Chapter-6

Catalytic hydrogen transfer reduction of nitrobenzene on MgO and modified MgO catalysts

“Making the simple complicated is commonplace; making the complicated simple, awesomely simple, that’s creativity.”

Charles Mingus
**Nomenclature**

MDI → Methylene diphenyl diisocynoate

CHTR → Catalytic hydride transfer reaction

TGA → Thermogravimetric analysis

PXRD → Powder X-ray diffraction pattern
6.1 Introduction

Aniline is an important raw material used in industries as a starting material mainly for the large-scale production of methylene diphenyl diisocyanate (MDI), an important monomer in the preparation of polyurethane. Aniline is also used as the starting material and as an intermediate for the production of rubber processing chemicals, such as vulcanization accelerators, antioxidants, stabilizers and inhibitors. Other consumers of aniline include dyes, pigments, pharmaceuticals, pesticides, fungicides, amino resins and photographic chemicals [1].

Currently, about 90 % of aniline is manufactured industrially by continuous high pressure catalytic hydrogenation of nitrobenzene by liquid phase or vapor phase methods in either a fixed-bed or a fluidized-bed reactor using suitable heterogeneous catalysts. The 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. Vapor-phase processes employ either fixed-bed or fluidized bed reactors and copper on silica is typically employed as a catalyst [2]. Instead of hydrogen, natural gas is also used for nitrobenzene hydrogenation, as demonstrated by Bayer workers using methane/water and copper chromite catalyst [3]. Aniline is also manufactured by liquid-phase processes. The same catalysts are also employed for vapor-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 continuous stirred tank reactor, in which the heat of reaction is removed by continuously distilling off the aniline product and water [4, 5]. Apart from these processes, aniline is also manufactured in large scale
by reduction of nitrobenzene in good yields with iron and hydrochloric acid in the Be´champ process [6]. The importance of this process has declined over the last few decades, but it is still used in the pigment and dyestuff industry and to make iron oxide pigments and aniline is produced as a by-product. But it has a distinct disadvantage of formation of iron sludges that are difficult to filter and always contain adsorbed reaction products and hence lead to disposal problems. Among these, the non-polluting hydrogenation using molecular hydrogen is the dominant production route, but the inevitable use of hydrogen under high pressure, presents considerable fire hazard as small hydrogen molecules can easily leak through the pinholes and storing hydrogen presents problems. The large scale use of hydrogen may disturb the balance of atmosphere and widen the ozone hole. Constant efforts are being made to find cheaper and safer alternatives to the conventional hydrogenation of this industrially important organic transformation.

In comparison with catalytic reduction using molecular hydrogen described above, catalytic hydrogen transfer reduction is one of the easiest, safest and highly selective methods to carry out the reduction and has received continuous recognition as an alternative route for the clean production of variety of chemicals under mild reaction conditions [7, 8]. Many researchers have reported the reduction of nitrobenzene by hydrogen transfer from the readily available hydrogen sources such as hydrocarbons [9], formic acid and its salts [10-13], hydrazine hydrate [14-15], alcohols [16-17].

Donor activity of cyclohexene and a series of n-alkanes in catalytic hydrogen transfer to various organic groups over magnesia as a catalyst have been reported [9]. Styrene,
phenyl acetylene, benzaldehyde and acetophenone were not reduced by cyclohexene in the temperature range 250 - 400 °C, were as, nitrobenzene was reduced to aniline by cyclohexene at 400 °C. The highest yield of aniline (57 %) from nitrobenzene was observed at 400 °C in the presence of n-decane from a series of C_6 - C_{16} n-alkanes used as hydrogen donors. Ammonium formate was reported to be most convenient and efficient hydrogen source in catalytic hydrogen transfer reductions. Reduction of aromatic nitro compounds with ammonium formate as hydrogen donor in different catalytic systems containing Pd/C, Ni, Zn and Mg [10-12]. Based on the research of ammonium formate, further catalysts were developed using hydrazinium monoformate as the hydrogen donor. The result indicated that reduction of nitro group was complete within 2-10 minutes at room temperature and all the compounds reduced by Raney Ni/N_2H_4•HCOOH and Zn/N_2H_4•HCOOH were obtained in good yields (90-95 %) [13].

