Chapter-4

Alkylation of aniline on MgO catalyst obtained from different precursors

"All truly wise thoughts have been thought already thousands of times; but to make them truly ours, we must think them over again honestly, till they take root in our personal experience."

Johann Wolfgang von Goethe
Nomenclature

NMA $\rightarrow$ N-methylaniline

NNDMA $\rightarrow$ N, N-dimethylaniline

LDH $\rightarrow$ layered double hydroxides

MgCO$_3$ $\rightarrow$ Magnesium carbonate

Mg(OH)$_2$ $\rightarrow$ Magnesium hydroxide

4Mg(OH)$_2$ $\rightarrow$ MgCO$_3$5H$_2$O Magnesium hydroxide carbonate

MgO $\rightarrow$ Magnesium oxide

PVA $\rightarrow$ Polyvinyl alcohol

NEA $\rightarrow$ N- monoethylaniline

NNDEA $\rightarrow$ N’, N-diethylaniline
4.1 Introduction

Alkylation of amines is one of the most fundamental and industrially important reaction as the alkylated products serve as vital precursors for bigger organic and drug molecular build ups [1-4]. The alkylation of aniline with methanol gives toluidine, N-methylaniline (NMA), and N, N-dimethylaniline (NNDMA) as major compounds. These are important intermediates in the manufacture of dyes, plastics, and explosives. The ethyl and benzyl anilines are also used widely in these applications. N-ethylaniline is important dyestuffs. N, N-diethylaniline is used as a cocatalyst in polymerization reaction and as an inhibitor of acid corrosion in metallic vessels as well as an antioxidant for lubricating oils. 2, 6-diethylaniline is an important intermediate in the synthesis of weedicide [5].

Traditionally, alkylation reactions of amines are carried out in liquid phase, using mineral acids as catalysts and alkyl halides or dimethyl sulfate as alkylation agents [6-8]. The intrinsic drawback with the processes coupled with increasing awareness of environmental issues has prevented their wide use. Scientists worldwide have been devoting their attention to the development of eco-friendly catalysts for the production of these industrially important chemical intermediates. Various heterogeneous catalysts and nontoxic alkylation reagents such as olefins, alcohols and dimethyl carbonates have been tested for the reaction [9-29]. These include oxides [9-12], ferrospinels [13], layered double hydroxides (LDH) [14], zeolites [15–20], AEL type molecular sieves [21-22], clays [23–26] and magnesium orthophosphate [27-28]. Many of these reports reveal the dependence of acid–base properties of the catalysts for aniline alkylation. The type and strength of acidic and basic sites have been an area of intense investigations. Thus, the design and development of catalyst materials with tunable surface and acid properties may potentially
extend the scope of this industrially useful organic transformation to obtain the desired activity and selectivity.

Nan Ko et al. [9] have studied the alkylation of aniline with methanol over γ-alumina in a fixed-bed and integral-flow reactor at atmospheric pressure and a temperature range of 300-425 ºC. N-methylation was the predominant reaction product with selectivity higher than 98 mol% over this temperature range. They also proposed a mechanism in which aniline and methanol are adsorbed undissociatively on the Lewis acid–base dual sites of gamma-alumina and electrophilic attack of the methyl group of methanol on the nitrogen atom of aniline results in favorable formation of N-methylated products.

Sugunan S et al. [13] have investigated various compositions of chromium manganese ferrospinels with general formula \( \text{Cr}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4 \) \( (x = 0, 0.2, 0.4, 0.6, 0.8 \text{ and } 1.0) \) as catalysts for the vapour phase alkylation of aniline with methanol. All the ferrites exhibited 100 percent selectivity for N-methyl aniline. Neither C-alkylated products nor any other side products were detected for all the catalyst samples. They found that catalytic activity of the samples was related to their acid–base properties and also on the cation distribution. Under the optimized reaction conditions all the systems showed constant activity for a long duration.

