

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

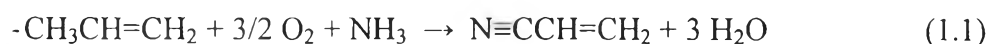
#### 2.1 Theoretical Background

##### 2.1.1 Nitrile

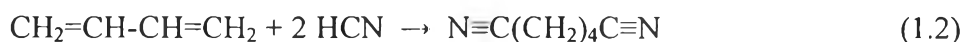
A nitrile is any organic compound that has a  $-C\equiv N$  functional group. Nitriles are found in many useful compounds, including methyl cyanoacrylate, used in super glue, and nitrile butadiene rubber, a nitrile-containing polymer used in latex-free laboratory and medical gloves. Organic compounds containing multiple nitrile groups are known as cyanocarbons. Inorganic compounds containing the nitrile group are not called nitriles, but cyanides instead. Though both nitriles and cyanides can be derived from cyanide salts, most nitriles are not nearly as toxic.

Industrially, the main methods for producing nitriles are ammoxidation and hydrocyanation. Both routes are green in the sense that they do not generate stoichiometric amounts of salts.

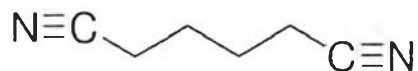
In ammoxidation, a hydrocarbon is partially oxidized in the presence of ammonia. This conversion is practiced on a large scale for acrylonitrile and a side product of this process is acetonitrile. Most derivatives of benzonitrile as well as Isobutyronitrile are prepared by ammoxidation.



Hydrocyanation is a popular method for producing nitriles from hydrogen cyanide and alkenes. The process requires homogeneous catalysts. An example of hydrocyanation is the production of adiponitrile from 1,3-butadiene:



### 2.1.1.1 Adiponitrile (ADN)



**Figure 2.1** Chemical structure of adiponitrile.

Adiponitrile (1,6-Hexanedinitrile) is the organic compound with the formula  $(\text{CH}_2)_4(\text{CN})_2$ . The molecule is a dinitrile, consisting of hexamethylene hydrocarbon chain terminated with nitrile functional groups. This dinitrile is an important precursor to the polymer nylon 6,6.

Because of the industrial value of adiponitrile, many methods have been developed for its synthesis. Early industrial routes started from furfural and later by the chlorination of butadiene to give 1,4-dichloro-2-butene, which with sodium cyanide, converts to 3-hexenedinitrile, which in turn can be hydrogenated to adiponitrile.



Adiponitrile has also been produced from adipic acid, by dehydration of the diamide, but this route is rarely employed.

In modern route, the majority of adiponitrile is prepared by the nickel-catalysed hydrocyanation of butadiene. The net reaction is



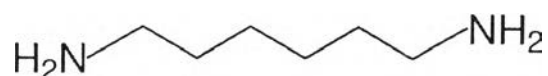
The other major industrial route involves electrosynthesis, starting from acrylonitrile, which is dimerized



**Table 2.1** Properties of adiponitrile

Properties	
Molecular formula	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub>
Molecular weight	108.14 g mol <sup>-1</sup>
Density	0.951 g mL <sup>-1</sup> at 25 °C
Melting point	1 – 3 °C
Boiling point	295 °C
Flash point	163 °C

### 2.1.2 Hexamethylenediamine (HMDA)

**Figure 2.2** Chemical structure of hexamethylenediamine.

Hexamethylenediamine (1,6-Hexanediamine) is the organic compound with the formula H<sub>2</sub>N(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>. The molecule is a diamine, consisting of a hexa-methylene hydrocarbon chain terminated with amine functional group. The colourless solid (yellowish for some commercial samples) has a strong amine odor. It is presently produced by the hydrogenation of adiponitrile:



The hydrogenation is conducted molten adiponitrile diluted with ammonia, typical catalysts being based on cobalt and iron. The yield is good, but commercially significant side products are generated by virtue of reactivity of partially hydrogenated intermediates. These other products include 1,2-diaminocyclohexane, hexamethyleneimine, and hexamethylenetriamine. An alternative process operates in diluted adiponitrile conditions using

hexamethylenediamine itself as a solvent and Raney-Ni as catalyst. This process operates without ammonia and at lower pressure and temperature.

Hexamethylenediamine is used almost exclusively for the production of polymers, an application that takes advantage of its bifunctional structure. The great majority of the diamine is consumed by the production of nylon 6-6 via condensation with adipic acid. Otherwise hexamethylene diisocyanate (HDI) is generated from this diamine as a monomer feedstock in the production of polyurethane. The diamine also serves as a cross-linking agent in epoxy resins.

