CHAPTER III

Design, Synthesis and Characterization of Magnesium Oxide Modified Mesoporous Carbon and its Application in the Synthesis of Sulfinamides
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Introduction

Sulfinamides play a very vital role in modern organic chemistry. In the recent years, several new methodologies for the synthesis of sulfoxides and sulfinamides have emerged. These are useful compounds and can be transformed to a number of other important functional groups such as sulfonimidoyl chlorides and cyclic sulfonimidates, which are valuable starting materials in the synthesis of various oxa- and aza-heterocyclic compounds. N-chloro sulfinamides were found to be the reactive intermediates in the oxidative chlorination of sulfinamides with tert-butyl hypochlorite.

Chiral sulfinamides have proven to be the building blocks in the asymmetric synthesis of various amine derivatives and as ligands in catalytic asymmetric reactions. Furthermore, sulfinamides can also act as N-sulfinyl protecting group which can be easily removed under mild conditions.

Several biologically active naturally occurring molecules like L-1-deoxyallonojirimycin and L-1-deoxymannojirimycin have sulfinamide moiety as an intermediate in their syntheses.

![Figure 1](image_url)
State of the Art

Various procedures have been reported for the preparation of sulfinamides. The conventional synthesis of these compounds refer to the treatment of sulfinyl chlorides with secondary amines or with Grignard reagents. Another method reported for the synthesis of these compounds is by the reaction of sulfinyl phthalimides with primary and secondary amines. But low yields of the desired products due to unstable precursor formation and concomitant side reactions were the major drawbacks of these methods.

Furukawa et al. reported the synthesis of sulfinamides from sulfinic acids using dicyclohexylcarbodiimide (DCC) as a dehydrating agent and 2-chloro-1-methylpyridinium iodide as a coupling reagent (Scheme 1).

Scheme 1

Davis et al. showed the synthesis of enantiopure sulfinimines from p-toluenesulfinate ester (Scheme 2).

Scheme 2

Uchino et al. reported the synthesis of sulfinyl chlorides from phthalimidomethyl sulfides in the presence of acetic acid and the corresponding preparation of the sulfinides.
Ellman and co-workers reported the synthesis of tert-butanesulfinamides via the oxidation of the corresponding disulfides (Scheme 3).\textsuperscript{14}

\[
\text{Scheme 3}
\]

Malacria and co-workers reported the synthesis cyclic sulfinates and sulfonamides through a hemolytic substitution at the sulfur atom.\textsuperscript{15}

These reactions often require two or more synthetic steps. In order to render this reaction more useful, an elegant single step process is desired.\textsuperscript{16} The recently reported but widely used method for the synthesis of sulfinamides is by amination of sulfinyl chlorides. Although, the preparation of sulfinyl chlorides is not exceptionally difficult, they are sensitive to hydrolysis and require preparation using highly toxic reagents as thionyl chloride. Therefore, mild and easier methods for the synthesis of sulfinamides are desired.

Recently, much effort has been directed towards a mild synthesis of these sulfinamides. Sharpless and co-workers reported the synthesis of sulfinate esters from sulfonyl chlorides by a one-pot reductive esterification reaction using phosphites as the reducing agents (Scheme 4).\textsuperscript{17}

\[
\text{Scheme 4}
\]
However, the attempts of this group to prepare sulfinamides were not successful. Toru and co-workers introduced the synthesis of chiral sulfinate esters by using triarylphosphines as reductants (Scheme 5).

\[
\begin{align*}
\text{Ph}^1 & \quad \text{Cl} \quad \text{Ph}^1 \\
\text{S} & \quad \text{Ph}^1 \quad \text{Ph}^1 \\
\text{Pr}^1 & \quad \text{Pr}^1 \quad \text{Pr}^1
\end{align*}
\]

Scheme 5

Very recently, Harmata et al.\(^\text{16}\) have reported the synthesis of sulfinamides from sulfonyl chlorides, using triphenylphosphine as the reductant and triethylamine as the base (Scheme 6).

\[
\begin{align*}
\text{Tol}^1 & \quad \text{S} \quad \text{O} \\
\text{Ph}^1 & \quad \text{Cl} \quad \text{Ph}^1 \\
\text{NH}_2 & \quad \text{NH}_2
\end{align*}
\]

Scheme 6

In the recent years the focus being shifted towards devising cleaner technologies for the synthesis of fine chemicals, more emphasis is being laid on the designing of methodologies using reusable catalysts.

To the best of our knowledge, no heterogeneous catalyst has been reported till date for the synthesis of sulfinamides from the corresponding sulfonyl chlorides.

