valuable intermediate *m*-aminophenol by Sumitomo and by Mitsui Chemical [38] (see Scheme 9).

Processes that have been described include vapour-, aqueous- and solvent-phase variants. For the vapour-phase reaction, oxides of Mo, W, Ga and Zn, and phosphoric acid on silica have been claimed [73]. Reactions in aqueous ammonia employ salts such as ammonium molybdate [74] and the phosphates of Fe, Ni or Zn [73]. For the solvent case, a recent development is the use of zeolites and montmorillonite clays in toluene or xylene [75].

An example of the application to an alkylaminophenol is the amination of resorcinol with butylamine and phosphoric acid catalyst as the first step in the preparation of the di-*N*-butyl derivative [76].

In an analogous way, the amination of hydroquinone, with ammonia or alkylamines, yields *p*-aminophenol and its *N*-alkyl derivatives. Catalysts patented for this process by Mitsui include zeolite H-USY



Scheme 9. Mitsui process for amination of resorcinol.

treated with ammonium fluoride [77] and the phosphates of Ti, Zr or Hf [78]; in the latter case, co-feeding phenol was essential to obtain a high selectivity of 78% at 93% conversion.

In the above processes further reaction leads to the formation of diamine by-products. Under appropriate conditions diamines become the main products; for example, hydroquinone can also be fully aminated to yield *p*-phenylenediamine [2] (d). A patent to Mitsui Petrochemical claims the use of aqueous ammonia and Pd/C catalyst in the presence of cyclohexanone to give *p*-phenylenediamine in 50% selectivity at 73% conversion [79].

2.2.3. *Haloarenes*

The amination of halobenzenes not possessing nitro or other activating groups requires a catalyst. The catalysed reaction of chlorobenzene with ammonia is the third process to have been employed commercially for the production of aniline [2] (a) (see Scheme 1). Dissolved copper salts such as 'Nieuwland catalyst', $CuCl/NH_4Cl$, were employed [4] (a).

Halide exchange is also employed in the preparation of aniline derivatives. Examples are the manufacture of *p*-nitrodiphenylamine from *p*-nitrochlorobenzene and aniline and of *N*-phenyl-*p*-phenylenediamine from *p*-chloronitrobenzene and aniline, both processes employing copper salts as catalysts. Copper salts are also employed in the preparation of *o*- and *p*-phenylenediamines by amination of the corresponding dichlorobenzenes. An example involving a bromine compound is the amination of *p*-bromofluorobenzene over cuprous oxide to give *p*-fluoroaniline in 91% yield [80].

Heterogeneous catalysis of halobenzene amination offers the advantages of simplified product/catalyst separation and waste reduction. Following incidental reports of the use of zeolitic catalysts for this reaction, a systematic investigation was conducted by Burgers [81]. In a screening comparison of various metal–ion-exchanged zeolites for the gas-phase amination of chlorobenzene, copper was confirmed as the most active and selective metal. When different Cu-zeolites were compared, the order of initial activity was found to be Y » L >> MOR > BEA > ZSM-5, which roughly parallels the increasing silica/alumina ratio. It is suggested that the higher surface polarity of the low-silica zeolites is responsible for the higher activity [82].