**Table 2.2** Properties of hexamethylenediamine

<b>Properties</b>	
Molecular formula	$C_6H_{16}N_2$
Molecular weight	$116.20 \text{ g mol}^{-1}$
Density	$0.89 \text{ g mL}^{-1}$ at $25 \text{ }^\circ\text{C}$
Melting point	$42 - 45 \text{ }^\circ\text{C}$
Boiling point	$204 - 205 \text{ }^\circ\text{C}$
Flash point	$80 \text{ }^\circ\text{C}$

### 2.1.3 Hydrogenation

Hydrogenation (treating with hydrogen) is a chemical reaction between molecules of hydrogen ( $H_2$ ) and another compound or element, usually in the presence of catalyst. The process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, generally an alkene. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperature. Hydrogenation can also reduce double and triple bonds in hydrocarbons.

Because of the importance of hydrogen, many related reactions have been developed for its use. Most hydrogenations use gaseous hydrogen ( $H_2$ ), but

some involve the alternative sources of hydrogen, not  $H_2$ : these processes are called transfer hydrogenations.

In general, hydrogenation has three components, the unsaturated substrate, the hydrogen (or hydrogen source) and a catalyst.

Typical substrates are listed in the table.

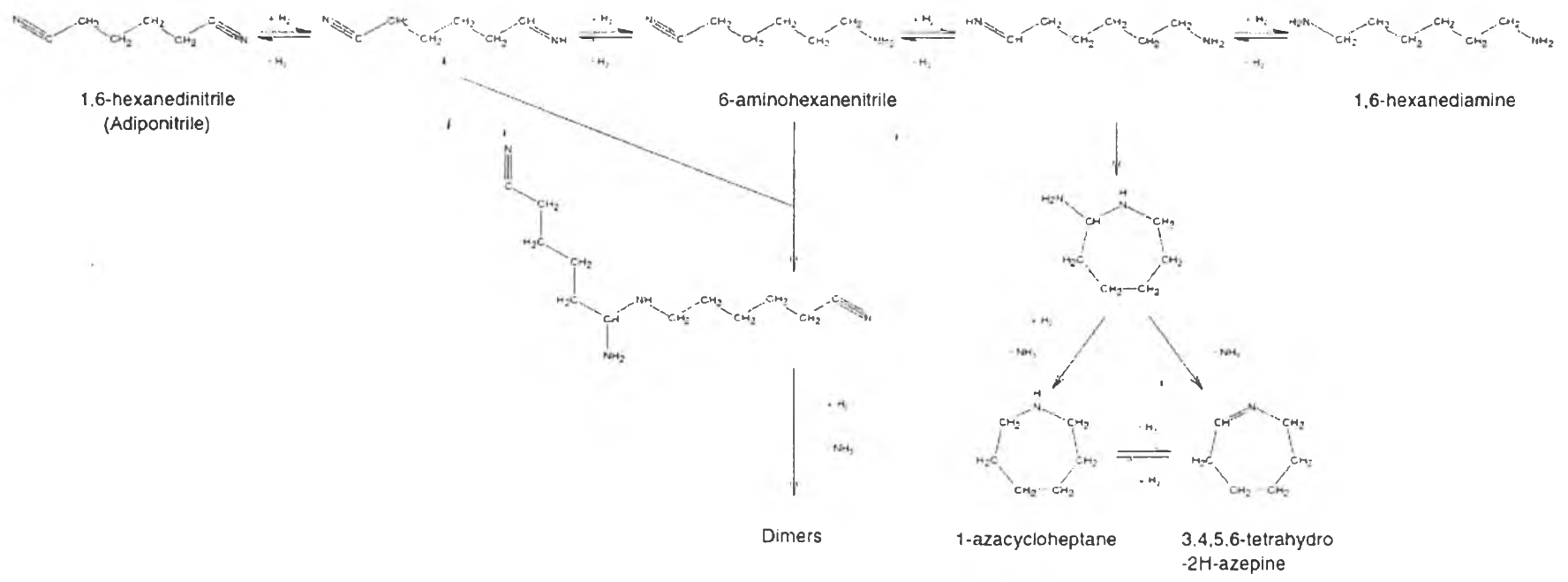
**Table 2.3** Substrates and products of hydrogenation

Substrates	- Products	Comments
alkene, $R_2C=CR'_2$	alkane, $R_2CHCHR'_2$	many catalysts, major application is margarine
alkyne, $RCCR$	alkene, $cis-RHC=CHR'$	over-hydrogenation to alkane can be problematic
aldehyde, $RCHO$	primary alcohol, $RCH_2OH$	easy substrate
ketone, $R_2CO$	secondary alcohol, $R_2CHOH$	more challenging than $RCHO$ , prochiral for unsymmetrical ketones
ester, $RCO_2R'$	two alcohols, $RCH_2OH + R'OH$	challenging substrate
imine, $RR'CNR''$	amine, $RR'CHNHR''$	easy substrate, often use transfer hydrogenation, actual precursor is N-protonated
amide, $RC(O)NR'_2$	amine, $RCH_2NR'_2$	challenging substrate
nitrile, $RCN$	primary amine, $RCH_2NH_2$	product amine reactive toward precursor nitrile in some cases
nitro, $RNO_2$	amine, $RNH_2$	commercial applications use heterogeneous Ni and Ru catalysts; major application is aniline