Solid bases like magnesium oxide, which exhibits excellent basic properties, has been used in many important synthetic procedures like condensation, dehydrogenation and dehydration. These reactions are indispensable for various fine chemical syntheses.\(^\text{19}\)
A diverse range valuable intermediates, bulk and fine chemicals like isophorone, calcium antagonists, cinnamaldehyde and ionones and others having a double bond conjugated with a carbonyl group are formed via the condensation reactions. But commercially available magnesium oxide has a very low surface area, which in its turn exposes a lesser number of active sites for catalytic reactions.

A catalyst with large active surface area is highly active. In order to address the difficulty of low surface area of commercial catalysts, synthesis of mesoporous and nanocrystalline magnesium oxide with high surface area and their application in a number of base catalyzed reactions has been taken up. Moreover, use of high surface area materials as catalyst supports offer another route to address this problem, which help to increase the surface area of the metal oxide.

Ordered mesoporous materials are promising candidates in the area of heterogeneous catalysis as they offer dual advantage of possessing a large surface area and offering a certain degree of size and shape selectivity. These materials are thus used as catalyst support in order to tailor the catalytic performance by increasing the surface area, altering the exposure of the active sites and modifying their nature by interaction with the support. The general method of synthesis of porous catalysts with basic properties are generally by post-synthetic doping of host materials with basic guest species such as zeolites with alkaline earth metal oxides, SBA-15 and MCM-41 with magnesium oxide. The catalysts synthesized by this method are found to be stable and very efficient for various base catalyzed reactions.

Ordered mesoporous carbon with a hexagonal symmetry is an important member of the group of mesoporous materials. The carbon materials combine chemical
inertness, biocompatibility, and thermal stability and are thus suitable for many applications, such as catalyst supports, adsorbents, and electrode materials for supercapacitors and fuel cells.\textsuperscript{29-32} The most promising pathway to synthesize these mesoporous carbon is by exotemplating or hard templating method to create ordered replicas.\textsuperscript{33} Ryoo et al. reported the first synthesis of mesoporous carbon materials (CMK-1, 4) \textit{via} a nanocasting route using mesoporous silica MCM-48 as a hard template.\textsuperscript{28} Later, various types of mesoporous silica and carbon precursors have been adapted to synthesize mesoporous carbons, such as CMK-1 from MCM-48,\textsuperscript{28} CMK-2 from SBA-1,\textsuperscript{34} CMK-3 and CMK-5 from SBA-15\textsuperscript{35} and so on. Using mesoporous carbon CMK-3 as a robust, neutral support, it was planned to synthesize a basic catalyst, having a high surface area by impregnation of magnesium oxide.

**Present Work**

Herein, the preparation and detailed characterization of MgO modified mesoporous carbon and its application in the synthesis sulfinamides by reductive amination from the corresponding sulfonyl chlorides using triphenylphosphine as the reducing agent has been described. This new method allows a facile reaction, followed by a simple work up procedure to give the corresponding products in moderate to good yields (Scheme 7 and 8).

\begin{center}
\textbf{Scheme 7}
\end{center}
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\[
\begin{align*}
\text{Scheme 8}
\end{align*}
\]

Results and Discussion

Synthesis and Characterization of CMK-3-MgO

SBA-15 was synthesized using the amphiphilic triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO20PO70EO20; average molecular weight, 5800; Aldrich). A typical synthesis was performed following the procedure available in the literature.\(^{36}\)

CMK-3 carbon was prepared according to the process described in the literature.\(^{37}\)

The CMK-3-MgO samples were synthesized using three varieties of CMK-3 synthesized at different temperatures \textit{viz.} CMK-3(100), CMK-3(130) and CMK-3(150), having different pore volumes and diameters.\(^{36}\)