Santhanalakshmi et al. [14] investigated the possibility of employing calcined Mg(II)-Al(III) LDHs as basic catalysts for the vapour phase alkylation of aniline with methanol. Only a single product (NMA) was formed with a maximum of 68 % conversion of aniline to NMA. The role of acidity-basicity on the catalytic behavior was analysed. They reported the combined catalytic effect of acidic and basic sites of the calcined hydrotalcites as the main reason for the absolute selectivity towards NMA.
Studies over various zeolites suggest that the major factors influencing the activity and selectivity of the gas-phase alkylation of aniline are the acid-base properties and shape selectivity of the solid catalyst. Change in selectivity towards N-alkylation of aniline using Faujacute’s acidic and basic property was studied by Barthomeuf et al. [15]. The alkylation of aniline with methanol was carried out at 400 °C on X and Y zeolites exchanged with Li, Na, K, Rb and Cs cations. The activity and selectivity were shown to be strongly dependent on the acid-base properties. The selectivity could be oriented towards alkylation on the nitrogen or on the aromatic ring. The X type zeolite was found to be more active than the Y ones but they deactivate quickly. The study made at equal conversion showed that the selectivity is governed by the balance between the basicity of the oxygen atoms of the framework and the Lewis acidity of the cations in the cages.

B.S. Rao et al. [21] examined aniline methylation over AEL type molecular sieves. The activity of AlPO-11 and derivatives of AlPO-11 on the product pattern of aniline methylation were investigated. They found AlPO-11 and its related materials were found to be active in aniline methylation, thereby decreasing acid strength and by increasing basic strength, N-monoalkylated product could be promoted while stronger acid sites enhance successive alkylation of monoalkylated product. Woo et al. [22] investigated the selective alkylation of aniline with methanol over several metallosilicates. They suggested that weak and moderate acid sites are sufficient for the N-alkylation whereas strong sites are mandatory for ring alkylation and coke formation. According to alkylation studies reported by Narayanan and Deshpande on clays [23-26], a combination of Brønsted and Lewis acid sites on the catalyst surface is more favorable for aniline alkylation.
Aramendía et al. [27, 28] studied the catalytic activity in the alkylation of aniline with methanol over Mg$_3$(PO$_4$)$_2$/MgO systems prepared from different proportions of the two components. The solids were studied in terms of surface chemical properties and of their catalytic activity in the alkylation of aniline with methanol. N-methylaniline and N, N-dimethylaniline were formed as major products over these solids. However, as expected, specific surface area and basicity decrease with increasing P content, and the alkylation activity and selectivity toward NNDMA was found to increase with increasing P content. Many of these reports reveal the dependence of acid–base properties of the catalysts and aniline alkylation; the type and strength of acidic and basic sites have been an area under discussion. Thus, the design and development of materials with tunable surface and acid properties may potentially extend the scope of this industrially useful organic transformation to obtain the desired activity and selectivity.

Magnesium oxide is a highly versatile metal oxide catalyst which is used for several base catalyzed organic transformations such as the Tishchenko reaction [29], the Meerwein-Ponndorf-Verley reaction [30], self-Michael addition to form methyl diesters [31], self-condensation of propanol [32], benzylation of aromatic compounds [33], aldol reaction [34] and Michael addition of malonates to enones [35]. We have earlier reported MgO as a catalyst for alkylation and benzylation of phenol [36, 37]. As part of the continued effort towards selective synthesis of chemicals and chemical intermediates using vapor phase alkylation over MgO catalyst, we have chosen the continuous vapor phase alkylation of aniline using alcohols in the present investigation. The selection of alcohols as alkylating agent is due to the fact that the use of alcohols does not generate harmful
byproducts and alcohols are more readily available than corresponding alkyl halides or dimethyl sulfate compounds.

The catalytic properties are generally recognized to be dependent on the preparation methods. The preparation consists of various factors which determine the property of the final product. These include precipitation method, ageing period, way of washing and calcination conditions. Amongst these, the kind of starting material and pretreatment conditions gives often large effect on catalytic property. The catalytic property of alkaline earth oxides is quite dependent on the starting material and pretreatment conditions. Hattori et al. [38] had studied the difference in surface and catalytic properties of two magnesium oxides prepared from hydroxide and carbonate hydroxide on the isomerization of butenes, while MgO prepared from hydroxide showed four times higher activity and selectivity than MgO prepared from carbonate. MgO was also reported to vary its catalytic property with the pretreatment for the isomerization of 1-butene and H2-D2 exchange reaction. Thus, it can be seen that precursor and catalyst preparation method influences basicity/base strength distribution and surface area of the synthesized catalyst.

The most conventional method reported for MgO synthesis is via the thermal decomposition of several magnesium salts [39, 40]. This is achieved in most cases by thermal decomposition of magnesium-compounds, which decomposes to magnesia and gaseous components. However, the resulting MgO particles inevitably possess relatively large and non-uniform particle sizes and low specific surface area, which are not preferable for the aforementioned applications. For most catalytic purposes of magnesia, high specific surface area is needed. Intensive research has been done on the preparation of highly active MgO from basic magnesium-carbonate. Recently, there have been some methods for the
synthesis of nanostructured mesoporous MgO, e.g., gel-templated technique [41], modified citrate precursor technique [42], microwave plasma torch technique [43] and combustion technique [44]. Sol–gel technique combined with a structure directing surfactant has also been applied for the synthesis of MgO nanoparticles [45].