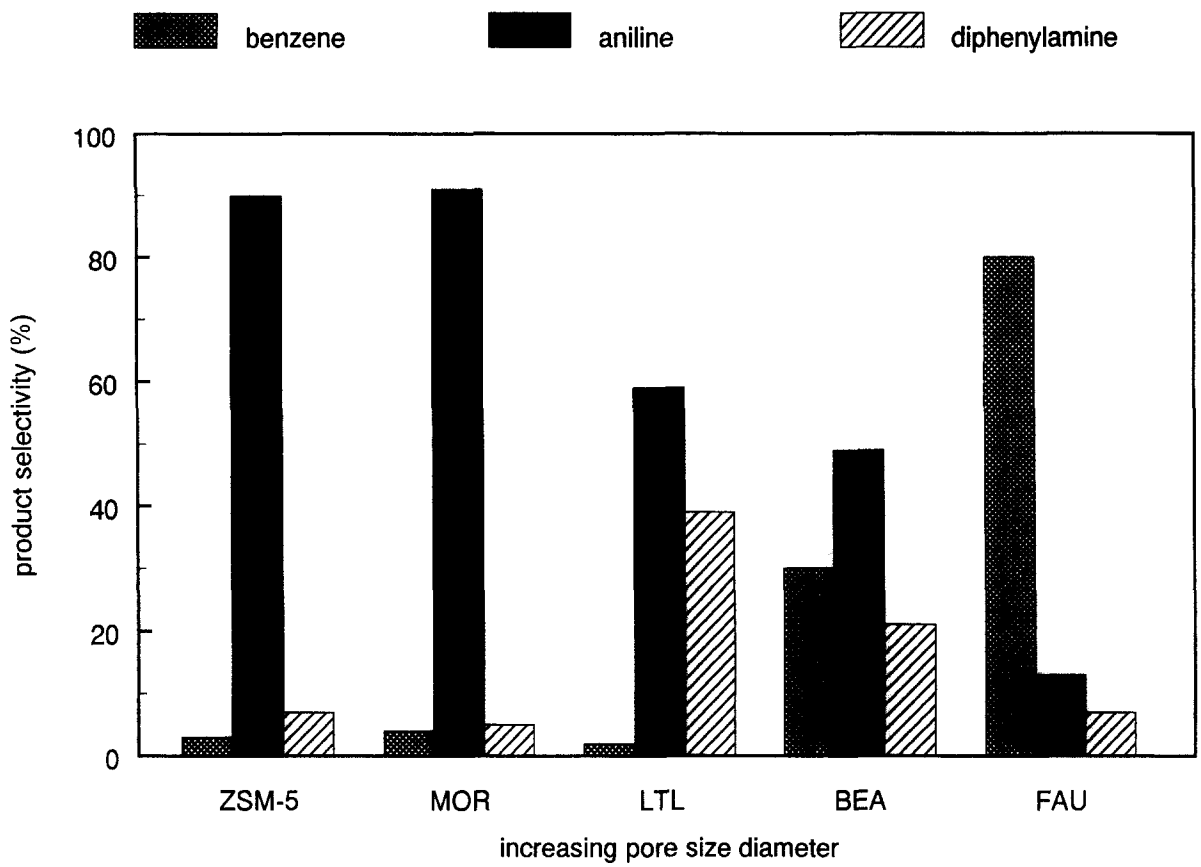


Fig. 1. Amination of chlorobenzene over various Cu-zeolites: influence of pore diameter on (by-)product distribution [81].

The principal by-products obtained are benzene and diphenylamine. Interesting selectivity differences between the various zeolites were observed. The lowest benzene and diphenylamine, and thus the highest aniline selectivity, were obtained with ZSM-5 and mordenite. This shape-selective advantage is lost as the pore size is increased, zeolite L giving increased diphenylamine, though benzene formation remained low. The still larger-pore materials BEA and Y gave substantially increased benzene but the diphenylamine selectivity, instead of increasing further, was once again found to be low (see Fig. 1). The proposed explanation of these trends was that benzene is formed, not via simple hydrodehalogenation of chlorobenzene by hydrogen formed from ammonia decomposition, but principally from the decomposition of heavy condensation products.

The various zeolites were also found to differ strongly in stability, the large-pore zeolites BEA and Y showing the most rapid deactivation during operation. The most stable operation was found at 400°C and two separate deactivation regimes were recognized, coke formation being the principal cause of activity loss at temperatures above 400°C and accumulation of by-products at lower temperatures. All the catalysts were found to be fully regenerable by means of a simple air burn-off at 450°C.