Different weight percentages of MgO modified CMK-3 was first synthesized by wet impregnation technique. Desired amount of magnesium acetate Mg(CH\(_3\)COO)\(_2\)\(\cdot\)4H\(_2\)O was dissolved in 50 mL of ethanol to prepare 60wt\%MgO-CMK-3, 40 wt\%MgO-CMK-3 and 20wt\%MgO-CMK-3 respectively. The ethanolic solution of Mg(CH\(_3\)COO)\(_2\)\(\cdot\)4H\(_2\)O was stirred at 50\(^\circ\)C for 10 min followed by addition of 1.0g of CMK-3. The reaction mixture was stirred at 50\(^\circ\)C for 3h to impregnate the mesopores with magnesium acetate. The reaction mixture was then filtered and the precipitate was dried in air. The resultant black coloured powder was then subjected to heating up to 300\(^\circ\)C under a low oxygen flow. Finally, the resulting catalyst was activated under nitrogen flow at 500\(^\circ\)C for 4 h to
remove any surface hydroxyl groups which may be formed during the impregnation procedure. The weight percent of MgO actually impregnated on the CMK-3 supports were determined by thermogravimetric analysis of the samples under flowing air to remove all the carbon material as oxide. A sharp peak was obtained around 520°C which indicates that the carbon is combusted at this temperature leaving behind the residual MgO (Figure 2). It was therefore found that the actual loadings of MgO on the CMK-3 supports are 44wt% MgO-CMK-3, 29wt% MgO-CMK-3 and 14wt%-MgO-CMK-3 respectively. The resulting material was then characterized thoroughly by various analytical techniques.
Figure 2. Thermogravimetric profile of (a) 14wt%-MgO-CMK-3 (b) 29wt%-MgO-CMK-3. (c) 44.41wt%-MgO-CMK-3.
Powdered X-ray diffraction (XRD)

Small angle X-Ray diffraction patterns of the samples exhibit the characteristic hexagonal structural ordering which is evident from the presence of the three XRD lines that can be indexed as (100), (110), and (200) reflections (Fig. 3a). Comparison of the diffraction pattern of CMK-3-MgO samples with that of the parent CMK-3 and SBA-15 shows a slight broadening of the peaks, which may be attributed to slight decrease in the structural order in the impregnated sample. Fig 3b shows the wide angle X-ray diffraction pattern of CMK-3-MgO, which exhibits all the characteristic reflections of MgO. Moreover, a broad pattern of diffraction indicates an amorphous nature of the material. Therefore it can be concluded that no crystallite formation of MgO has taken place and the impregnated magnesia is well dispersed into the pores of the CMK-3 structure.

Figure 3. (a) Small angle powder X-ray diffraction diagrams of CMK-3-MgO, CMK-3 and SBA-15. (b) Wide angle powder X-ray diffraction diagrams of CMK-3-MgO.
**Transmission electron microscopy (TEM)**

Transmission electron microscopy (TEM) however, shows a regular long range periodic order and hexagonal symmetry in the MgO impregnated CMK-3 structure (Fig 4).

![Figure 4. TEM image of CMK-3-MgO](image)

**X-ray photoelectron spectroscopy (XPS)**

Deconvolution of the high resolution narrow scan for O 1s in XPS spectrum (Fig 5) of the sample shows the presence of three distinct peaks. The lower binding energy (LBE) peak at 529.9 eV is attributed to the lattice oxygen O$^{2-}$ of the MgO while the higher binding energy (HBE) peaks at 531.9 eV and 534.6 eV are attributed to the presence of surface hydroxyl and carbonate species which may have formed on the
surface of the sample due to exposure of the sample to air. The presence of carbonate
groups are confirmed by the C 1s binding energy at 288.1 eV. The C 1s binding energy at
284.3 eV is due to the impurity in the system during XPS measurements. This is in
agreement with previous studies reported in the literature. The binding energies of Mg
2p also suggest the presence of Mg^{2+} in the MgO lattice. It is known that the negative
shift in the O 1s binding energy indicates a higher effective negative charge on surface
oxygen atoms. This leads to an increase in the electron-donating ability of the surface
oxygen atoms. The increased electron pair donating ability is believed to originate from
the formation of basic sites. Thus the surface O^{2-} ions are more basic.

Table 1. XPS data for the binding energies (eV) of elements in CMK-3-MgO

<table>
<thead>
<tr>
<th>XPS peak</th>
<th>CMK-3-MgO (BE in eV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>529.9, 531.9, 534.6</td>
</tr>
<tr>
<td>Mg 2p</td>
<td>51.4, 53.2</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.6, 286.1, 288.1, 290.2</td>
</tr>
</tbody>
</table>

* BE= Binding energy
Figure 5. XPS High resolution narrow scans of (a) Mg 2p (b) C 1s and (c) O 2p.

Temperature Programmed Desorption (TPD) of CO$_2$

Magnesium oxide is a well known basic catalyst. The basicity of the CMK-3-MgO was measured by Temperature Programmed Desorption (TPD) of CO$_2$. The TPD measurement was carried out for CMK-3-MgO catalysts to know the total basic strength of the catalyst. The corresponding TPD profile is illustrated in Fig. 6. The desorption profile of the catalyst shows a low-temperature CO$_2$ desorption peak around 100–150°C. This peak is attributed to the interaction of CO$_2$ with weak basic sites present in the catalyst. On the other hand, the peak appearing at 300–450 °C is due to the interaction of CO$_2$ with moderate basic sites of the catalyst. Another desorption peak appeared in the
temperature range of 600–800 °C resulting from the interaction of CO₂ with strong basic sites of the catalyst.