MgO is considered to be essentially a strongly basic oxide by virtue of the presence of O$_2^{-}$ surface ions capable of accepting protons. However, it is also a weak Lewis acid on account of its Mg$^{2+}$ ions (46). There are three main methods used to explore basic strength and basicity; first, benzoic acid titration using indicators, the adsorption of gaseous acids and using test reactions. The benzoic titration method is generally not suitable for measuring the basicity of a catalyst because it is carried out at room temperature which is significantly different from the usual operating conditions of catalytic reactions. Adsorption of acidic gases is therefore preferred and the most widely used for the measurement of basicity. Probe molecules which have been used include carbon monoxide, carbon dioxide, sulphur dioxide, hydrogen, phenol, water, pyrole. The third option is to employ test reactions such as, decomposition of alcohol; this reaction is also regarded as a typical reaction for investigating the acid-base properties of catalysts. Some authors have ascribed the dehydrating ability of a solid to its surface acidity [47] and its dehydrogenating action to its basicity [48]; others, however, assume that the dehydrogenation is catalyzed by both acid and basic sites through a concerted mechanism [49].

In this endeavor, we have prepared MgO with high surface area by controlled thermal decomposition of various magnesium salts such as (i) magnesium carbonate, MgCO$_3$ (ii) Magnesium hydroxide, Mg(OH)$_2$ (iii) Magnesium hydroxide carbonate 4Mg(OH)$_2$.MgCO$_3$.5H$_2$O and (iv) neat Magnesium Oxide, MgO for comparison purpose.
Structure directing nonionic surfactant, polyvinyl alcohol (PVA) was employed to obtain catalyst with the required pore characteristics. Thus, this technique provides a conventional procedure with the advantages of mild conditions, low cost, ease of work-up and promising large-scale production possibilities. The catalysts were examined for their surface properties and catalytic activity for the vapor phase alkylation of aniline using primary and aromatic alcohols such as methanol, ethanol and benzyl alcohol. A systematic study has been made which includes preparation of above-mentioned catalysts, characterization by XRD, BET and thermal analysis. The solids were used as catalysts for the transformation of benzyl alcohol and the alkylation of aniline with methanol, ethanol and benzylalcohol. Dehydrogenation selectivity in the benzyl alcohol reaction was used to study the basicity of the prepared solids. We have made an attempt to relate catalytic activity of MgO obtained from different precursors towards selective N-alkylation of aniline with their physico-chemical properties.

4.2 Experimental

4.2.1 Catalyst preparation

MgO catalysts in the size range of 800 to 1000 µm were prepared by using various magnesium salts namely i) Magnesium carbonate \([\text{MgCO}_3]\) ii) Magnesium hydroxide \([\text{Mg(OH)}_2]\) ii) Magnesium hydroxide carbonate \([4\text{Mg(OH)}_2\cdot\text{MgCO}_3\cdot5\text{H}_2\text{O}]\) and iv) Magnesium oxide \([\text{MgO}]\). The following step wise protocol was used individually for each precursor to obtain different MgO catalysts. To 100 g of magnesium salt, 400 cm\(^3\) of water containing 0.5 % PVA was added slowly over a period of about five minutes, and stirred further at room temperature for about 15 min. The resulting slurry was heated to 80 °C for 6 h with occasional stirring to remove excess of water. The blend was palletized in a
palletizing machine (Carver press) by applying about 7 tons of pressure to obtain 2 mm thickness and 2 cm diameter pellets. The catalyst was then broken down to obtain uniform particles in the size range of 800 to 1000 µm. Further, the catalyst particles were dried at 100 °C for 12 h in a hot air oven and further calcination at 480 °C for 10 h under nitrogen (30 cm³/min) in a tubular furnace to obtain the modified MgO catalyst.