With rare exceptions, no reaction below 480 °C (750 K or 900 °F) occurs between H<sub>2</sub> and organic compounds in the absence of metal catalysts. The catalyst binds both the H<sub>2</sub> and the unsaturated substrate and facilitates their union. Platinum, palladium, rhodium, and ruthenium form highly active catalysts, which operate at lower temperatures and lower pressures of H<sub>2</sub>. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives, but they are often slower or require higher temperatures.

For hydrogenation, the obvious source of hydrogen is H<sub>2</sub> gas itself, which is typically available commercially within the storage medium of a pressurized cylinder. The hydrogenation process often uses greater than 1 atmosphere of H<sub>2</sub>, usually conveyed from the cylinders and sometimes augmented by "booster pumps". Gaseous hydrogen is produced industrially from hydrocarbons by the process known as steam reforming.

An illustrative example of a hydrogenation reaction is the hydrogenation of adiponitrile to form hexamethylenediamine (Figure 2.3), important substance in the production of nylon 6,6.



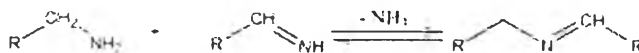
**Figure 2.3** Scheme of possible product obtained by catalytic hydrogenation of adiponitrile (Serra *et al.*, 2002).

### 2.1.3.1 Hydrogenation of Nitrile to Amine

The hydrogenation of nitriles is one of the main methods used in industrial chemistry for synthesis of primary amines. The product is always a mixture of primary, secondary and tertiary amines. The selectivity of this catalytic reaction depends on several factors: The nature of the catalyst (metal and support), the addition of ammonia, the temperature and the solvent used.

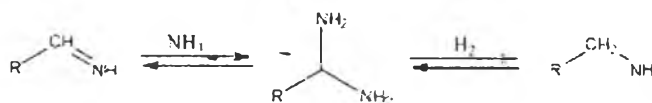
The effect of ammonia on selectivity was first investigated by Braun *et al.*, 1923. All authors describe a higher selectivity towards the primary amine if ammonia is added to the reaction mixture. Another effect is that the reaction rates are higher if ammonia is added up to a certain ammonia concentration and are then again lowered (Degischer *et al.*, 2001). Several explanations were put forward:

- Ammonia influences the equilibrium between the amine, the imine and the azomethine (Cabello *et al.*, 1997).



**Figure 2.4** Equilibrium of amine, imine, azomethine and ammonia.

- Ammonia reacts with the primary imine to produce the 1-aminoamine which is hydrogenolysed to form the primary amine (Christen *et al.*, 1992).



**Figure 2.5** Addition of ammonia to the double bond of the imine and hydrogenolysis of the 1-aminoamine.

- Ammonia poisons the acid site of the catalyst, inhibiting the acid-catalysed side reaction (Verhaak *et al.*, 1994).
- Ammonia modifies the electronic properties of the catalyst, preventing the unwanted side reactions.



Influence of the solvent, The investigation of the effect of various solvents on the selectivity and the activity by comparing the polarity of the solvent with the selectivity towards the primary amine. It was found that the more polar solvent, the higher selectivity. In addition, the activity in different alcohols was investigated, and it was found that the reaction rate increased as the number of C-atoms in the alcohol increased. The solubility of hydrogen in the solvent also influences the hydrogenation reaction (Besson *et al.*, 1991).

Generally, the selectivity decreases as the temperature increases (Bellefon *et al.*, 1994). Degischer *et al.* found that within the range of 60-140 °C the selectivity increased linearly with increasing temperature. At temperature above 160 °C, the selectivity decreased with increasing temperature. This change may be due to different activation energies at higher temperature (kinetic control) or a shift towards equilibrium at higher temperatures (thermodynamic control) (Degischer *et al.*, 2001).

Influence of the hydrogen pressure, a higher hydrogen pressure causes a higher reaction rate. Furthermore, a higher pressure, in general, leads also to a higher selectivity. However, if raney-nickel is employed, a higher hydrogen pressure surprisingly yields a lower selectivity towards the primary amine (Bellefon *et al.*, 1994).

#### 2.1.4 Catalysts

Catalysis is the increase in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents in the chemical reaction, a catalyst is not consumed. A catalyst may participate in multiple chemical transformations. The effect of a catalyst may vary due to the presence of other substances known as inhibitors or poisons (which reduce the catalytic activity) or promoters (which increase the activity).