![Graph](image)

**Figure 6.** TPD profile of CMK-3-MgO.

The results of energy disperse X-ray (EDX) analysis confirms that magnesium is present in its oxide form. Moreover, the absence of any hydroxyl peak in FT-IR of the calcined sample, confirmed the absence of any surface hydroxyl group in the CMK-3-MgO sample.

**Nitrogen physisorption analysis**

The mesoporous character of the catalyst was confirmed by nitrogen physisorption analysis. A characteristic type IV isotherm is obtained which exhibits a H1 hysteresis loop. The surface area (SA) of the MgO impregnated CMK-3(130) is 999 m²/g. Comparing the surface area of CMK-3-MgO catalyst with that of parent CMK-3 shows a slight decrease. This may be attributed to the impregnation of the MgO inside the
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channels of the porous structure of CMK-3, therefore blocking the cavities, which in its turn decreases the surface area of the catalyst (Fig.5a). A slight decrease of the pore volume was also found when compared to that of the parent CMK-3(130). The pore volume of the impregnated CMK-3-MgO sample is found to be 1.23 cm$^3$/g (Fig 7b).

![Graph](image)

**Figure 7.** (a) Nitrogen adsorption isotherm of CMK-3-MgO at 77 K and (b) BJH pore size distributions of CMK-3-MgO (open symbols: adsorption; closed symbols: desorption).

**Catalytic activity of CMK-3-MgO in sulfinamide synthesis**

In order to understand the relationship between structure and reactivity, CMK-3-MgO catalyst (SA: 999 m$^2$/g) was applied to the synthesis of sulfinamides. The reactivity of this catalyst was compared to commercially available MgO (SA: 25 m$^2$/g). It was observed that a mere 20% of the corresponding product could be isolated, when commercial MgO was used as the catalyst in the reaction of $p$-toluenesulfonyl chloride with benzyl amine in presence of triphenylphosphine as the reducing agent, whereas the yield of the corresponding product was 85% when CMK-3-MgO was used as the catalyst. Moreover, the selectivity of the catalyst to form the corresponding sulfinamide was also found to be greater in case of the CMK-3-MgO. The earlier reports of the synthesis of the
sulfinamides suggest that basic sites are necessary in the catalyst to trigger this reaction.\(^{39}\)

In this context, a thorough insight into the structure of MgO suggests that it is composed of Lewis acidic Mg\(^{2+}\) and Lewis basic O\(^{2-}\).\(^{22,23}\) This greater reactivity may be attributed to the higher surface area of the catalyst, which in its turn exposes a greater number of basic sites.

**Screening of the catalysts**

To optimize the reaction conditions and to find out the suitable catalyst, MgO supported on CMK-3(100), CMK-3(130) and CMK-3(150) were used as catalysts in the synthesis of the sulfinamides. The results are summarized in Table 1.

It was found that CMK-3(130) containing 44.41%wt of MgO acts as the best catalyst. Therefore this catalyst was then used for all further reactions.

**Table 1:** Screening of different catalysts for the reaction of \(p\)-toluenesulfonyl chloride and benzyl amine.\(^{a}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Sulfinamide 1(%)</th>
<th>Sulfonamide2(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CMK-3(100) MgO</td>
<td>65, 30(^{c})</td>
<td>10, 28(^{c})</td>
</tr>
<tr>
<td>2</td>
<td>CMK-3(130) 44wt%MgO</td>
<td>72</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>CMK-3(130) 29wt%MgO</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>CMK-3(130) 14wt%MgO</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>CMK-3(150) MgO</td>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Commercial-MgO</td>
<td>45</td>
<td>30</td>
</tr>
</tbody>
</table>

\(^{a}\)Reaction conditions: \(p\)-toluenesulfonyl chloride (1mmol), triphenylphosphine (1mmol), benzyl amine (1mmol), catalyst (50 mg), solvent (4 ml), stirred at 0°C for 1h.