Representation of catalysts used in the present investigation is as follows: The solids examined included magnesium oxides obtained by calcination of MgCO₃,Mg(OH)₂, MgCO₃-Mg(OH)₂ and MgO, and were designated MgO (I), MgO (II), MgO (III) and MgO (IV) respectively. For instance MgO (I), represents MgO that was obtained by slurrying MgCO₃ with aqueous 2 % PVA solution, followed by drying overnight at 100 °C in a hot air oven and sifting through 800-1000 µm mesh, prior to use, all solids were subjected to the same thermal treatment, namely, calcination at 400 °C for 10 h, with a ramp rate of 5 °C/min under 30 cm³/min under nitrogen atmosphere. The prepared catalysts were stored in a desiccator under dry nitrogen atmosphere. These catalysts were characterized by using various physico-chemical techniques and evaluated for vapor phase transformation of benzyl alcohol and alkylation of aniline with various alcohols such as methanol, ethanol and benzyl alcohol.

4.2.2 Catalyst characterization

The following characterization has been made on the catalyst materials. XRD was measured on a Philips X-ray diffractometer with Ni filtered Cu-Kα radiation over the range of 2θ from 5 to 80° with the intensity data for each point being collected at a 4 second interval. Surface area, pore volume and pore size distribution presented in this research were measured by nitrogen adsorption at -197 °C with an ASAP-2010 porosimeter from
Micromeritics Corporation (Norcross, GA). Surface area was measured by the BET method. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all the mesopores were filled with condensed nitrogen in the normal liquid state. Pore size distributions were estimated using the BJH algorithm. The samples were degassed at 100 °C at 10⁻⁵ torr overnight prior to the adsorption experiments.

4.2.3 Vapor phase alkylation

Vapor phase catalytic activity of the prepared catalysts was tested in a specially designed and in-house fabricated vapor phase quartz reactor placed in a programmable tubular furnace as shown in Fig. 4.1. The reactor was heated to the requisite temperature with the help of a digital temperature controller cum indicator. The catalyst bed was kept packed at a constant set temperature in the center portion of the reactor. The bottom of the reactor was connected to a liquid condenser and a receiver to collect the products. Reactants were fed into the reactor using a syringe infusion pump. The quartz reactor was specially designed for carrying out the vapor phase reactions. It consists of three main parts, the upper part is coiled, which acts as pre evaporation chamber for the reactants before they reach the catalyst bed kept between two quartz plugs in the middle part, the bottom part consists of hollow tube connected to a liquid condenser and a receiver to collect the products.
Fig. 4.1 Reactor setup used for carrying out vapor phase reactions.

Calcination of catalyst sample was accomplished by using the following procedure. Around 5 g of the sieved catalyst particles were loaded into the reactor tube to form a catalyst bed and pre-treated by calcination at 480 °C for 10 h under nitrogen flow at 30 cm³/min (ramp rate of 5 °C/min). In a typical reaction, 3g of pre-calcined catalyst was heated to the reaction temperature of 480 °C (ramp rate of 5 °C/min), after which the liquid organic feed containing a mixture of aniline and alcohols of desired molar ratio was introduced to carry out the catalytic reactions using a syringe pump at a constant flow rate of 1.2 cm³/h. Evolved gases emerging from the reactor outlet were passed through a liquid condenser onto a collector that allowed liquids to be withdrawn at different times. Following four reactions were studied independently over the four MgO catalyst prepared from different sources at 480 °C.

i. Partial oxidation of benzyl alcohol to benzaldehyde.

ii. Alkylation of aniline with methanol (1:3 molar ratio)

iii. Alkylation of aniline with ethanol (1:3 molar ratio)
iv. Benzylolation of aniline with benzylalcohol (1:3 molar ratio)

All the reactions were carried out for a period of 4 h, the liquid products were taken every hour and analyzed for product compositions by gas chromatograph (Shimadzu 2010), equipped with FID and HP-5, 30 m capillary column using a linear temperature program (from 60 °C to 300 °C at 10 °C min⁻¹). Authentic standards and Agilent 5973 GCMS (EI, 70 eV) was used for confirmation of products.

4.3 Results and discussion

4.3.1 Catalyst characterization

4.3.1.1 Textural properties

Table 4.1 shows the specific surface area, cumulative pore size, and average pore diameter for the calcined catalysts. Surface area was found to be decrease in the following order MgO (III) > MgO (I) > MgO (IV) > MgO (II). Magnesia obtained from decomposition of MgCO₃,Mg(OH)₂ and Mg(OH)₂ had the highest and least surface area of 308.5 m²/g and 62.5 m²/g respectively. The corresponding pore diameter for these two catalysts was found to be 53.4 and 141.9 respectively. The difference in surface area may be attributed to the evolution of the carbon dioxide and water from the precursors and the pore formation. As such magnesium oxide is slightly hygroscopic and absorbs moisture from atmosphere, many of these magnesium compounds will have a few molecules of water adhered to them and upon heating they leave the pores and the pores that are formed contribute for the surface area. Further, the processing temperature of these inorganic compounds may lead to sintering and pore collapsing that results in less surface area with magnesium hydroxide precursor [38].
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO (I)</td>
<td>278.8</td>
<td>0.609</td>
<td>71.6</td>
</tr>
<tr>
<td>MgO (II)</td>
<td>62.5</td>
<td>0.22</td>
<td>141.9</td>
</tr>
<tr>
<td>MgO (III)</td>
<td>308.5</td>
<td>0.5</td>
<td>53.4</td>
</tr>
<tr>
<td>MgO (IV)</td>
<td>186.5</td>
<td>0.272</td>
<td>58.2</td>
</tr>
</tbody>
</table>

