Synthesis of nano-MgO and identification of the destructive product of its reaction with 2-chloroethyl phenyl sulfide

Bozorgmehr Maddah*, Amir Aminifar & Hossein Chalabi
Department of Chemistry, Imam Hossein University, Tehran, Iran
Email: bozorgmaddah@yahoo.com

Received 29 March 2011; revised and accepted 23 August 2011

Nanocrystalline magnesium oxide has been prepared by the sol-gel method and characterized by X-ray diffraction, N$_2$-BET, SEM and infrared spectroscopic techniques. Results confirm the formation of nano-MgO materials with crystallite size in the range of 5-20 nm and surface area of 336-556 m$^2$/g. The product has been tested as destructive adsorbent for the decontamination of (2-chloroethyl) phenyl sulfide, a mimic of bis(2-chloroethyl) sulfide (HD or mustard gas). Destructive adsorbent reaction has been carried out in heptane and methanol media and investigated by GC-FID and GC-MS techniques. Reaction rate in heptane is observed to be higher than in methanol. It seems that a nonpolar media aids material transfer to the reactive surface sites without blocking these sites.

Keywords: Nanomaterials, Decontamination reaction, Magnesium oxide, Destructive adsorbent

The surface of metal oxides plays an important role in various reactions occurring in nature and in industrial processes. Metal oxides are found to be promising adsorbents for the degradation of environmental pollutants both in normal and light irradiated conditions. Their reactivity towards the toxic chemicals under normal conditions can be attributed to Lewis acid, Lewis base and Bronsted acid sites of varying coordination and the surface hydroxides. Nano-MgO, CaO, ZnO and Al$_2$O$_3$ adsorb polar organics such as aldehydes, alcohols, ketones, and other polar organics in very high capacities, and substantially outperform the activated carbon samples that are normally employed for such purposes. On the other hand, metal oxides have been established as potential adsorbent material for the decontamination of chemical warfare agents (CWA). Due to their high surface area, a large number of highly reactive edges, corner defect sites, unusual lattice planes and high surface-to-volume ratio, nanocrystalline metal oxides possess enhanced reactive properties towards chemical warfare agents and have been successfully tested for decontamination applications. The adsorption ability of nanocrystalline ionic metal oxides, in particular MgO, can be attributed to morphological features; a high proportion of edge/corner sites is available due to their polyhedral shapes. Both Lewis base and Lewis acid sites at the edge/corner are stronger due to coordinative unsaturation. Indeed, several models suggest that at least 20% of the surface ions are positioned on the edge/corner. Furthermore, according to magnetic susceptibility studies, other types of surface defects such as ion vacancies and electron-deficient and electron-rich sites exist. Nano-MgO is commonly obtained by thermal decomposition of magnesium hydroxide or carbonate and by sol-gel process. The oxide morphology, particle size and specific surface area depend on the preparation conditions (pH, gelling agent, calcinations rate and temperature). There is considerable interest in the synthesis of nanoscale magnesium oxide particles via the magnesium alkoxide, Mg(OR)$_2$, route. Generally, an alkoxide is hydrolyzed in an alcohol solvent to yield the hydroxide, which is followed by isolation and thermal dehydration. Stengl and co-workers have described the preparation of magnesium hydroxide aerogels on the basis of the hydrolysis and condensation reactions of the alkoxide. They carried out the hydrolysis of Mg (OCH$_3$)$_2$ in a water-methanol-toluene mixture and, after autoclave hypercritical drying, obtained magnesium oxide aerogels with surface areas of about 537 m$^2$/g.

The objective of the work reported herein is to improve upon these earlier preparation by using a modified aerogel procedure, employing an alcohol-toluene solvent mixture, rapid hydrolysis and gelation, supercritical drying of solvent, and determining the relationship between MgO surface area and reaction rate in detoxification activity of the prepared samples. The detoxification activity of the prepared samples of nano-MgO was evaluated by using HD-simulated 2-chloroethyl phenyl sulfide and identification of the destructive products.
Experimental

Analytical grade methanol, n-heptane, n-octane, toluene, Commercial magnesium oxide (CM-MgO) with BET 50 m$^2$/g and magnesium ribbons were purchased from Merck and 2-chloroethyl phenyl sulphide was purchased from Aldrich.