\(^{b}\)Isolated yields

\(^{c}\)Yield in THF as solvent.
Screening of solvents

Screening of various solvents for this reaction showed that a very low yield of the desired sulfinamide was realized in THF, acetonitrile and chloroform while the reaction in toluene showed only a trace amount of conversion of the starting materials. Therefore, using CMK-3(130)-MgO as the catalyst and \( p \)-toluenesulfonyl chloride, benzyl amine and triphenylphosphine as the model substrates, it was found that the reaction proved to be most facile when dichloromethane was used as solvent (Table 2). The selectivity of the reaction was found to be the maximum towards the formation of the corresponding sulfinamide when a mixture of benzyl amine and triphenylphosphine in dichloromethane was added slowly over 1 h to a stirred solution of the catalyst and \( p \)-toluenesulfonyl chloride in DCM at 0°C.

Table 2: Screening of various solvents for the reaction of \( p \)-toluenesulfonyl chloride and benzyl amine.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Sulfinamide 1(%)</th>
<th>Sulfonamide 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>72</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>30</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>Acetonitrile</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>4</td>
<td>CHCl(_3)</td>
<td>21</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>0</td>
<td>trace</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: \( p \)-toluenesulfonyl chloride (1mmol), triphenylphosphine (1mmol), benzyl amine (1mmol), catalyst (50 mg), solvent (4 ml), stirred at 0°C for 1 h.

\(^b\)Isolated yields
Optimization of reaction conditions

In order to optimize the yield of the desired product, three different methods of addition of substrates were adopted to maximize the yield of the sulfinamide product. In the first one, all the reactants were taken consecutively in the round-bottomed flask and then the catalyst was added to it. It was then stirred at 0°C, for 1 h. In the second method, p-toluenesulfonyl chloride and triphenylphosphine were taken in a round-bottomed flask and the catalyst was added to it. To this stirred reaction mixture, benzyl amine was added slowly over 1 h. In the third one, a solution of benzyl amine and triphenylphosphine in DCM was added slowly over 1 h to a stirred solution of p-toluenesulfonyl chloride and the catalyst in DCM. It was found that the maximum amount of the sulfinamide was formed in the reaction in which the third method of addition was followed. Therefore, this method was then used for all other reactions. The selectivity of the reaction was found to be the maximum towards the formation of the corresponding sulfinamide when a mixture of benzyl amine and triphenylphosphine in dichloromethane was added slowly over 1 h to a stirred solution of the catalyst and p-toluenesulfonyl chloride in DCM at 0°C.

Studying the effect of temperature over this reaction showed that a poor yield of the desired sulfinamide was obtained at room temperature. The results are furnished in Table 3. It was seen that, although p-toluenesulfonyl chloride underwent complete conversion at this temperature at a faster rate, the major amount of the isolated product was the corresponding sulfonamide. At -10°C, the reaction became very sluggish and resulted in a conversion of a mere 40% after 3 h. The results are shown in Table 3.
Optimum yield of the desired product was obtained when the reaction was conducted at 0°C.

It was seen that the use of 2 equivalents of the reductant triphenylphosphine did not help to improve the yield of the corresponding sulfinamide. Therefore, 1 equivalent of triphenylphosphine is used as the reducing agent in all the reactions.

**Table 3:** Effect of temperature for the reaction of \( p \)-toluenesulfonyl chloride and benzyl amine.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature(°C)</th>
<th>Sulfinamide 1(%)(^b)</th>
<th>Sulfonamide 2(%)(^b)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>50</td>
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</tr>
<tr>
<td>2</td>
<td>0</td>
<td>72</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>-10</td>
<td>34</td>
<td>12</td>
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</table>

\(^{[a]}\)Reaction conditions: \( p \)-toluenesulfonyl chloride (1mmol), triphenylphosphine (1mmol), benzyl amine (1mmol), catalyst (50 mg), DCM (4 ml), stirred at 0°C for 1h.

\(^{[b]}\)Isolated yields.

Using these optimized reaction conditions, a variety of aliphatic, aromatic, cyclic amines and amino acid derivatives were made to undergo this reaction. The results are summarized in **Table 4**.