Catalyzed reactions have lower activation energy (rate-limiting free energy of activation) than the corresponding uncatalyzed reaction, resulting in a higher reaction rate at the same temperature. However, the mechanistic explanation of catalysis is complex. Catalysts may affect the reaction environment favorably, or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds, or form specific intermediates that are not produced

naturally, such as osmate esters in osmium tetroxide catalyzed dihydroxylation of alkenes, or cause dissociation of reagents to reactive forms, such as chemisorbed hydrogen in catalytic hydrogenation.

Kinetically, catalytic reactions are typical chemical reactions; i.e. the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slowest step, and rates are limited by amount of catalyst and its "activity". In heterogeneous catalysis, the diffusion of reagents to the surface and diffusion of products from the surface can be rate determining. A nanomaterial-based catalyst is an example of a heterogeneous catalyst. Analogous events associated with substrate binding and product dissociation apply to homogeneous catalysts.

Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated, or destroyed by secondary processes.

In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid-liquid system or evaporate in a solid-gas system.

Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst. The following is a typical reaction scheme, where C represents the catalyst, X and Y are reactants, and Z is the product of the reaction of X and Y:



Although the catalyst is consumed by reaction 1, it is subsequently produced by reaction 4, so for the overall reaction:



As a catalyst is regenerated in a reaction, often only small amounts are needed to increase the rate of the reaction. In practice, however, catalysts are sometimes consumed in secondary processes.

As an example of this process, in 2008 Danish researchers first revealed the sequence of events when oxygen and hydrogen combine on the surface of titanium dioxide ( $\text{TiO}_2$ ) to produce water. With a time-lapse series of scanning tunneling microscopy images, they determined the molecules undergo adsorption, dissociation and diffusion before reacting. The intermediate reaction states were:  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ , then  $\text{H}_3\text{O}_2$  and the final reaction product (water molecule dimers), after which the water molecule desorbs from the catalyst surface.

In part of catalyst, two broad families of catalysts are known - homogeneous catalysts and heterogeneous catalysts.

#### *2.1.4.1 Homogeneous Catalyst*

Homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the reactants. Most commonly, a homogeneous catalyst is co-dissolved in a solvent with the reactants. The activity and selectivity of homogeneous catalysts is adjusted by changing the ligands. For prochiral substrates, the selectivity of the catalyst can be adjusted such that one enantiomeric product is favored. Asymmetric hydrogenation is also possible via heterogeneous catalysis on a metal that is modified by a chiral ligand.

#### *2.1.4.2 Heterogeneous Catalyst*

Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid and gas, but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids.

## 2.2 Literature Review

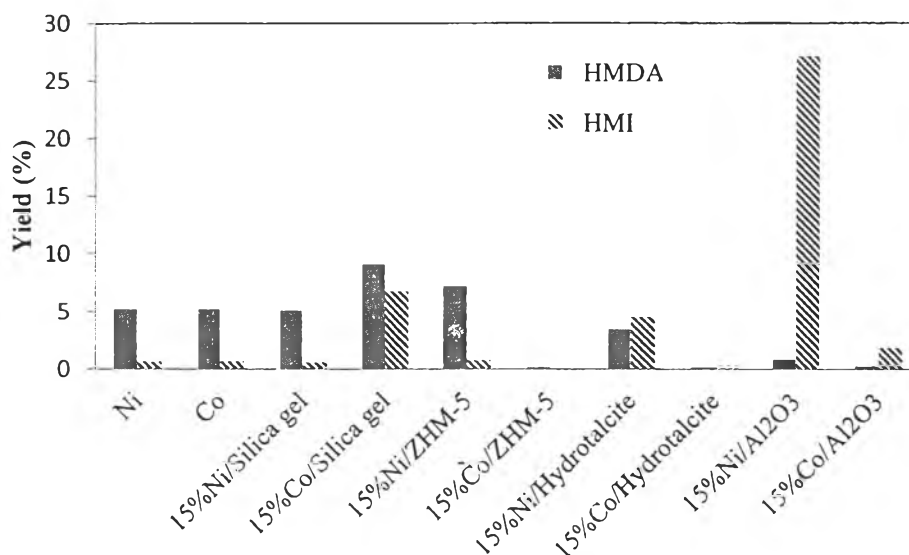
The influence of the nature of metal in adiponitrile hydrogenation investigated at 180 °C, 25 bar of total pressure, and 20 bar of H<sub>2</sub> with Ni, Co and Ru based monometallic catalysts are reported in Table 2.4.