Hydrazine hydrate has been an attractive alternative reducing agent for nitro compounds due to its stereo and functional selectivity. Further, the reduction with hydrazine hydrate produced harmless by-products such as nitrogen gas and water. In recent years, several papers about hydrazine reduction of nitro compounds over zinc and magnesium have been published. The reduction of nitro compounds could be accomplished with commercial zinc dust or magnesium dust within three to ten minutes. All the compounds reduced by this system were obtained in 90-95 % yields [14]. The reduction of aromatic nitro compounds with hydrazine hydrate over Mg-Fe hydrotalcite and Fe-Mg-Al hydrotalcite respectively have also been reported to produce good yield and selectivity [15]. The potential of these catalysts was tested for reduction of a variety
of substituted nitro aromatics. The catalyst was found to be highly active and 100 % selective.

Recently, nitro compounds reduction via hydride transfer using mesoporous mixed oxide using 2-propanol as a hydrogen donor and NaOH have been studied over different NiCo$_2$O$_4$ catalysts [16]. NiCo$_2$O$_4$ prepared by the alkyl polyglucoside (C10) template was found to be the best catalyst that gave 100 % selectivity towards amine. Template assisted route led to increase in the surface area compared to co-precipitated NiCo$_2$O$_4$. Enhancement in the surface area was found to enhance the reaction towards amine. CHTR of nitroarenes with propan-2-ol and KOH/NaOH over several mixed metal oxides, such as ZrO$_2$-NiO, ZrO$_2$-CoO and ZrO$_2$-Fe$_2$O$_3$ have also been published. The studies indicate that ZrO$_2$-NiO was the most effective catalyst in their research system [17].

With the advent of microwave irradiation technology and ultrasound-promoted organic synthesis, several research groups have employed these technologies as a convenient method for the reduction of nitroarenes. The reaction on Al$_2$O$_3$ support in presence of sodium hydrogen sulphide under microwave condition enhanced the speed dramatically. The reaction time could be shortened from several hours in thermal conditions to several minutes in microwave conditions. Further, the yields could be improved greatly [18]. Ultrasound-promoted, highly efficient reduction of several aromatic nitro compounds to the aromatic amines was achieved by samarium/ammonium chloride mediated reaction [19].

The literature summarized in the above section indicates that several attempts to improve the selectivity for amines have been made and the nature of investigation was
mainly performance evaluation of catalyst / promoter systems. However, most of these methods require long reaction times, as they are batch processes and involve liquid phase CHTR. Hence, it was considered worthwhile to investigate the vapor phase CHTR of nitrobenzene into aniline on inexpensive catalysts such as MgO and doped MgO catalyst system, using abundantly available methanol as the hydrogen donor. MgO is reported to be a versatile material used as the catalyst for several base catalyzed organic transformations [20-22]. It’s one of the most active catalysts in Meerwein-Ponndorf-Verley (MVP) reduction, which involves hydrogen transfer reactions between an alcohol and carbonyl group of aldehydes and ketones [23]. Further, modified magnesium oxide catalysts have received considerable attention for their enhanced catalytic performance. There have been various metals and metallic oxides which have been used to modify MgO to obtain the desirable catalytic properties for a specific reaction, like Diez et al. have doped MgO with Li and found that the catalytic activity of MgO is enhanced for aldol condensation of citral with acetone [24]. Similarly, Vijayraj and Gopinath have also found that MgO doped with alkali metal ions has higher activity as compared to MgO for O-methylation of dihydroxy benzene with dimethyl carbonate [25]. Alkali metal ions have also been used for oxidation of CO to CO$_2$ [26], oxidative cracking of propane [27] and hexane [28], Ni modified MgO has been used for oxidative and thermal reforming of butane [29], Klicpera and Zdrazil have modified MgO with MoO$_3$ for Hydrodesulphurisation of benzothiophene [30], Wang et al. have modified MgO with Ru and CeO$_2$ for synthesis of ammonia [31]. Reddy et al. have also found that when MgO is modified with vandium and calcium oxide it can be used for selective oxidation of $p$-methoxy toluene to $p$-methoxybenzaldehyde [32]. Kanaia et.al. have used MoO$_3$
modified MgO for selective epoxidation of allyl acetate [33]. We have earlier published work on modified MgO as a catalyst for selective alkylation and benzylation of phenol [34-35].