A modified autoclave hypercritical procedure was developed to prepare nano-MgO particles. This method involves the preparation of Mg(OCH$_3$)$_2$ by the reaction of the magnesium metal with methanol (8 % w/v), hydrolysis of Mg(OCH$_3$)$_2$ in the presence of toluene; after hydrolysis of Mg(OCH$_3$)$_2$, the hydroxide gel was transferred to the reactor and then the reactor was pressurized with nitrogen gas to obtain the desired pressure of 110 psi. Finally, the reactor was slowly heated to 275 °C at a rate of 2 °C/min for 2 hours. The temperature was allowed to equilibrate for 30 minutes at 275 °C followed by a quick release of the pressure. The reactor was allowed to cool for 1 hour. The resulting product was a light brown powder which was calcined at 500 °C and stored in a vial in a desiccator for future use.

XRD patterns were obtained in a Scintag-XDS 2000 spectrometer. The light source used was Cu-K$_\alpha$ radiation with an applied voltage and current of 40 kV and 40 mA, respectively. The 2$\theta$ angles ranged from 10$^\circ$ to 100$^\circ$ at a speed of 2$^\circ$/min. Scanning electron micrograph was obtained with a HITACHI S-300N instrument. Surface areas were obtained by the BET method with a Quantachroma nova series 1200 instrument. The samples (150 mg) were heated under vacuum at the desired temperature, usually 300 °C for several hours, followed by cooling and then N$_2$ adsorption measurements were made 77 K at different pressures. In order to identify the products of degradation of CEPS, n-heptane was used to extract the sample CEPS over the oxides. The extractants were analyzed by a HP-Agilent GC-MS system and Varian Star 3400 CX gas chromatograph with a flame ionization detector (FID). A fused-silica capillary column DB-1701 (30 mx0.25 mmx0.25 µm) was used. The initial and final temperature of the oven was programmed to 60 °C (held for 6.00 min) and 200 °C respectively, to reach the final temperature (after 6.00 min); the temperature was increased at a rate of 20 °C/min. The products were identified by comparing their experimental mass spectra with references.

For GC and GC-MS studies, the reaction was set up in a round bottom flask, 100 mg of nano-MgO (or CM-MgO) was added to 5 µl CEPS, 5 µl for n-octane (internal reference) and 10 mL heptane (or methanol), under N$_2$ atmosphere and room temperature. The liquid fraction (10 µl) was drawn through a serum-septum periodically (5, 15, 30, 60, 120, 360, 720 min) and was injected directly to the column with a microliter syringe.

Results and discussion

The purity and structure of MgO powders were determined through X-ray diffraction (XRD) measurements. Figure 1 shows the XRD of MgO for batch 6 (Table 1). The spectra were comparable to JCPDS 45-0946. The mean crystallite size of the nanocrystalline MgO materials was estimated by using the Scherrer formula and was found to be in the range of 4-20 nm, while it was 0.15 µm for the bulk materials (as per the catalogue). Figure 2 shows the typical surface section SEM micrograph of the obtained MgO powder (batch 6). Most MgO particles are of a similar size.

<table>
<thead>
<tr>
<th>Batch</th>
<th>M/S</th>
<th>$P_{N_2}$(psi)</th>
<th>$S_{BET}$(m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50/100</td>
<td>0</td>
<td>218</td>
</tr>
<tr>
<td>2</td>
<td>50/100</td>
<td>110</td>
<td>336</td>
</tr>
<tr>
<td>3</td>
<td>50/100</td>
<td>220</td>
<td>340</td>
</tr>
<tr>
<td>4</td>
<td>40/100</td>
<td>110</td>
<td>425</td>
</tr>
<tr>
<td>5</td>
<td>30/100</td>
<td>110</td>
<td>500</td>
</tr>
<tr>
<td>6</td>
<td>20/100</td>
<td>110</td>
<td>556</td>
</tr>
<tr>
<td>7</td>
<td>15/100</td>
<td>110</td>
<td>540</td>
</tr>
<tr>
<td>8</td>
<td>10/100</td>
<td>110</td>
<td>535</td>
</tr>
<tr>
<td>9</td>
<td>20/100</td>
<td>0</td>
<td>366</td>
</tr>
<tr>
<td>10</td>
<td>20/100</td>
<td>220</td>
<td>546</td>
</tr>
</tbody>
</table>