**Table 4.1** Surface area, pore volume and pore diameter for the calcined catalysts.

4.3.1.2 Thermal characterization

As mentioned earlier in surface area characterization to get the right surface characteristics, such as surface area and pore size, it is very important and essential to pretreat or activate the catalysts at the right temperature. To obtain the right temperature, few desorption experiments were carried out with the temperature required to remove the adsorbed species like carbonate and hydroxide from the magnesium precursor. These studies were carried out by pyrolysis-MS technique; evolved gases were monitored over a temperature range of 80 °C to 700 °C. During the experimentation, the evolved gas of the pyrolysed sample was continuously fed to the mass spectrometer and observed for molecules that were evolved by mass fragments. Single Ion Mode (SIM) was used to scan the evolved water (m/z 18) and carbon dioxide (m/z 44). Furnace temperature was ramped from 80 °C to 700 °C at the rate of 40 °C/min. Total ion chromatogram obtained by mass spectrometer detector for the evolved gases for different catalyst precursors by pyrolysis-MS are shown in Fig. 4.2. The X axis is shown in time (min), which is converted to temperature while calculating the evolving temperature based on the ramp rate and initial
set temperature. The inferences when the magnesium compounds are studied with the above said pyrolysis studies include the following. Evolution of water from magnesium hydroxide was observed from around 320 °C and completely evolved by 420 °C, whereas, with magnesium carbonate, complete evolution of water was observed below 320 °C and evolution of carbon dioxide was observed between 340 °C to 480 °C.

**Fig. 4.2** Schematic diagram of pyrolyser GC-MS unit.

In the case of magnesium hydroxide carbonate, water evolved in the same manner as that of magnesium carbonate, however, evolution of carbon dioxide pattern showed a different behavior, carbon dioxide continued to evolve beyond 480 °C and continued up to 520 °C. The difference in carbon dioxide evolution can be attributed to different kind of basic sites present on magnesium carbonate and magnesium hydroxide carbonate material.
Fig. 4.3  Ion chromatogram of evolved gases (SIM mode; m/z 18 and m/z 44) for a) Mg(OH)$_2$ b) MgCO$_3$ c) Mg(OH)$_2$MgCO$_3$ obtained by mass spectrometer detector.

The XRD pattern (Fig. 4.3) shows intense peaks at 2θ values of 37, 42.8 and 62.3 for the calcined samples, which clearly shows that the studied powder sample have rock salt structure, the only crystalline form of magnesium oxide (JCPDS 71-1176). Broadness of peak for MgO obtained from Mg(OH)$_2$MgCO$_3$ and MgCO$_3$ indicates their amorphous nature compared to MgO and Mg(OH)$_2$. 
**4.4** XRD spectra of MgO catalysts calcined at 480 °C. a) Mg(OH)₂MgCO₃ b) MgO c) MgCO₃ d) Mg(OH)₂

**4.3.1.3. Surface acid-base properties**

In our efforts to study the surface acid-base properties of different MgO catalysts, we have employed conversion of benzyl alcohol to benzaldehyde as a test reaction. MgO obtained from different precursors of magnesium exhibited fairly high selectivity for benzaldehyde and toluene was the only by-product formed in this reaction, whereas, other secondary products were formed in trace levels. Partial oxidation reaction of benzyl alcohol is shown in Scheme 4.1.
Scheme 4.1 Vapor phase oxidation reaction of benzyl alcohol on MgO catalyst.