The active site in these catalysts is considered to be the Cu(I) ion. The reduction of the as-synthesized Cu(II) zeolite, prepared by ion-exchange, to the active Cu(I) form by ammonia generates protons by charge compensation and catalysts formed in this way will be acidic. To study the effect of this acidity, a Cu-mordenite prepared in this way was compared with a non-

acidic Cu-MOR prepared by impregnation with $CuCl_2$, followed by ammonia reduction [83]. It was found that the activity of the acidic catalysts is higher than that of the non-acidic. This, coupled with the fact that the rate of chlorobenzene amination is higher than that of bromobenzene [84], i.e. opposite to the order observed in the case of homogeneous catalysis, leads to the suggestion that the rate-determining step is the decomposition of, or the elimination of HX from, the copper-product complex, which is mediated by H^+.

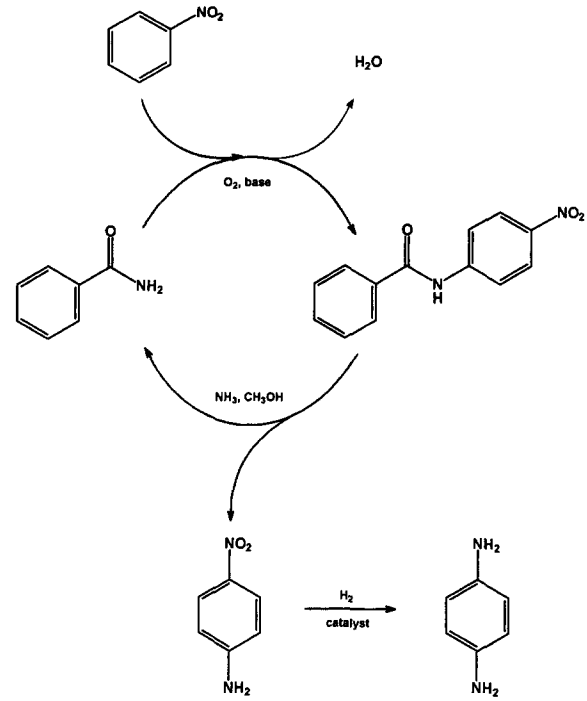
Copper mordenite was also found to be active for the amination of the chlorotoluenes [83]. The extension of the reaction to dichlorobenzenes would represent an alternative to the hydrogenation of the dinitro compounds [2] (d) for the production of diamines. However, the catalysts Cu-mordenite and Cu-L proved inactive for the transformation of *p*-dichlorobenzene to *p*-phenylenediamine [83] although other copper catalysts may be employed, for example, CuO [85] and copper salts in aqueous ammonia [3].

2.2.4. *Other arene starting materials*

The direct amination of benzene and other arenes has been named by James F. Roth as one of "ten challenges that typify the present needs of industrial catalysis" [86]. However, rather less progress appears to have been made in this area than with the direct amination of olefins, which has been commercialized by BASF for the production of *t*-butylamine from ammonia and isobutene. Du Pont developed the use of oxide catalysts such as ZrO_2-promoted Ni/NiO to give aniline from benzene and ammonia with high selectivity of 97%, though at a low benzene conversion of 13% [4] (a) [87]. A catalyst reoxidation step is necessary to maintain the catalytic cycle. Aniline itself can be aminated to phenylenediamines [88] and toluene to toluenediamines [89].

A more recent example is the production of small amounts of aniline (2%) and phenol (4%) from benzene (at 6% conversion) and aqueous ammonia, employing a copper/calcium phosphate catalyst [90].

Indirect methods, involving the use of hydroxylamine salts or reductive amination, are also known [41]. A recent example of the latter is the amination of toluene by sodium amide, catalysed by Rh/C and other hydrogenation catalysts [91].