Although the use of MgO for reduction of nitrobenzene is known [36,37], there have been no reports on reduction of nitrobenzene with the help of MgO doped catalysts and detailed study on the formation of each of the intermediates during the course of reduction. In this chapter, we report the CHTR of nitrobenzene to aniline using i) ZnO ii) ZrO$_2$ doped MgO catalyst system. The motivation for using ZnO and ZrO$_2$ as dopant on MgO was due to the fact that both these metal oxides have received considerable attention for the production of hydrogen from methanol for the fuel cell [38-40]. Methanol as hydrogen donor was selected for the current study because it is an excellent hydrogen carrier with very high hydrogen to carbon ratio. It being one of the largest bulk chemicals in the world makes its availability easier and it can be readily converted into hydrogen at moderate temperatures. The side products like HCHO, CH$_4$, CO$_2$, CO formed due to the decomposition of methanol are volatile [41]. Therefore, it is easy to remove them from the reaction product compared to the side products obtained by other facile hydrogen donors such as isopropanol, hydrazine, sugars, benzyl alcohol, cyclohexene and formic acid.

Catalytic activity is known to be largely dependent on catalyst preparation method. Hence, it is very desirable to develop methods to produce in a controllable manner highly porous MgO with high specific surface area. The modified MgO, ZrO$_2$/MgO and ZnO/MgO catalysts were prepared by dry blending method and PVA was used as soft
template followed by controlled calcination under nitrogen atmosphere. To pin point the influence of ZrO\textsubscript{2} and ZnO species on the MgO support, a systematic study has been made which includes preparation of above-mentioned catalysts, determination of their physicochemical properties by using various techniques such as multipoint BET method, PXRD, SEM and TGA/DTA. Catalytic activity studies on all the three catalyst systems for the vapor phase reduction of nitrobenzene using methanol as hydrogen donor was performed using the in-house designed and fabricated vapor phase pulse reactor described in chapter 5. The influence of feed composition, flow rate and reaction temperature were investigated to obtain maximum aniline selectivity. Further, we have made an attempt to relate catalytic activity of MgO supported catalysts with their physico-chemical properties.

6.2 Experimental

6.2.1 Catalyst preparation

6.2.1.1 Preparation of magnesium oxide catalyst

MgO catalyst in the size range of 800 to 1000 µm was prepared by using magnesium carbonate [MgCO\textsubscript{3}]. 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 ton 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 cm$^3$/min) in a tubular furnace to obtain the modified MgO catalyst.

6.2.1.2. ZrO$_2$ and ZnO doped magnesium oxide catalyst

MgO catalysts containing transition metal oxide dopants such as ZnO and ZrO$_2$ (2 % by weight of MgO) were prepared by doping ZnO and ZrO$_2$ with magnesium carbonate followed by calcination at 480 °C. To obtain good dispersion of dopants in the final MgO catalyst, 2 g each of ZnO or ZrO$_2$ was separately dry mixed with 98 g of MgCO$_3$ for 12 h on a planetary ball mill operating at 300 rpm. The dry blends were then slurried with 400 cm$^3$ water containing 0.5 % PVA for 15 minutes and processed further as described in the previous section to obtain ZnO and ZrO$_2$ doped MgO catalysts in the size range of 800 to 1000 µm. The catalysts are represented as ZnO/MgO and ZrO$_2$/MgO respectively. All the three, MgO, ZnO/MgO and ZrO$_2$/MgO 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 catalytic hydride transfer reduction of nitrobenzene to aniline using methanol as in-situ hydrogen donor.

6.2.2 Catalyst characterization
The TGA and DTA profiles of MgCO\(_3\), ZnO/MgCO\(_3\) and ZrO\(_2\)/MgCO\(_3\) were recorded to study the thermal decomposition pattern of all the prepared catalysts. This data was used to set an appropriate calcination condition to obtain catalysts with high surface area and activity. BET surface area and pore volume of calcined catalysts were calculated from nitrogen adsorption and desorption isotherms at -196 °C using the multipoint-BET and pore size by BJH method. The samples were degassed at 90 °C for 12 h prior to actual measurement in a vacuum oven. The crystallographic phases of the prepared catalysts were measured on a Philips X-ray diffractometer with Ni filtered Cu-K\(\alpha\) radiation over the range of 2\(\theta\) from 10 to 85° with the intensity data for each point being collected at a 4 second interval.