The results obtained in the dehydration-dehydrogenation of benzyl alcohol over catalysts of the MgO obtained from various precursors are shown in Table 4.2. The enhanced catalytic activity of all the catalysts may be explained as follows. It is evident that the catalytic selectivity for benzaldehyde is generally high for all the solids. This was expected as the dehydrogenating activity is usually lower than the dehydrating activity on equal reaction temperature. Regarding the surface acid–base properties, the population of basic sites exceeds the acid sites. The enhanced basic site is due O\(^{2-}\) and Lewis acidity due to Mg\(^{2+}\). The percent conversion of benzyl alcohol on the MgO catalysts prepared from different precursors was found to be in the order of MgO > MgCO\(_3\) > Mg(OH)\(_2\) MgCO\(_3\) > Mg(OH)\(_2\) and the selectivity towards benzaldehyde was found to be in the order of Mg(OH)\(_2\) MgCO\(_3\) >Mg(OH) > MgCO\(_3\) > MgO. This observation indicates that MgO obtained from Mg(OH)\(_2\) MgCO\(_3\), is more basic than MgO obtained from MgCO\(_3\). This is in accordance with the basicity observed by the evolved gas analysis by pyrolysis-MS technique.

Further, it is interesting to note that MgO obtained by calcination of Mg(OH)\(_2\), with least surface area (78 m\(^2\)/g), gave comparatively low conversion, whereas no regularity was observed in the increase in the total conversion of benzyl alcohol with surface area was observed. Thus, our investigation on the decomposition of alcohols to form benzaldehyde
and toluene revealed the varying strength of both the acid-base properties of MgO catalysts obtained from different precursors. The dehydrating ability of MgO catalyst can be ascribed to its surface acidity and its dehydrogenating action to its basicity. The possible mechanism for hydride transfer reaction of benzyl alcohol on MgO can be explained on the basis of reported mechanism by Nagraju et al. [50]. The basic nature of catalyst enhances the formation of benzyl oxide ion intermediate. The benzyl oxide ions thus formed get adsorbed on the surface of the catalyst. Benzyl ion can be formed over acid sites. Transfer of hydride ion takes place from one benzyl oxide ion to the adjacent benzyl ion. The species donating hydride ion undergoes oxidation to benzaldehyde and automatically the benzyl ion converts to toluene (Scheme 4.2).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of benzyl alcohol (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>MgO(I)</td>
<td>37.2</td>
<td>78.7</td>
</tr>
<tr>
<td>MgO(II)</td>
<td>22.4</td>
<td>80.7</td>
</tr>
<tr>
<td>MgO(III)</td>
<td>31.4</td>
<td>86.6</td>
</tr>
<tr>
<td>MgO(IV)</td>
<td>38.3</td>
<td>73.3</td>
</tr>
</tbody>
</table>

**Table 4.2** Oxidation of benzyl alcohol to benzaldehyde. Conversion and selectivity profile on different MgO catalysts at 480 °C, 4h.
**Scheme 4.2** Plausible mechanism for hydride transfer reaction.

**4.3.2 Catalytic studies**

The three vapor phase alkylation reactions were tested in the sequence mentioned below on all the four calcined catalysts ii) Alkylation of aniline with methanol (1:3 molar ratio) iii) Alkylation of aniline with ethanol (1:3 molar ratio) iv) Benzylation of aniline with benzylalcohol (1:3 molar ratio).

**4.3.2.1. Alkylation of aniline with methanol**

Selective methylation of aniline to mono N-methylaniline is very critical, as methylation of aniline can lead di-N-alkylation and C-alkylation products leading to poor selectivity for the synthetically more important monosubstituted product. Scheme 4.3 shows the alkylation of aniline with methanol.

**Scheme 4.3** Reaction scheme for N-methylation of aniline with methanol.

Our studies on MgO obtained from different precursors of magnesium have shown a very high selectivity for the required N- mono methyl aniline (NMA) and minor amount of
NNDMA. Activity and selectivity for samples taken at 4 h for different catalysts are shown in Table 4.3. The conversion for all the catalysts did not differ much and were found to be in the range of 15 to 24 % and the selectivity towards N-methyl aniline was in the range of 79 to 90 %. The catalytic activity follows the order: MgCO$_3$ > Mg(OH)$_2$ > MgO > Mg(OH)$_2$ MgCO$_3$ and the selectivity was found to follow the order Mg(OH)$_2$ MgCO$_3$ > MgCO$_3$ > MgO > Mg(OH)$_2$. Low conversion of aniline for all the catalysts indicates that the presence of surplus active base sites, which does not alter the activity, and there is no linear relationship between basicity/acidity and activity [14]. However, a comparison of the catalytic performance (Table 4.3) with surface properties (Table 4.1) of the catalysts indicates that there is a direct relationship between their catalytic selectivity towards the N-alkylation of aniline and their surface area. The surface area values of the systems were also found to follow the same order as selectivity towards NMA.