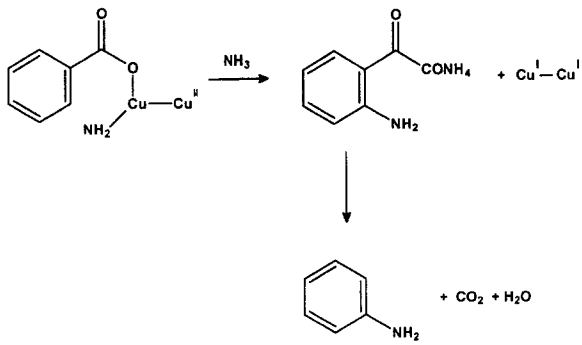


Scheme 10. Monsanto route to *p*-phenylenediamine [92].

An interesting Monsanto process for *p*-phenylenediamine provides an example of a more environmentally acceptable route than existing processes which generate chlorine-containing waste streams [92]. The starting material, nitrobenzene, reacts in the first step with benzamide, in the presence of a base and molecular oxygen, to give 4-nitrobenzanilide. This compound, with methanolic ammonia, regenerates benzamide and yields *p*-nitroaniline, which is catalytically hydrogenated to *p*-phenylenediamine. Formally, the reaction sequence is a nucleophilic substitution of NH_2 for aryl hydrogen (see Scheme 10).

A final example of the use of copper to effect a formal nucleophilic amination is the reaction of benzoic acid and alkylbenzoic acids to (alkyl)anilines under ammonia pressure, employing homogeneous copper compounds, as described by Arzoumanidis and Rauch [93]. Substitution proceeds via *ortho*-attack of coordinated amide (see Scheme 11).

The decarboxylation is accompanied by reduction of Cu(II) to Cu(I), which may be reoxidized by atmospheric oxygen. So far, it has not proved possible to



Scheme 11. Proposed mechanism for benzoic acid amination [93].

combine these two steps to achieve a truly catalytic cycle.

2.2.5. *Diarylamines*

The use of aniline or a derivative, instead of ammonia, leads to the formation of diarylamines from anilines, phenols or halobenzenes [3]. The self-condensation of aniline with acid catalysts forms the basis of manufacturing processes for diphenylamine. Heterogeneous catalysts such as alumina may be used, but high temperatures are required, resulting in coke formation. A patent to Uniroyal [94] claims that the use of a suitable large-pore alumina enables the temperature to be lowered from above 450°C to around 400°C.

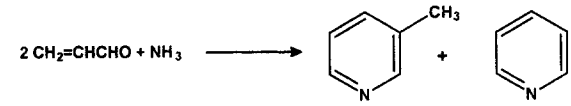
Mechanistically, the situation is analogous to the amination of phenol; aniline in its imine form is subject to nucleophilic attack by a second aniline molecule.

The use of zeolites NaHY and rare-earth exchanged REY for the self-condensation of aniline was studied by Warawdekar and Rajadhyaksha [95]. Interesting observations were the maximum activity of NaHY at an intermediate level of exchange and the negative temperature dependence of the reaction. As in the case of the phenol-to-aniline reaction, a mechanism involving both cations and protons was proposed.

3. Heterocyclics

3.1. *Pyridine and derivatives*

In this section, catalytic amination reactions leading to pyridines are discussed. Condensation reactions and



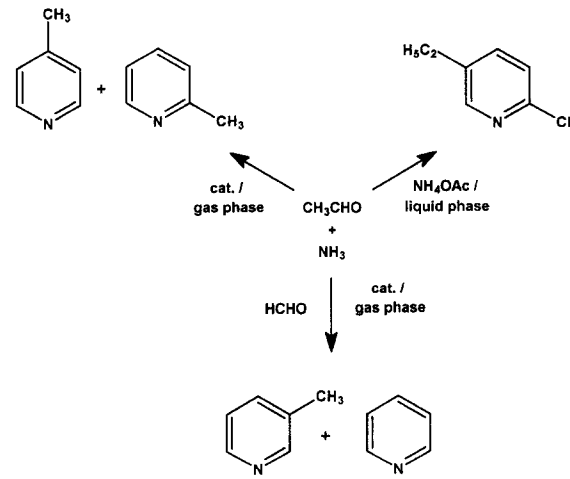
Scheme 12. Pyridine and 3-picoline from acrolein.

aniline rearrangements yielding these compounds form the subject of a separate article in this issue [96] and are not included here.