6.2.3 Catalytic activity studies

Prior to the start of the reduction reaction, the calcined catalyst (about 150 mg) was taken in the reactor tube and pre-treated in an atmosphere of flowing helium (200 cm\(^3\)/min) at 480 °C for 1 h. In a typical reaction, 0.1 µL of the reactants (nitrobenzene and methanol) was injected inside the fixed bed reactor. Reactions were carried out independently on MgO, ZrO\(_2\)/MgO and ZnO/MgO catalysts, by keeping a constant gas hourly space velocity (GHSV) of 33,000 h\(^{-1}\) which is calculated from the equation GHSV = [Total gas flow rate at standard temperature and pressure / Volume of the catalyst bed]

6.3 Results and discussion
6.3.1 Thermal analysis

TGA/DTA profiles of MgCO$_3$, ZnO/MgCO$_3$ and ZrO$_2$/MgCO$_3$ are shown in Fig 6.1. All the three catalyst systems were found to have similar thermal behavior. The DTA curves for all the three catalysts indicate two endotherms with maxima at 285 °C and 431 °C with a corresponding weight losses of 20 and 24 % representing loss of hydroxyl and carbon dioxide respectively as observed in TGA. The loss of water and carbon dioxide was confirmed by performing evolved gas analysis using mass spectrometry. No weight loss was observed after 460 °C, the maximum temperature for complete decomposition of MgCO$_3$ and hence 480 °C as activation temperature was adopted. All the catalysts were prepared by heating the corresponding pellets at

![Graph showing TGA/DTA profiles](a)
Fig. 6.1 TGA/DTA profiles of the three as prepared catalysts pellet under nitrogen atmosphere a) ZnO/MgCO\textsubscript{3} b) ZrO\textsubscript{2}/MgCO\textsubscript{3} c) MgCO\textsubscript{3}

480 °C for 10 h under nitrogen atmosphere, which resulted in mesoporous MgO with high catalytic activity.

### 6.3.2 Surface area, pore size and pore volume of the catalysts

The BET surface area of ZnO/MgO, ZrO\textsubscript{2}/MgO and MgO catalysts were found to vary in the following order: Catalyst (m\textsuperscript{2}/g); ZnO/MgO (229) > MgO (221) > ZrO\textsubscript{2}/MgO (191). It was observed that ZrO\textsubscript{2}/MgO had the least surface area of 191 m\textsuperscript{2}/g compared to MgO and ZnO/MgO, which were in the range of 220- 230 m\textsuperscript{2}/g. Nitrogen adsorption-
desorption isotherms of MgO, ZnO/MgO and ZrO$_2$/MgO are shown in Fig. 6.2. All the catalysts exhibited an isotherm similar to type II, with H3-type hysteresis loop. According to IUPAC recommendations [42], this type of isotherm, is the normal isotherm with a non-porous or macro porous adsorbent and represents unrestricted monolayer-multilayer adsorption. The beginning of the almost linear middle section of the isotherm in the BET curve is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin. The type H3 loop, which does not exhibit any limiting adsorption at high P/P$_0$ corresponds to aggregates of plate-like particles giving rise to slit-shaped mesopores. The pore size distribution calculated from the corresponding isotherms (Fig. 6. inset) by BJH method, indicates that all the materials had bimodal pore size distributions of meso and macropores with most of the mesopores centered around 30 Å and macropores have a spread up to 500 Å.
Fig. 6.2 Nitrogen adsorption-desorption isotherm of a) ZnO/MgO b) ZrO$_2$/MgO c) MgO calcined catalyst samples. Corresponding pore size distribution (inset).
Pore size and pore volume were found to vary in the following order (Catalyst average pore diameter in Å): MgO (90.5) > ZnO/MgO (77.9) > ZrO$_2$/MgO (74). Pore volume (cm$^3$/g): MgO (0.49) > ZnO/MgO (0.44) > ZrO$_2$/MgO (0.35). The lower pore size and pore volume further confirms the low surface area observed for ZrO$_2$/MgO, which could be due to the location of ZrO$_2$ in MgO pores. High surface area and the presence of larger mesopores in MgO enable the reactant molecules easy access to the active sites present in the material [40].