**Table 2.4** The comparison of the monometallic catalysts in the catalytic hydrogenation of adiponitrile

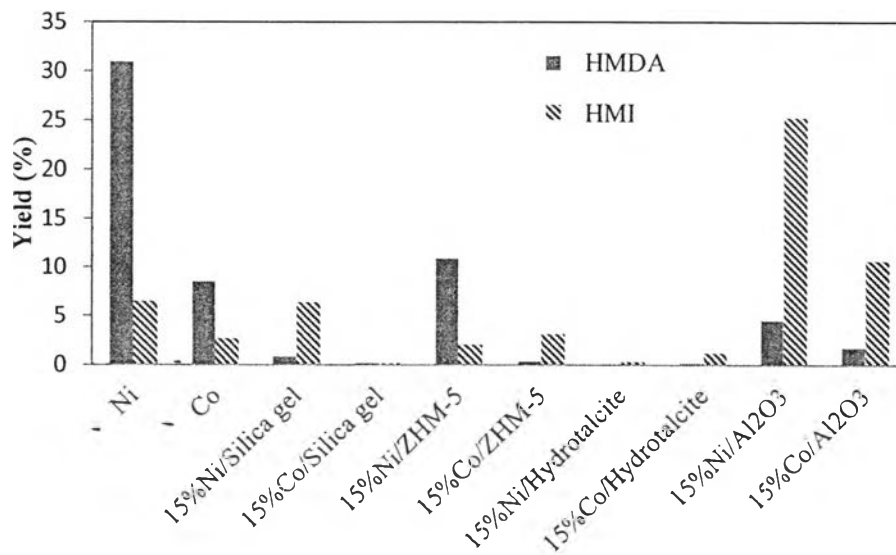
Catalyst	Conversion (%mol)	Average activity (mmol H <sub>2</sub> /g <sub>cat</sub> )	HMDA Selectivity (%mol)
Ni	100	10.1	42
Cu	100	2.1	71
Ru	97.5	0.14	84

Ni has highest average activity at 10.1 mmol H<sub>2</sub>/g<sub>cat</sub>, followed by Co at 2.1 and Ru at 0.14 mmol H<sub>2</sub>/g<sub>cat</sub> but the reverse order in hexamethylenediamine (HMDA) selectivity, 42, 71 and 84 mol% (Balladur *et al.*, 1995). Ni showed much different in average activity but less in HMDA selectivity so Ni was interesting for further studies to increase the HMDA selectivity.

Figures 2.6 and 2.7 shows the results of preliminary work of adiponitrile hydrogenation over various catalysts at 200 °C, time on stream = 2 h and hydrogen to adiponitrile ratio = 5000 and 17000. The range of 0-10 %yield of HMDA was observed at 5000 ratio so there is no significantly different but at 17000 ratio, yield of HMDA from Ni catalyst was much higher than the others. Ni catalyst showed the highest yield of HMDA ca. 31% but yield of hexamethyleneimine (HMI) also increase with increasing yield of HMDA (internal communication of Pengpanich, S. *et al.*,). This result suggests to studying the Ni based catalysts to increase yield of HMDA and decrease yield of HMI.



**Figure 2.6** Yield (%) of HMDA and HMI for the hydrogenation of adiponitrile over various catalysts at 200 °C, hydrogen to adiponitrile ratio = 5000 and time on stream = 2 h (internal communication of Pengpanich, S. *et al.*,).



**Figure 2.7** Yield (%) of HMDA and HMI for the hydrogenation of adiponitrile over various catalysts at 200 °C, hydrogen to adiponitrile ratio = 17000 and time on stream = 2 h (internal communication of Pengpanich, S. *et al.*,).

The study of evolution of several Ni and Ni–MgO catalysts during the hydrogenation reaction of adiponitrile. The changes of the surface properties of two bulk Ni (commercial Raney-Ni and prepared crystalline Ni) and two Ni–MgO catalysts were studied after the hydrogenation of adiponitrile in the gas phase at atmospheric pressure for 216 h at two different reaction conditions. Catalysts before and after the catalytic reaction were characterized by different techniques. Raney-Ni and Ni–MgO catalysts show an evolution of activity with the reaction time until reaching constant conversion and selectivity values. The metallic area decreases after reaction for all catalysts. Interestingly, this decrease is lower and the surface area slightly increases when using reaction conditions of high space velocity, which favour the desorption of condensation products and results in a certain disagglomeration of particles. The high hydrogenation ability of Raney-Ni and the basicity of Ni–MgO catalysts allow them to achieve much higher conversions than the bulk Ni catalyst prepared. The presence of defined octahedral particles, observed for the crystalline Ni and Ni–MgO catalysts by SEM, has been related to the constant high value of selectivity to 6-aminohexanenitrile (around 80%) maintained after 216 h of reaction at less hydrogenating conditions (Serra *et al.*, 2004).