Fig. 1−X-ray diffraction pattern of the synthesized nano-Mgo (batch 6).
Specific surface areas of ten batches of representative nano-MgO precursors prepared under different experimental conditions are presented in Table 1. The data show extremely high specific surface areas (218-556 m$^2$/g), compared to that of the commercial sample (50 m$^2$/g). Indeed, the experimental conditions used in our experiment were modified from those of Stengl and co-workers, altering the magnesium oxide aerogels with surface areas of about 537 m$^2$/g. Such modification had a great impact on the specific surface area of the resulting products. This improvement could result from two major factors. First, the use of an excess of toluene solvent may affect the hydrolysis-cocondensation process. As stated by Hubert-Pfalzgraf, the hydrolysis-polymerization reactions are governed by several parameters including solvent and dilution. The interaction between the OH group and toluene solvent may help to protect the gel structure. The incorporation of a hydrophobic organic solvent may reduce liquid-pore wall interaction, which is one of the major causes of the capillary force and the stress formation. On the other hand, the hydrolysis of Mg(OCH$_3$)$_2$ depends on the solvent used. When a low dielectric constant solvent (or mix solvents) is employed, the hydrolysis and gelation are faster and the surface area of the dried gel is higher. With increase toluene solvent was used, i.e. methoxide solution/toluene solvent (M/S), the surface area increased from 336 to 556 m$^2$/g. The use of M/S ratio, equal to 20/100 seemed to yield the most optimized surface area (556 m$^2$/g) probably because of its effect on the hydrolysis process and protecting the gel structure of methoxide solution. The large excess amount of toluene solvent, i.e. M/S=15/100 and 10/100 solution, did not improve the surface area of the final product any further.

Secondly, the introduction of nitrogen gas to the gel before the autoclave treatment may cause shrinkage of the gel during the drying process. This effect was reported in the preparation of autoclave dried silica gel. It was demonstrated that the application of an inert gas, N$_2$, in the autoclave provided control of the shrinkage of the gels and a pressure of 80 bars was necessary to avoid any shrinkage. In our experiment, a pressure of 110 psi (7.5 bars) was found to be optimum condition. Application of a higher pressure of N$_2$ at 220 psi (15 bars) does not improve the specific surface area of the product.

The prepared MgO samples were also characterized by FTIR. The presence of hydroxyl groups on the surface of the product has been shown by the appearance of IR absorption peaks at 3431 cm$^{-1}$. In addition, Mg–O absorption at 540 cm$^{-1}$ was also observed. As the material was calcined at 500 °C and stored in an air tight bottle, the possibility of the presence of moisture is negligible. FTIR spectrum of the synthesized MgO (not shown here) is similar to that reported in literature.

The effect solvent the rate of the destructive adsorption process was studied. Without a solvent, the complete reaction can take days or weeks to complete. Heptane was initially chosen as a solvent since it is inert and facilitated CEPS transfer to the MgO surface. Several preparative batches of nano-MgO and CEPS adsorption reaction were carried out in heptanes in order to determine the relationship of MgO surface area and reaction rate (Table 1). The reaction rate of adsorption and decomposition of CEPS with MgO has been verified by GC for these reactions. We found that the reaction rate in heptane is directly related to the surface area of the nano-MgO. For example, over 59.6 % of the CEPS was consumed with batch 6 (556 m$^2$/g surface area in 30 min), less than 47.5 % disappeared with batch 2 (336 m$^2$/g), and less than 27.1 % disappeared with CM-MgO (50 m$^2$/g) (see Fig. 3). However, it may be noted that CM-MgO, which is very different morphologically, exhibited a far lower rate. It is clear that crystal shapes as well as surface area are effective in the reaction adsorption. Aerogel prepared-MgO crystallites are polyhedral, while...
CM-MgO is polycrystalline and exists mainly as cubes\textsuperscript{9,10}. The initial rapid rate of these reactions markedly slowed down after about 30 min; this behavior has also been observed earlier\textsuperscript{4,9-12}. It is likely that an array of site reactivity is involved, and the most active sites are consumed first (edges, corners, defects), followed by the less reactive sites (such as planar surfaces).