Woo et al. [22] investigated the selective alkylation of aniline with methanol over various metallosilicates. They suggested that strong, medium, and weak acid sites are active sites to produce the C-alkylate and coke, NNDMA and N-methyl toluidine and NMA respectively. Our results are consistent with this assertion, as expected, the weak acidity of magnesium oxides prevented the formation of C-alkylated products. The possible reaction mechanism for the vapor phase alkylation of aniline with methanol on MgO is shown in Scheme 4.4. This mechanism can be explained on the basis of mechanism established by Nan Ko et al. [9], according to which Lewis acid sites of the metal oxide systems interact with the methoxy species and the hydrogen atoms of the undissociated hydroxyl groups interact with the Lewis basic sites. Electrophilic attack of the methyl group
of methanol and on the nitrogen atom of the adsorbed aniline leads to NMA, which on subsequent methylation leads to NNDMA. Thus the mechanism accounts for the need of moderate amounts of both acidic and basic Lewis sites for the system.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aniline</td>
<td>NMA</td>
</tr>
<tr>
<td>MgO (I)</td>
<td>20.5</td>
<td>86.2</td>
</tr>
<tr>
<td>MgO (II)</td>
<td>15</td>
<td>78.7</td>
</tr>
<tr>
<td>MgO (III)</td>
<td>23.9</td>
<td>89.3</td>
</tr>
<tr>
<td>MgO (IV)</td>
<td>22.1</td>
<td>81.9</td>
</tr>
</tbody>
</table>

Table 4.3 Vapor phase alkylation of aniline with methanol. Conversion and selectivity profile on different MgO catalysts at 480 °C, 4h.

\[
\begin{align*}
\text{I} & : \quad \text{H}_2\text{N} - \text{Mg} - \text{O} - + \text{Mg} - \text{O} - \rightarrow \text{H}_2\text{N} - \text{Mg} - \text{O} - \\
\text{II} & : \quad \text{H}_3\text{C} - \text{O} - + \quad \text{H}_3\text{C} - \text{O} - \rightarrow \text{H}_3\text{C} - \text{O} - \\
\text{III} & : \quad \text{H}_2\text{N} - \text{Mg} - \text{O} - + \text{H}_3\text{C} - \text{O} - \rightarrow \text{H}_2\text{N} - \text{CH}_3 + \text{H}_2\text{O}
\end{align*}
\]
Scheme 4.4 Plausible reaction mechanism for the vapor phase alkylation reaction of aniline with methanol over MgO system.

4.3.2.2 Alkylation of aniline with ethanol

Scheme 4.5 Reaction scheme for N-ethylation of aniline with ethanol.

The catalytic activity and selectivity for aniline alkylation with ethanol over different MgO catalysts are shown in Table 4.4. It can be clearly seen from the table that conversion of aniline was less compared to methylation experiment. Ethylation showed poor catalytic activity compared to the previous studies of aniline alkylation with methanol and also poor selectivity for the required N- monoethylaniline (NEA) was observed, the conversion and selectivity for all the catalysts were in the range of (15 to 20 %) and (5 to 12 %) respectively; other secondary products formed were ethylene, N-ethylimine and N,N’-diethylaniline (NNDEA). Presence of strong basic sites and high vapor phase temperature could be disadvantageous, as it may cause cracking of alcohol and hence some would not be available for the reaction. Thus, conversion is dependent on the chain length of the alkyl group of the alcohol. The highest conversion was observed when methanol was used as the
alkylating agent and the conversion gradually decreases as the chain length increases, this observation is in agreement with that reported in literature [51].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aniline</td>
<td>NEA</td>
</tr>
<tr>
<td>MgO (I)</td>
<td>18.6</td>
<td>12.4</td>
</tr>
<tr>
<td>MgO (II)</td>
<td>18</td>
<td>6.4</td>
</tr>
<tr>
<td>MgO (III)</td>
<td>16.3</td>
<td>5.4</td>
</tr>
<tr>
<td>MgO (IV)</td>
<td>19.5</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Table 4.4 Vapor phase alkylation of aniline with ethanol. Conversion and selectivity profile on different MgO catalysts at 480 °C, 4h.