Because Ni acts as a catalyst in the reaction so the more molecule of Ni expects to increase the performance of catalyst in activity and selectivity so the support will use to disperse the molecule of Ni catalyst. The comparison of Ni dispersion of the Ni supported catalysts shows in Figure 2.5. 15% Ni/Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> catalyst showed the highest dispersion at 2.88% (Bampenrat *et al.*, 2010).

**Table 2.5** Degree of Ni dispersion of the Ni supported catalysts

Catalyst	Ni dispersion (%)
15% Ni/ $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	0.47
15% Ni/Ce <sub>0.75</sub> Zr <sub>0.25</sub> O <sub>2</sub>	2.88
15% Ni/Ce <sub>0.75</sub> Zr <sub>0.15</sub> Mn <sub>0.10</sub> O <sub>2</sub>	1.46
15% Ni/Ce <sub>0.75</sub> Zr <sub>0.05</sub> Mn <sub>0.20</sub> O <sub>2</sub>	1.19
15% Ni/Ce <sub>0.75</sub> Mn <sub>0.25</sub> O <sub>2</sub>	0.98

GB1196208A(1970) in the topic of Preparation of Hexamethylenediamine from Adiponitrile claimed the reaction in presence of ammonia which comprises conducting the hydrogenation reaction in at least two reactor zones in series, the ammonia present in each reaction zone. The weight ratio of adiponitrile to ammonia at the start of the hydrogenation reaction in each reaction zone is substantially the same. Hexamethylenediamine is removed from the reaction mixture in each zone and the remaining reaction mixture, together with additional adiponitrile, is passed to the next reaction zone.

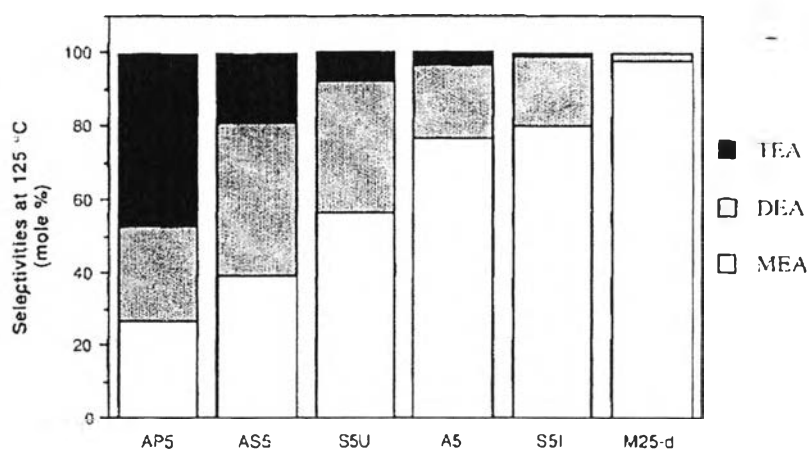
GB1284348A(1972) in the topic of Process for the Manufacture of Hexamethylenediamine claimed the catalytic hydrogenation of adiponitrile with finely Raney catalyst in liquid phase, at 20 to 50 atmospheric pressure and temperature from 60 to 100 °C, that hydrogen and adiponitrile are fed into a liquid reaction medium consisting of hexamethylenediamine, water and a caustic alkali.

The addition of basic substances, ammonia and a caustic alkali, in both mentioned patents due to the basicity can suppress the deamination reaction that convert 6-aminohexanenitrile to hexamethyleneimine (by-product) so in this research will try to use basic support instead of caustic alkali to increase the basicity of the system.

The study of gas-phase hydrogenation of adiponitrile with high selectivity to primary amine over supported Ni-B amorphous catalysts. Gas phase hydrogenation of adiponitrile was performed at 1 atm pressure over the Ni-B/SiO<sub>2</sub> amorphous catalyst, which exhibited high selectivity to HMDA at 100% adiponitrile conversion. The selectivity to HMDA could be further enhanced by MgO doped to support (Ni-B/SiO<sub>2</sub>-MgO). The product analysis revealed that the selectivity to HMDA was mainly dependent on the contents of AHN and HMI formed during the adiponitrile hydrogenation. The AHN was an intermediate in the reaction; it resulted from the half-hydrogenation of adiponitrile; and its content was strongly affected by the activity of the catalyst. The HMI was a side-product (secondary amine) formed via the nucleophilic addition of the primary amine on one side of adiponitrile chain to the aldimino carbon atom on the other side which was adsorbed by the Ni active sites. The electronic density of the Ni active sites played a key role in determining the content of HMI. The presence of the alloying B resulted in the electron-enriched

Ni active sites which effectively inhibited the formation of HMI and in turn, resulted in the high selectivity to HMDA (Li *et al.*, 2001).