GC-MS analysis was carried out 720 min after starting the reaction. Two peaks were eluted at 3.8 and 5.9 minutes. The eluents were fragmented using electron ionization. Figure 4 shows both products, viz., CEPS has a molecular weight of 172 which matches the M peak, with M+2 from the \textsuperscript{37}Cl isotopes, and the largest fragmentation at 123 from the loss of CH\textsubscript{2}=Cl, this fragmentation matches up with the CEPS standard and the second spectra is attributed to phenyl vinyl sulfide, MW=136, the fragmentation peak, at 109 m/z, is C\textsubscript{6}H\textsubscript{5}-S from the loss of CH\textsubscript{2}-CH\textsuperscript{*}.

The suggested MgO-CEPS destructive adsorption reaction has been depicted in Scheme 1. It may be observed that isolated OH groups working in tandem with non hydroxylated MgO moieties (thus Mg\textsuperscript{2+} ion binds to the sulfur of CEPS) could lead to the bound substitution (alkoxide) product. For the vinyl product formation, it may be that isolated OH groups are capable of causing E2 elimination as shown in Scheme 1. These suggestions correspond very closely to the results reported for the reaction of 2-CEES (2-chloroethyl ethyl sulfide) with MgO\textsuperscript{7}.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>In methanol</th>
<th>In heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.81</td>
<td>2.01</td>
</tr>
<tr>
<td>15</td>
<td>18.18</td>
<td>47.97</td>
</tr>
<tr>
<td>30</td>
<td>22.86</td>
<td>59.59</td>
</tr>
<tr>
<td>60</td>
<td>25.28</td>
<td>65.72</td>
</tr>
<tr>
<td>120</td>
<td>26.39</td>
<td>65.99</td>
</tr>
<tr>
<td>360</td>
<td>27.69</td>
<td>67.99</td>
</tr>
<tr>
<td>720</td>
<td>28.15</td>
<td>70.29</td>
</tr>
</tbody>
</table>

With methanol the results were very different to those in heptane. The amount of CEPS consumed in heptane was two to three times greater over the same period of time. The results with methanol show (see Table 2), however, that polar solvents hinder the
reaction, even though polar reaction transition state must be involved. These data indicate that polar solvents can compete with reactive sites on the MgO surface, including Bronsted acid and Lewis acid sites. In particular, the blocking of Lewis acid site would hinder the coordination of the CEPS. Since methanol is such a strong hindrance to the reaction, this tends to lend further support to the idea that methanol simply blocks access to the sorbent surface. The formation of substitution product (likely in the deported alkoxide state) could not be followed by GC during this reaction because the substitution product had bonded very strongly to the surface. Narske co-workers reported similar result when working with CaO reaction with 2-CEES.

In the present study, nano-MgO was prepared by sol–gel method with crystallite size in range of 5-20 nm and surface areas of 336-556 m²/g. The data show extremely high specific surface areas, compared with the work of Stengl. This may be due to two major factors. Firstly, the use of an excess amount of toluene solvent may affect the hydrolysis-cocondensation process. Secondly, the introduction of nitrogen gas to the gel before the autoclave treatment may cause shrinkage of the gel during the drying process. The amount of CEPS consumed with heptane was two to three times greater than that with methanol over the same period of time. Polar solvent can compete with reactive sites on the MgO surface thus; blocking the Lewis acid site which may hinder the coordination of CEPS. The present results show that nano-MgO with high specific surface areas can be used effectively for decontaminating (2-chloroethyl) phenyl sulfide.

References