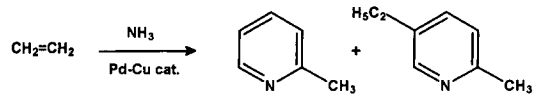
The growing demand for pyridine and its derivatives, traditionally products of coal-tar distillation, by the fine-chemicals industry has led to the development of synthetic methods for their production. Several amination processes for pyridine itself and its alkyl derivatives are commercially operated [2] (e) [4] (b) [59] (b). In Japan, pyridine and 3-picoline are manufactured from acrolein and ammonia (see Scheme 12).

The niacin intermediate 2-methyl-5-ethylpyridine is obtained from acetaldehyde and aqueous ammonia using ammonium acetate as catalyst (see Scheme 13). Acetaldehyde and ammonia react in the gas phase, over silica–alumina catalyst containing proprietary promotors, to give 2- and 4-picolines, while pyridine and 3-picoline are produced in a gas-phase process from acetaldehyde and formaldehyde (see Scheme 13).

In a developmental process of Nippon Steel the two most important derivatives, 2-picoline and 2-methyl-5-ethylpyridine, are produced from ethylene and



Scheme 13. Pyridine and derivatives from acetaldehyde.



Scheme 14. Alkylpyridines from ethylene.

ammonia, using as catalyst an ammoniacal palladium solution with a copper redox system [4] (b) (see Scheme 14).

Acetone and furfuryl alcohol also represent potential commercial feedstocks for pyridines via amination processes [59] (b) and many other starting materials have been described. Crotonaldehyde [97] and acetylene [98] have been investigated by Russian workers. The use of ethanol is discussed at more length below.

Catalysis development for the amination of aldehydes, ketones and alcohols to pyridines, and in particular the investigation of zeolitic catalysts, represents a very active area of research. The suitability of pentasil-type zeolites for this application was demonstrated by Mobil workers [99]. The results described below are from gas-phase experiments at atmospheric pressure and temperatures in the range 350–450°C.

3.1.1. *Pyridines from aldehydes and ketones*

For the amination of acetaldehyde alone, which yields predominantly 2- and 4-picolines, Chang and Lang showed ZSM-5 zeolite to be superior in activity to amorphous catalysts and in stability to mordenite. The highest selectivity of 13% to the desired 2-picoline was obtained with cadmium-modified ZSM-5 [99]. Picolines are also obtained in high yield from propylene glycol, when HZSM-5 is employed [100].

Faujasite zeolites have been used to catalyse this reaction by Roy et al. Cadmium gave improvements in this case also, but the highest activity was found with silica–alumina modified with ZnO, which gave a yield of 70% [101,102].

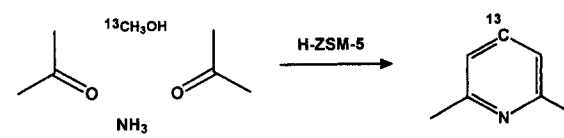
In contrast to the amination of acetaldehyde alone, the inclusion of formaldehyde and/or methanol in the feed yields pyridine as main product, together with 3-picoline [97]. Adjustment of the product distribution is demonstrated in a process modification of Feitler and Wetstein employing a pentasil-type zeolite catalyst, containing also kaolin and amorphous silica–alumina, and a ternary aldehyde mixture containing acetaldehyde, formaldehyde and propionaldehyde [103,104]. A pyridine/picolines molar ratio of 0.55 was obtained, at a 66% selectivity to total pyridine bases, compared with a ratio of 2.2 without propionaldehyde.