The study of the selective hydrogenation of acetonitrile on supported nickel catalysts. Figure 2.8 shows the selectivity of ethyl-, diethyl-, and triethylamine at 125 °C of the catalysts.

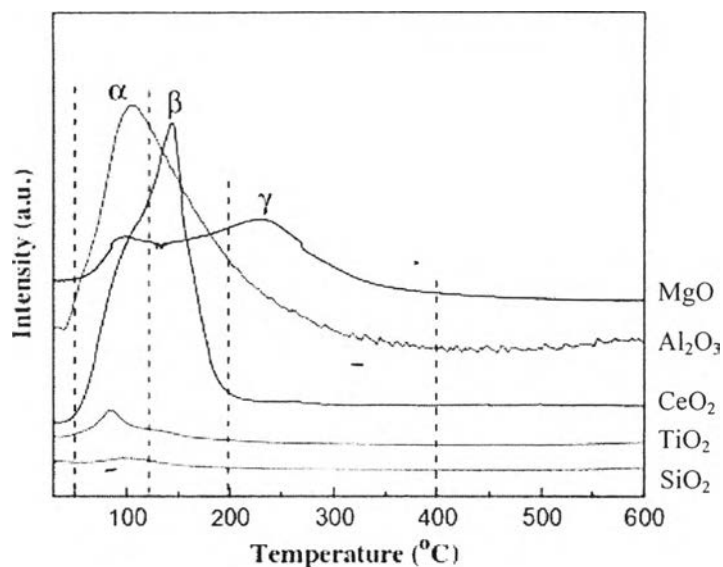


**Figure 2.8** Selectivity in the hydrogenation of acetonitrile at 125 °C for several nickel catalysts containing supports of different basicity. MEA = monoethylamine, DEA = diethylamine and TEA = triethylamine (Verhaak *et al.*, 1994).

Going from left to right, the catalyst basicity increases. In this sequence, the selectivity toward the primary amine ranges from ca. 25 mol% (catalyst AP5) to ca. 98 mol% (catalyst M25-d). It showed that the higher basicity of the catalysts can increase the selectivity of primary amine (monoethylamine, MEA) (Verhaak *et al.*, 1994).

The study of effect of support's basic properties on hydrogen production in aqueous-phase reforming (APR) of glycerol and correlation between water gas shift and APR. MgO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> supports were compared the basicity.





**Figure 2.9** TPD profiles of CO<sub>2</sub> adsorbed on the supports (Guo *et al.*, 2012).

TPD profiles of CO<sub>2</sub> adsorbed on the different supports are reported in Figure 2.9. The basic surface sites were classified according to their basic strength, which depend on the different desorption temperature of CO<sub>2</sub>. As shown in the figure, there were three kinds of desorption peaks between 50 and 400 °C, denoted as  $\alpha$  peak (between 50 and 120 °C),  $\beta$  peak (between 120 and 200 °C) and  $\gamma$  peak (between 200 and 400 °C), respectively. In these three peaks,  $\alpha$  and  $\beta$  peaks are related to the weak basic surface sites while  $\gamma$  peak is related to the strong basic sites. The SiO<sub>2</sub> support showed only one very weak  $\alpha$  peak of CO<sub>2</sub> desorption. TiO<sub>2</sub> support showed  $\alpha$  and  $\beta$  peaks. For CeO<sub>2</sub>, there was a narrow  $\beta$  peak with high intensity. Besides, a shoulder  $\alpha$  peak could also be observed in the profile of CeO<sub>2</sub>. It is worth to remark that there was a broad and strong peak in the temperature range of 50 to 400 °C with a peak of 100 °C in the profile of Al<sub>2</sub>O<sub>3</sub>, indicating that all of the three kinds of basic surface sites existed and the weak basic surface sites were dominant in Al<sub>2</sub>O<sub>3</sub>. Although there were also three kinds of basic surface sites were contributed by the  $\gamma$  peak. From these data, a basicity scale of support can be established, according to the CO<sub>2</sub>-TPD, as follows: MgO > Al<sub>2</sub>O<sub>3</sub> > CeO<sub>2</sub> > TiO<sub>2</sub> > SiO<sub>2</sub> (Guo *et al.*, 2012).