Aniline and the substituted anilines showed excellent selectivity towards the formation of sulfinamides, no formation of sulfonamides were noticed in these cases (Table 2, entries 8-11). Proline methyl ester showed a poor selectivity towards the formation of the desired sulfinamide (Table 2; entry 12). But no diastereoselective products were formed.
Table 4: Synthesis of a series sulfinamides using $p$-toluenesulfonyl chloride and various amines$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Amines</th>
<th>Sulfinamide 1 (%)$^b$</th>
<th>Sulfonamide 2 (%)$^b$</th>
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most of the cases aryl sulfonamides were formed as a minor side product. Resulted in 74% of the desired product in a very short reaction time (Table 2; entry 1). Aliphatic amines, like butyl amine showed a good selectivity towards the formation of amine afforded moderate yield of the sulfinamide product. This may be attributed to the reduction by triphenylphosphine, undergoes a facile reaction with these amines to form the final product in moderate yield (Table 2; entry 3). Good yields of the aryl sulfinamides were also obtained in case of the cyclic primary amines, where as the side product, aryl sulfonamides were formed in a very small amount of only 10% (Table 2; entry 4). Piperidine afforded a poor yield of the desired sulfinamide whereas, morpholine showed a much higher selectivity towards the formation of the corresponding sulfinamide product (Table 2; entries 5-6).

\[ \text{Reaction conditions: } p\text{-toluenesulfonyl chloride} (1 \text{mmol}), \text{ triphenylphosphine} (1 \text{mmol}), \text{ amine} (1 \text{mmol}), \text{ catalyst} (50 \text{ mg}), \text{ DCM} (4 \text{ ml}), \text{ stirred at } 0^\circ\text{C for 1h.} \]

\[ \text{Isolated yields} \]
Various substituted aryl sulfonyl chlorides yielded the corresponding sulfinamides in moderate to good yields when subjected to reductive amination with a series of amines. The results are summarized in Table 5.

**Table 5:** Synthesis of a series sulfinamides using various arylsulfonyl chlorides and various amines

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Amine</th>
<th>Sulfinamide (%)</th>
<th>Sulfonamide (%)</th>
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[a] *Reaction conditions:* arylsulfonyl chloride (1mmol), triphenylphosphine (1mmol), amine (1mmol), catalyst (50 mg), DCM (4 ml), stirred at 0°C for 1h.

[b] Isolated yields.
From the results it was observed that benzenesulfonyl chloride shows a moderate selectivity towards the formation of the corresponding sulfinamides (Table 3; entries 1 and 2). Comparatively, lesser amount of aryl sulfinamide formation was found in case of both ortho and para substituted nitro benzenesulfonyl chlorides (Table 3; entries 3-6). 2,4, 6 tri-isopropyl benzenesulfonyl chloride on the other hand was found to afford the desired product in good yield.

**Reusability study of the catalyst**

After the completion of the reaction, the catalyst was separated by simple filtration and washed several times with ethyl acetate to remove any traces of organic compounds and was dried at 100°C, in a hot air oven and re-used for further cycles without any re-activation. Yields of the products obtained in the consecutive reaction cycles are similar to that of the first one. The results are summarized in Table 6.

**Table 6.** Recovery and reuse of CMK-3-MgO catalyst for reductive amination of p-toluenesulfonyl chloride with benzyl amine.\(^a\)

<table>
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<tr>
<th>Entry</th>
<th>No of cycles</th>
<th>Isolated yields 1(%)</th>
<th>2(%)</th>
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<tr>
<td>1</td>
<td>1</td>
<td>72</td>
<td>8</td>
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<tr>
<td>2</td>
<td>2</td>
<td>70</td>
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<td>70</td>
<td>10</td>
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<tr>
<td>5</td>
<td>5</td>
<td>70</td>
<td>10</td>
</tr>
</tbody>
</table>

\(^a\)Reaction conditions: p-toluenesulfonyl chloride (1mmol), triphenylphosphine (1mmol), benzyl amine (1mmol), catalyst (50 mg), DCM (4 ml), stirred at 0°C for 1h.
Plausible Mechanism

A plausible mechanism can be proposed for the synthesis of sulfinamides via reductive amination of sulfonyl chloride on the basis of the literature reports.\textsuperscript{17,22,23} The CMK-3-MgO catalyst (1) contains both Mg\textsuperscript{2+} and O\textsuperscript{2-} in the MgO lattice, so it can stabilize both positive and negative charges. Therefore, in the first step triphenylphosphine (PPh\textsubscript{3}) attacks the S=O bond, taking up the Cl\textsuperscript{-} ion forming an ion-pair species (2) which in its turn forms the intermediate Ar-S(O)-OPPh\textsubscript{3} (3). The electron deficient phosphine moiety then leaves off forming triphenylphosphine oxide (O=PPh\textsubscript{3}). The Cl\textsuperscript{-} ion then back attacks to form the intermediate sulfinating species Ar-S(O)Cl (4), which in the next step undergoes nucleophilic attack by the amine (5) to form the final product (Scheme 9).

\begin{center}
\textbf{Scheme 9}
\end{center}
Conclusions

In summary, a highly basic catalyst with very high surface area has been designed and synthesized. Thorough characterization of the catalyst showed a highly ordered characteristic mesoporous structural arrangement. Excellent activity of this catalyst has been observed for the synthesis of sulfinamides from aryl sulfonyl chlorides using various amines in presence of triphenylphosphine as reductant. The catalyst is highly stable and can be reused for several cycles with consistent activity.