Modifications of ZSM-5 with palladium [105], thallium [106] or both thallium and palladium [107] are claimed to increase the pyridine selectivity. A systematic comparison of various zeolites and silica–alumina was conducted by Sumitomo workers [108,109]. The highest pyridine selectivity was obtained with HZSM-5. Thallium and other modifiers such as lead, cobalt and zinc were found to be beneficial and both the total pyridines yield (76–81%) and the pyridine selectivity were found to be maximized by the use of Tl-ZSM-5 with intermediate Si/Al ratios in the 30–120 range.

The amination of acetaldehyde/formaldehyde has also been studied over the mesoporous zeolite MCM-22; the product distribution is qualitatively similar to that obtained with ZSM-5 [110].

The amination of acetone over HZSM-5 leads to the formation of dimethylpyridines (lutidines) and more highly alkylated derivatives [99]. Different zeolites were compared in the reaction of acetone and methanol with ammonia by Van der Gaag et al. [111]. With HZSM-5, the selectivity to 2,6-lutidine was found to increase with the Si/Al ratio; by co-feeding water, the selectivity could be increased to around 20%. No activity was shown by silicalite catalyst (all-silica ZSM-5) showing that the presence of acid sites is required. Very low activity was shown by mordenite, which has a low Si/Al ratio of 6–7. The introduction of ^{13}C -labelled methanol yielded 2,6-lutidine with ^{13}C exclusively at the 4-position (see Scheme 15). This is consistent with mechanisms proceeding via methyl vinyl ketone or imines formed from acetone or its condensation products but does not permit of an unambiguous assignment.

A recent paper of Rama Rao et al. compares various zeolites and amorphous catalysts in the amination of acetone/formaldehyde/methanol mixtures [112]. As in the example above, with HZSM-5 zeolites the 2,6-lutidine selectivity (and also the 2-picoline selectivity)



Scheme 15. 2,6-lutidine from acetone / methanol.

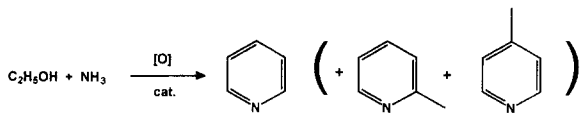
increased with Si/Al ratio, but fell again at the highest Si/Al of 280. At acetone conversions of 50–60%, 2-picoline yields of 30–47% were obtained. A lead-promoted silica–alumina was higher in activity than that of any of the unmodified HZSM-5 catalysts, but gave a product mix containing much more 2,6-lutidine and less 2-picoline. The modification of ZSM-5 with lead gave the most active catalyst tested.

Still more highly alkylated pyridines have been prepared via the reaction of acrolein with alkanals such as butanal, employing pentasil-type zeolites. The major products were 3-ethylpyridine and 3-picoline [113]. Acrolein and formaldehyde, together with acetaldehyde or propionaldehyde, were aminated using CdO/silica–alumina catalyst. Acetaldehyde gave chiefly pyridine (50%), with 3-picoline as main by-product (22%) [114,115], while propionaldehyde yielded principally 3-picoline (57%) and some 3,5-lutidine (13%).

3.1.2. *Pyridines from alcohols*

Van der Gaag et al. showed that pyridine, together with 2-and 4-picolines as minor products, could be obtained by the oxidative amination of ethanol, in selectivities approaching 50%, using HZSM-5 catalyst [116] (see Scheme 16). No pyridine was obtained in the absence of oxygen. Co-feeding water was found to have a positive effect on both pyridine selectivity and catalyst stability. A mechanism proceeding via oxidation of ethanol to acetaldehyde was proposed. LeFebre showed zeolite Nu-10 also to be an effective catalyst for the reaction, giving a maximum of 80% (alkyl)-pyridines. In further mechanistic studies the involvement of both acetaldehyde and formaldehyde, formed by radical fragmentation from ethanol, was invoked to explain the preponderance of pyridine itself among the products [117].