The study of the effect of surface acidic and basic properties on the hydrogenation of laurionitrile over the supported nickel catalysts. Supported nickel

catalysts with different supports (MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgAlO and SiAlO) were prepared by the co-precipitation method. Nickel was found to be relatively easier to reduce in Ni/MgO and Ni/SiO<sub>2</sub> than in Ni/Al<sub>2</sub>O<sub>3</sub>, while nickel was higher dispersed in Ni/SiO<sub>2</sub> than in Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/MgO. Thus, the reducibility and dispersion of nickel in Ni/MgAlO and Ni/SiAlO were significantly enhanced, leading to the high active nickel surface areas (75 m<sup>2</sup>/g<sub>cat</sub>). Acetonitrile was found to be adsorbed on the reduced nickel and acidic sites. The strong surface basicity of Ni/MgO was found to favour the selectivity to the primary amine, but inhibited the conversion of laurionitrile. On the other hand, the conversion of laurionitrile was high over the Ni/SiO<sub>2</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiAlO with strong surface acidity, but the selectivity to the primary amine was relatively low. The Ni/MgAlO with intermediate strengths of surface acidity and basicity exhibited the high conversion of laurionitrile and high selectivity to the primary amine (Chen *et al.*, 2012).

The study of the effect of surface acidic and basic properties on the hydrogenation of aromatic rings over the supported nickel catalysts. Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/MgAlO and Ni/MgO catalysts containing about 60 %wt. of nickel were prepared by the co-precipitation method. It was found that these catalysts possessed high surface areas of active nickel due to the high loading and dispersion of supported nickel. Nickel was relatively easier to reduce in Ni/MgO than in Ni/Al<sub>2</sub>O<sub>3</sub>, while it was more highly dispersed in Ni/Al<sub>2</sub>O<sub>3</sub> than in Ni/MgO. Thus, both the reducibility and dispersion of nickel in Ni/MgAlO were quite high, leading to the highest area of active nickel (78 m<sup>2</sup>/g<sub>cat</sub>) in the three catalysts studied in this work. Microcalorimetric adsorption of NH<sub>3</sub> and CO<sub>2</sub> showed the acidic surface of Ni/Al<sub>2</sub>O<sub>3</sub>, but basic surface of Ni/MgO, both after the reduction. The reduced Ni/MgAlO exhibited both the surface acidity and basicity. Its surface acidity was weaker than Ni/Al<sub>2</sub>O<sub>3</sub>, but stronger than Ni/MgO, while its surface basicity was weaker than Ni/MgO, but stronger than Ni/Al<sub>2</sub>O<sub>3</sub>. The initial heat was measured to be about 108, 113 and 127 kJ/mol for the adsorption of CO on the Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/MgAlO and Ni/MgO, respectively, indicating that the basic support MgO might donate electron charges to, while the acidic support Al<sub>2</sub>O<sub>3</sub> might withdraw electron charges from the supported nickel atoms. Thus, the surface charge density of nickel might be changed by the surface acid–base properties of supports (Hu *et al.*, 2010).

There are several patents deal with gas and suspension phase adiponitrile hydrogenation reaction with various catalysts either in form of free metals or oxide or salt such as nickel, cobalt, copper, zinc, iron, platinum, palladium, rubidium and ruthenium.

**Table 2.6** Review of the patents

Patent	Catalysts	Temperature (°C)	Pressure (atm)
GB1070031A(1967)	Ni, Co, Cu, Zn, Pt, Pd, Rb, Ru as free metals, oxides or salts	120 - 170 °C	270 - 400
GB1196208A(1970)	Ni, Co, Cu, Zn, Pt, Pd, Rb, Ru as free metals, oxides or salts	135 - 150 °C	333
GB1284348A(1972)	Raney-Ni or Raney-Ni containing small amount of other metals such as chromium	60 - 100 °C	20 - 50
GB1328333A(1973)	Cobalt oxide	85 - 185 °C	200 - 400
GB1379250A(1975)	Iron catalyst	70 - 260 °C	250 - 400
US4064172(1977)	Iron oxide	80 - 200 °C	20 - 500
WO 98/43940(1998)	sponge Co (Raney Co) modified with 0.5 - 6 weight % of at least one of the group consist of Ni, Cr, Fe, Mo	25 - 150 °C	< 140

Patent	Catalysts	Temperature (°C)	Pressure (atm)
US5874607A(1999)	Co and/or Fe	40 - 150 °C (suspension) 30 - 200 °C (fixed bed reactor)	20 - 200 (suspension) 20 - 300 (fixed bed reactor)
US5900511(1999)	sponge Co modified with 0.5 - 6 weight % of at least on of Ni, Cr, Fe, Mo	25 - 150 °C	< 140
US6080883A(2000)	nickel	40 - 150 °C (suspension) 20 - 150 °C (fixed bed reactor)	20 - 200 (suspension) 20 - 300 (fixed bed reactor)
EP0971876B1(2002)	sponge Co modified with 0.5 - 6 weight % of at least on of Ni, Cr, Fe, Mo	25 - 150 °C	< 135
US6359178B1(2002)	catalysts based on elemental iron	70 - 220 °C	100 - 400
EP1107942B1(2004)	based on elemental iron	70 - 220 °C	100 - 400