Experimental Section

General

X-ray photoelectron spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg-Kα anode. The pressure in the spectrometer was about \(10^{-9}\) Torr. For energy calibration the carbon 1s photoelectron line is used. The carbon 1s binding energy was taken to be 285.0 eV. The spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products which were not obtained as pure species were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were in general, reproducible to within \(\pm 0.1\) eV.

Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer as KBr pellets. Thermogravimetric (TG), differential thermal analysis (DTA) the catalyst were studied on TGA/SDTA Mettler Toledo 851\(^{e}\) system coupled to MS Balzers GSD 300T, using open alumina crucibles, containing samples weighing
about 8-10mg with a linear heating rate of 10°C min$^{-1}$. Nitrogen adsorption and
desorption isotherms were measured at −196 °C on a Quantachrome Autosorb 1C
sorption analyzer. All samples were outgassed at 250 °C for 24 h. The specific surface
area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size
distributions were obtained from the adsorption branch of the nitrogen isotherms by
Barrett-Joyner-Halenda method. Temperature programmed desorption (TPD) profiles of
the catalysts were generated on an on-line quartz micro reactor interfaced to a thermal
conductivity detector (TCD) equipped with a gas chromatograph (Varian CP 3800 USA)
and the profiles were recorded using GC software. Transmission electron micrographs
were carried out in a Philips Tecnai G$^2$ FEI F12 electron microscope for probing particle
size. The samples were ultrasonically dispersed in ethanol before loading onto a carbon-
coated copper grid and then allowed to dry at room temperature before recording the
micrographs. SEM-EDX (scanning electron microscopy- energy dispersive X-ray
analysis) was performed on a Hitachi SEM S-520, EDX-Oxford Link ISIS-300
instrument. Bruker Avance (300 MHz), Varian Unity (400 MHz) spectrometer using
TMS as an internal standard and CDCl$_3$ as solvent. Mass spectra were obtained at an
ionisation potential of 70 eV [scanned on VG 70-70H (micro mass)]. Only selected ions
are presented here. Tri-block copolymer P$_{123}$ (EO20PO70EO20, EO= ethylene oxide,
PO= propylene oxide, 5800) was obtained from Aldrich. TEOS (Aldrich) was used as a
source of silicon. Analytical grade magnesium acetate was purchased from Wako
Chemicals, Japan. Sulfonyl chlorides, triphenylphosphine and amines were obtained from
Aldrich or Fluka and used without any further purification. All the other solvents and
chemicals were obtained from commercial sources and purified using standard methods.
ACME silica gel (100–200 mesh) was used for column chromatography. Thin-layer chromatography was performed on Merck-precoated silica gel 60-F254 plates. All the other solvents and chemicals were obtained from commercial sources and purified using standard methods.

**Synthesis of CMK-3-MgO catalysts**

**Synthesis of silica template SBA-15**

A typical synthesis was performed following the procedure available in the literature. SBA-15 was synthesized using the amphiphilic triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO20PO70EO20; average molecular weight, 5800; Aldrich). A typical synthesis was performed as follows: 4 g of the amphiphilic triblock copolymer was dispersed in 30 g of water and 120 g of a 2 M HCl solution and stirred for 5 h. Thereafter, 9.5 g of tetraethyl orthosilicate (TEOS) was added to the homogeneous solution under stirring. The resulting gel was aged at 40 °C for 24 h and finally heated to 100 °C for 24 h. In a second set of experiments, the gels were prepared as described above and crystallized at different temperatures between 100 and 150 °C. After synthesis, the obtained solids were calcined in flowing air at 540 °C to decompose the triblock copolymer.

**Synthesis of CMK-3**

CMK-3 carbon was prepared according to the process described in the literature. In a typical synthesis of mesoporous carbon, 1 g of template was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H₂SO₄ in 5 g of water, and keeping the mixture in an oven for 6 h at 100 °C. Subsequently, the oven temperature was raised to 160 °C for another 6 h. To obtain fully polymerized and carbonized sucrose
inside the pores of the silica template, 0.8 g of sucrose, 0.09 g of H$_2$SO$_4$, and 5 g of water were again added to the pretreated sample and the mixture was subjected to the thermal treatment described above. The template-polymer composites were then pyrolyzed in a nitrogen flow at a heating rate of 5 °C min$^{-1}$ up to 900°C and kept under these conditions for 6 h to carbonize the polymer. The mesoporous carbon was recovered by filtration after dissolution of the silica framework in 5wt% hydrofluoric acid, washed several times with ethanol and dried at 120°C.