6.3.3 X-Ray diffraction analysis

Powder X-ray diffraction patterns of the calcined catalysts and pure dopants are shown in Fig 6.3. All the calcined catalysts were amorphous, which exhibited broad peaks characteristic of MgO at 2θ = 42.8 and 62.3, [JCPDS (71-1176)], which establish the formation of a homogeneous compound with rock salt structure. ZnO doped MgO showed peaks with 2θ values is in agreement with JCPDS card for ZnO [JCPDS 36-1451] in addition to 2θ values of MgO, indicating no solid solution formation between MgO and ZnO. In the case of ZrO$_2$ doped MgO, monoclinic crystallographic phase (2θ = 24.1°, 28.4°, 31.4°) of ZrO$_2$ was evident [JCPDS No. 37-1484]. However, lower intensities of MgO peaks observed for the ZrO$_2$/MgO calcined catalyst may be due to the probable interaction of the two phases at the calcination temperature.
Fig. 6.3 Powder XRD pattern of MgO, ZnO/MgO, ZrO₂/MgO and ZnO and ZrO₂ catalysts.

6.3.4 SEM studies
SEM micrographs of all the calcined catalysts were taken to investigate any possible differences in the morphology of the three catalysts, which could have resulted in the decrease in surface area observed in the case of ZrO$_2$/MgO as compared to MgO and ZnO/MgO. In the case of ZrO$_2$/MgO slightly different particle morphology in terms of size and shape was observed. The bigger particles are more predominant in this case as compared to the other two catalysts (Fig. 6.4), where more of smaller particles are observed. This could be due to sintering effect in the case of ZrO$_2$/MgO sample. This further confirms lower surface area and diffraction intensities observed for this sample by BET and XRD.

![SEM micrographs of a) MgO b) ZrO$_2$/MgO c) ZnO/MgO catalysts.](image)

**Fig. 6.4** SEM micrographs of a) MgO b) ZrO$_2$/MgO c) ZnO/MgO catalysts.

### 6.3.5 Catalytic activity studies on MgO, ZrO$_2$/MgO and ZnO/MgO catalyst system

Catalytic tests were carried out on the in-house developed microreactor GC-MS system. Schematic representation of the on-line setup and details of the setup is described under the experimental section of chapter 5. A weighed amount of the pre-calcined catalyst is placed in the reactor tube supported on either side by quartz wool to hold the catalyst bed in the reactor tube. The outlet of the quartz tube was connected to the inlet
port of a GC-MS with a 0.1 mm inner diameter stainless steel tube. It was wrapped with heating tape set at 150 °C to prevent the condensation of the products. Prior to the start of the reduction reaction, the calcined catalyst (about 150 mg) was taken in the reactor tube and pre-treated in an atmosphere of flowing helium (200 cm³/min) at 480 °C for 1 h. In a typical reaction, 0.1 µL of the reactants (nitrobenzene and methanol) was injected inside the fixed bed reactor. Reactions were carried out independently on MgO, ZrO₂/MgO and ZnO/MgO catalysts to investigate the catalytic activity of the MgO and doped MgO catalysts on the hydrogen transfer reduction of nitrobenzene with methanol. The initial experiments were carried out with only nitrobenzene to detect the probable intermediates to understand the mechanism of the catalyst action. The reaction was carried out at three different temperatures 360, 420 and 480 °C using MgO as a catalyst.

Table 6.1 shows the conversion of nitrobenzene and the various products formed at three different temperatures. The conversion of nitrobenzene at 360 °C is about 67.5 %; however, at temperatures 420 °C and 480 °C all the nitrobenzene is converted. The major products obtained are azobenzene, aniline, pyridine, biphenyl, benzonitrile and carbazole. There are several other compounds formed in comparatively trace amounts, as can be seen from the Table 6.1. The amount of these compounds depends on the set reaction temperature. As the temperature is increased from 360 °C to 420 °C the selectivity towards azobenzene slightly increases from 31 to 37 %, however when the temperature was further increased to 480 °C the selectivity decreases to about 5 %. It is observed that though selectivity towards azobenzene decreases but the selectivity towards benzene, pyridine and aniline was found to increase with increase in temperature. The selectivity
towards benzene increases from 3.4 % at 360 °C to 9.4 % at 420 °C and finally to 16.4 % at 480 °C, whereas the selectivity for aniline increases from 6.94 to 25.3 % from 360 °C to 480 °C. This partial reduction of nitrobenzene to azobenzene and aniline in the absence of any external hydrogen source could be due to the presence of proton and hydroxyl species bound to low coordination sites of MgO surface, which requires evacuation at 800 °C [37].