Kulkarni et al. achieved the non-oxidative amination of ethanol over HZSM-5 catalysts by incorporating formaldehyde in the feed, thereby eliminating yield losses through carbon dioxide formation [118]. Pyridine yields of 20–40%, with 10–25% picolines, were obtained. The reaction is proposed to proceed via the formation of ethylamine, which dehydrogenates to an imine; the reaction of two molecules of this with formaldehyde produces pyridine, while the condensation of three molecules of imine gives picolines.



Scheme 16. Pyridine and picolines from ethanol.

The non-oxidative amination of ethanol is also effected using a heteropoly acid catalyst supported on gamma-alumina [119]. This system yields 2- and 4-picolines with >55% selectivity at 94% alcohol conversion.

For the amination of tetrahydrofurfuryl alcohol, Choi et al. employed palladium on various carriers and identified carrier acidity and the palladium loading and dispersion to be the critical factors determining the pyridine selectivity [120]. The highest selectivities were obtained with gamma-alumina carrier and a Pd particle size of 3–4 nm.

3.2. *Pyrrole and derivatives*

Pyrroles may be manufactured by the amination of furans and butynediol [2] (f) with ammonia or amines. Solid acids such as silica–alumina and zeolites, and also transition-metal catalysts, are employed. Recent developments by BASF workers include the production of pyrrole, in up to 86% selectivity at complete conversion, from 1,4-dimethoxytetrahydrofuran [121], over acid catalysts including a borosilicate zeolite, and of 1-methylpyrrole from 2-butene-1,4-diol and methylamine employing a copper catalyst [122].

Martin and Lücke employed HZSM-5 to obtain 2-methyl- and 1,2-dimethylpyrrole in almost quantitative selectivity at 40% and 70% 2-methylfuran conversions with ammonia and methylamine, respectively [123].

4. Conclusions; future trends

Manufacturers of aromatic amines, in common with others in the chemicals industry, are increasingly required to reduce the environmental impact of their processes and to increase their feedstock and energy efficiency. The replacement of traditional operations involving dissolving metal reductions and acidic reagents by catalytic processes is an effective way

to reduce waste streams and achieve these goals and, as has been shown above, catalytic processes already dominate this branch of the industry. It is to be expected that producers of aniline and other bulk products will continue to improve their proprietary technology; such evolutionary improvements are seldom reported in the literature, however. Nevertheless, in the absence of the introduction of revolutionary technology, such as the direct amination of benzene, which would have an impact comparable to that of the phenol-to-aniline process, progress in future is likely to continue to be of this kind.

With regard to smaller-scale production, the increasing sophistication of homogeneous catalytic systems can be expected to enable further improvements in the selectivity to multifunctional amines, for example, those containing other reducible groups. Although homogeneous catalysts are at a disadvantage compared with heterogeneous, with respect to product and catalyst recovery, the use of new phase-transfer and biphasic systems will make the use of homogeneous catalysts increasingly practicable and enable their potential for selectivity tuning to be realized.

The emphasis in current work on processes, such as hydrogen-transfer and CO/H_2O reductant systems, which frequently employ benign solvent systems such as aqueous ethanol, reflects the trend to reduce the use of environmentally unacceptable solvents. It is likely that alternatives for processes involving chlorine-containing intermediates, where the final product does not contain chlorine, will continue to be actively sought.

5. Glossary of trivial names and abbreviations

acac	acetylacetonato (2,4-pentanedione)
acrolein	2-propenal
anisidine	methoxyaniline
BEA	zeolite beta
cresol	methylphenol
CSTR	continuous-flow, stirred-tank reactor
furfuryl alcohol	2-(hydroxymethyl)-furan
lutidine	dimethylpyridine
MOR	zeolite mordenite
niacin	nicotinic acid; pyridine-3-carboxylic acid
picoline	methylpyridine
REY	rare-earth Y zeolite

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