**Synthesis of MgO modified CMK-3.**

In a typical synthetic procedure of different weight percentages of MgO modified CMK-3, desired amount of magnesium acetate Mg(CH$_3$COO)$_2$.4H$_2$O was dissolved in 50 mL of ethanol to prepare 60wt%MgO-CMK-3, 40 wt%MgO-CMK-3 and 20wt%MgO-CMK-3 respectively. The ethanolic solution of Mg(CH$_3$COO)$_2$.4H$_2$O were stirred at 50°C for 10 min followed by addition of 1.0g of CMK-3. The reaction mixture was stirred at 50°C for 3h to impregnate the mesopores with magnesium acetate. The reaction mixture was then filtered and the precipitate was dried in air. The resultant black coloured powder was then subjected to heating up to 300°C under a low oxygen flow. Finally, the resulting catalyst was activated under nitrogen flow at 500°C for 4 h to remove any surface hydroxyl groups which may be formed during the impregnation procedure. The weight percent of MgO actually impregnated on the CMK-3 supports were determined by thermogravimetric analysis of the samples under flowing air to remove all the carbon material as oxide. A sharp peak was obtained around 520°C which indicates that the carbon is combusted at this temperature leaving behind the residual MgO. It was
therefore found that the actual loadings of MgO on the CMK-3 supports are 44wt% MgO-CMK-3, 29wt% MgO-CMK-3 and 14wt% MgO-CMK-3 respectively.

**Typical Experimental Procedure for the synthesis of sulfinamides**

To a stirred solution of \( p \)-toluenesulfonyl chloride (190 mg, 1 mmol) and CMK-3-MgO catalyst (50 mg) in dichloromethane (2 mL) at \( 0^\circ \)C, was added a solution of triphenylphosphine (262 mg, 1 mmol) and benzyl amine (107 mg, 1 mmol) in dichloromethane (2 ml) via a syringe over a period of 1h. The reaction was monitored by TLC for the complete conversion of the \( p \)-toluenesulfonyl chloride. After the completion of the reaction the reaction mixture was filtered to remove the catalyst and washed several times with ethyl acetate. The combined organic extracts were concentrated under reduced pressure and subjected to purification by column chromatography over a silica gel column (60-120 mesh) to afford the pure product (eluent: 20% ethyl acetate: hexane) as white solid. The catalyst was dried at \( 100^\circ \)C in a hot air oven and preserved for the next run. The products were identified by NMR and mass spectroscopic analysis and comparison with the data available in the literatures.\(^{16}\)

**Representative examples**

**1-(\( p \)-tolylsulfinyl)-4-methoxyaniline (Table 4, entry 1).**

**Figure 8.** \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.62 (d, \( J=8.4 \) Hz, 2H), 7.18-7.31 (m, 7H), 4.24-4.30 (t, \( J=5.5 \) Hz, 1H), 4.14 (dd, \( J=4.8, 13.2 \) Hz, 1H), 3.76 (dd, \( J=7.3, 13.5 \) Hz, 1H), 2.35 (s, 3H).

**Figure 9.** \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 21.31, 55.38, 114.42, 114.44, 122.61, 125.52, 129.53, 132.97, 141.52, 156.55.

**Figure 10.** ESI-(MS) (m/v) (Relative intensity) 284 (M+23, 55%).
N-cyclohexyl-2, 4, 6-triisopropylsulfinamide (Table 5, entry 8)

**Figure 11.** $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.02 (s, 2H), 4.23 (m, 1H), 4.0 (m, 2H), 3.44 (m, 1H), 2.85 (m, 1H), 2.09 (m, 2H), 1.76 (m, 2H), 1.62 (m, 1H), 1.12=1.48 (m, 20H).

**Figure 12.** $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 23.99, 24.24, 25.45, 28.19, 33.66, 34.21, 35.32, 54.32, 122.86, 147.17, 151.44.

**Figure 13.** ESI-(MS) (m/z) (Relative intensity) 350 (M+1, 100%).

Rest of the products were characterized similarly and the results obtained were similar to that reported in the literature.$^{16}$
Chapter III

References


10. S. R. Wilson, M. E. Walters, B. Orbaugh, personal communication.