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>360</th>
<th>420</th>
<th>480</th>
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<tbody>
<tr>
<td>% Conversion</td>
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<tr>
<td>Nitrobenzene</td>
<td>67.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>% Selectivity</td>
<td></td>
<td></td>
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<tr>
<td>Benzene</td>
<td>3.4</td>
<td>9.4</td>
<td>16.4</td>
</tr>
<tr>
<td>Pyridine</td>
<td>0.7</td>
<td>2.3</td>
<td>7.6</td>
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<tr>
<td>Nitrobenzene</td>
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<tr>
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<td>6.94</td>
<td>19.4</td>
<td>25.3</td>
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<td>Benzonitrile</td>
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<td>3.7</td>
<td>7.0</td>
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<td>Isoquinoline</td>
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<td>4-methylquiniline</td>
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<td>2.4</td>
<td>8.7</td>
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<tr>
<td>Dibenzofuran</td>
<td>0.9</td>
<td>1.4</td>
<td>2.8</td>
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<td>Benzenamine, N-phenyl</td>
<td>---</td>
<td>---</td>
<td>8.9</td>
</tr>
<tr>
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<td>2.2</td>
<td>---</td>
</tr>
<tr>
<td>9-Phenyl-9H-Carbazole</td>
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<td>1.3</td>
<td>2.8</td>
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Table 6.1 Distribution of reaction products formed during the vapor phase reaction of nitrobenzene on MgO catalyst at different temperatures.

At temperatures lower than 420 °C, more of azobenzene was formed, whereas at temperature higher than 420 °C, biphenyl and benzene are observed. This could be due to the degradation of nitrobenzene on the surface of MgO catalyst at reaction temperatures
higher than 420 °C. It is also observed that absence of methanol leads to very fast deactivation of the catalyst due to coke formation.

In our efforts to understand the effect of mole ratio and reaction temperature on the CHTR on the prepared catalyst systems, we systematically carried out vapor phase reduction reactions using methanol as hydrogen donor independently on MgO, ZnO/MgO and ZrO₂/MgO catalyst systems. Effect of three different mole ratio’s of nitrobenzene to methanol (1:3, 1:6 and 1:10) and three different reaction temperatures (400, 420 and 440 °C) were investigated. All the catalysts showed 100 % conversion of nitrobenzene at all the studied temperatures and mole ratios. The product distribution and selectivity data for the reduction of nitrobenzene over MgO, ZnO/MgO and ZrO₂/MgO at three different mole ratio’s of nitrobenzene to methanol (1:3, 1:6 and 1:10) and three different reaction temperatures (400, 420 and 440 °C) is presented in Table 6.1. An outstanding selectivity of 87.5 % for aniline was observed in the case of zinc doped magnesium oxide catalyst, followed by pure MgO (81.5 %) and ZrO₂/MgO (76.2 %). The balance of the products, other than those mentioned in the distribution Table 6.2, consisted of by-products such as toluene, pyridine, biphenyl, azobenzene, phenazine and N-phenyl-1,4-benzenediamine.

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>ZrO₂/MgO</th>
<th>ZnO/MgO</th>
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<td><strong>Mole ratio</strong></td>
<td><strong>Temperature °C</strong></td>
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<tr>
<td>NB:M</td>
<td>400</td>
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<thead>
<tr>
<th><strong>Aniline %</strong></th>
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<tr>
<td>1:3</td>
<td>69.1</td>
<td>68.6</td>
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<td>1:6</td>
<td>79.3</td>
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Table 6.2 Product distribution and selectivity data for the reduction of nitrobenzene (NB) using methanol (M) as hydrogen donor over MgO, ZrO$_2$/MgO and ZnO/MgO catalysts.