4.3.2.3. Benzylation of aniline

Unlike other aliphatic alkylation reaction, where we obtained N-alkylated products, benzylation of aniline with benzyl alcohol gave benzylimine (Schiff base) as a major product. This could be due to the reaction of benzaldehyde with aniline. Very high conversion of aniline was observed for all the catalyst system. N-Benzylanilne, the required product along with other by-products such as di-N benzyl anilne, toluene and benzaldehyde were formed in very less quantity (Table 4.5). Although the mechanism for the present reaction is not completely clear yet, a possible mechanism is shown in Scheme 4.6. The first step of the reaction would involve catalytic oxidation of an alcohol to the corresponding carbonyl compound. We have already revealed the catalytic activity of MgO towards oxidation of benzylalcohol (A) to benzaldehyde (B), under section 4.3.1.3. The carbonyl intermediate B would readily react with aniline (D) to afford benzimine (E). The
species E would react with another molecule of benzylalcohol (A) to give product N-Benzyylaniline (F) by hydride transfer reaction. Thus, the reaction may proceed through an imine intermediate, which is reduced to an amine. This is in accordance to the mechanism reported earlier by Sipra Naskar [51].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzyllimine</td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>MgO (I)</td>
<td>97.3</td>
<td>77.9</td>
</tr>
<tr>
<td>MgO (II)</td>
<td>96.7</td>
<td>86.6</td>
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<tr>
<td>MgO (III)</td>
<td>93.9</td>
<td>86.8</td>
</tr>
<tr>
<td>MgO (IV)</td>
<td>96.7</td>
<td>78.1</td>
</tr>
</tbody>
</table>

**Table 4.5** Vapor phase benzylation of aniline with benzyl alcohol. Conversion and selectivity profile on different MgO catalysts at 480 °C, 4h.
Scheme 4.6 Reaction scheme for N-benzylation of aniline with benzylalcohol.

In our studies using benzyl alcohol as alkylating agent, interestingly, we found maximum conversion of aniline (> 90 %) and selectivity towards Schiff base (> 75 %), indicating that basic-acid strength do not have any influence on the catalytic activity of the studied catalysts. The main reason for this behavior could be attributed to the formation of stable intermediate (Schiff base) with the minimum available active basic-acidic sites. The Schiff base could not be further reduced to N-benzyl aniline due to stearic bulk of the benzyl group in the benzylimine intermediate.
4.4 Conclusions

MgO having very high surface area could be obtained by controlled thermal decomposition with the aid of structure directing nonionic surfactant, polyvinyl alcohol. This technique provides a conventional procedure with the advantages of, low cost and promising large-scale production to obtain high surface area MgO catalyst. Novel application of pyrolysis- MS technique to study the evolved gas has enabled us in better understanding of the nature of evolved species from different starting materials. This in-turn could be correlated to the nature of surface basic sites that can be present on the final MgO catalyst; evolution of CO\textsubscript{2} at relatively higher temperature in the case of MgCO\textsubscript{3},Mg(OH)\textsubscript{2} leads to the generation of highly basic MgO catalyst as compared to MgO obtained from calcination of neat MgCO\textsubscript{3}. Thus, the surface and chemical properties of the four MgO solid base catalysts prepared from different starting materials were not the same.

The results for benzyl alcohol conversion to benzaldehyde and toluene indicate the potential use of this reaction to determine the acid–base properties of metal oxides. For the vapor phase oxidation of benzyl alcohol to benzaldehyde, the catalytic performance was found to be strongly influenced by the starting material used for preparation of MgO catalyst. Selective formation of benzaldehyde and toluene indicate the presence of active basic and acidic sites on the surface of MgO catalyst. The enhanced basic site is attributed to O\textsuperscript{2−} and Lewis acidity due to Mg\textsuperscript{2+}. Dehydrogenation selectivity was found to be highly correlated with basicity of the solid.
Vapor phase alkylation of aniline with methyl alcohol resulted in highly selective mono N-alkylated products of aniline, whereas reaction of ethyl alcohol gave very poor selectivity for N-ethylaniline. Thus, conversion is dependent on the chain length of the alkyl group of the alcohol. The highest conversion was observed when methanol was used as the alkylation agent and the conversion gradually decreases as the chain length increases. Further, MgO prepared by activation of commercial MgO and by calcination of MgCO$_3$ showed better selectivity for NMA compared to MgO obtained from Mg(OH)$_2$ and Mg(OH)$_2$.MgCO$_3$(magnesium carbonate hydroxide) due to presence of higher Lewis acid sites on the surface of MgO catalyst. Reaction of benzyl alcohol resulted in the formation of N-benzyldieneaniline with a very good conversion of aniline. The size of the alkylation species, steric hindrance and their electrophilicity could be some of the major factors resulting in the formation of Schiff base.
References cited