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Fig. 6.5 shows increase in selectivity towards aniline when ZnO/MgO is used as the catalyst over ZrO$_2$/MgO and MgO at a mole ratio of 1:10 nitrobenzene to methanol. The selectivity towards aniline increases with increase in temperature for all the three catalysts. The selectivity towards aniline increases from about 69 % to 82 % for MgO when the temperature is increased from 400 °C to 440 °C. When ZrO$_2$/MgO is used as the catalyst the selectivity towards aniline increases from about 72 % to 76 % and when ZnO/MgO is used as the catalyst it increases from about 86 % to 88 %, when the temperature is raised from 400 °C to 440 °C. As anticipated, increase in methanol concentration in the feed, also led to increase in the N-methylation of aniline, in the MgO and ZrO$_2$/MgO catalyst systems, N-methylaniline ranging from 10 to 19 % was formed. It is also observed that N-methylated product was not favored in the case of ZnO/MgO, as less than 5 % of N-
methylaniline was observed at all the studied temperatures and mole ratios of nitrobenzene to methanol. This could be attributed to complete decomposition of methanol into CO and H₂ under high temperatures (> 400 °C) on the ZnO doped MgO catalyst. Formation N-methylaniline in the case of MgO and ZrO₂/MgO could be attributed to the stabilization of methoxy species on the lewis acid sites of these catalysts. Electrophilic attack of the methyl group of the methanol on the nitrogen atom of the adsorbed aniline leads to N-alkylation of aniline. Methoxy species on zirconia is known to decompose very slowly [41], accordingly a maximum of 19.2 % N-methylaniline was observed on ZrO₂/MgO at 400 °C. Our observation is in accordance to that in literature, where ZrO₂ is known to catalyze N-methylation of aniline with methanol [42]. It’s also observed from Table 6.1, that presence of excess methanol in the feed retards the decomposition of nitrobenzene to benzene by favoring reduction product of nitrobenzene at most of the studied temperatures. Mechanism for the formation of benzonitrile, which is consistently formed in all the three catalyst systems in the order ZnO/MgO < ZrO₂/MgO < MgO is not very clear.
Fig. 6.5 Selectivity of aniline on MgO, ZrO$_2$/MgO, ZnO/MgO catalysts at different temperatures at 1:10 mole ratio of nitrobenzene to methanol.

6.4 Conclusions

The catalytic activities of MgO, ZnO/MgO, ZrO$_2$/MgO have been investigated in the vapor phase reduction of nitrobenzene to aniline using methanol as hydrogen donor. The use of locally designed and fabricated pulse reactor coupled to a GC-MS as an on-
line reaction testing technique enabled the rapid catalytic reaction testing with a small amount of the solid catalyst. The influence of parameters such as feed composition, reaction temperature and the effect of dopants such as ZnO and ZrO$_2$ on the catalytic behavior of MgO were evaluated. The reaction mechanism was postulated by identification and structural information of the entire product formed using on-line mass spectrometry.

The parametric study reveals that the selectivity towards aniline depends on the mole ratio of nitrobenzene to methanol and the reaction temperature. Clear differences were observed between MgO, ZnO/MgO and ZrO$_2$/MgO. For instance, though complete nitrobenzene conversion was observed on all the three catalysts, maximum aniline selectivity of (87 %) was obtained in the case of ZnO/MgO, while a high amount of N-methylanilne (19 %) was observed with ZrO$_2$/MgO. Synergetic effect of acid- base properties of the catalyst surface seem to play an important role in deciding the activity of the catalyst. Presence of ZnO, an amphoteric oxide, on the surface of MgO was possibly decomposing the methanol completely into CO and H$_2$, thereby reducing the chance of further alkylation of aniline. When ZrO$_2$, an amphoteric oxide with slightly higher acidic sites, is doped on MgO, it leads to further alkylation of aniline to N-methylaniline. ZnO/MgO was found to be the best catalyst giving complete conversion of nitrobenzene and very high selectivity towards aniline. The formation of these products at varying levels indicate that for the ZnO and ZrO$_2$ doped MgO catalyst, the physico-chemical properties and hence active sites on the catalyst surface vary, which in turn has significant influence on catalytic efficiency for the reduction of nitrobenzene to aniline.
Studies of parameters which include temperature, flow rate and mole ratio highlight their influence at different operating conditions. Finally, the ZnO/MgO catalyst which gave the highest selectively compared to ZrO$_2$/MgO and MgO seems to be a promising catalyst for vapor phase catalytic hydride transfer reduction of nitrobenzene using methanol as in-situ hydrogen donor.
References cited


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