JOURNAL OF
Materials
CHEMISTRY

Synthesis of carbon-coated MgO nanoparticles

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Received 14th August 2002, Accepted 20th August 2002
First published as an Advance Article on the web 5th November 2002

Carbon-coated MgO nanoparticles, with carbon forming a porous coating on the surface of MgO nanoparticles, have been prepared by two different techniques. Resorcinol has been found to be an efficient agent for the modification of magnesium methoxide leading to carbon-coated MgO nanocrystals of small crystallite size and high surface area. Decomposition of dry magnesium methoxide under an inert gas flow proved to be another efficient and economical way to synthesise carbon-coated MgO. The carbon coating acts as a hydrophobic barrier partially protecting the core metal oxide from water adsorption and conversion to magnesium hydroxide. However, destructive adsorption reactions can still proceed on the metal oxide surface, as evidenced by the dehydrochlorination of 2-chloroethyl ethyl sulfide (2-CEES) and 1-chlorobutane. The overall stability of the material in the presence of water vapor is significantly improved in comparison with non-coated nanocrystalline MgO.

Introduction

Nanocrystals of common metal oxides such as MgO, CaO, ZnO, TiO_2, Al_2O_3, and Fe_2O_3, have been shown to be highly efficient and active adsorbents for many toxic chemicals including air pollutants, chemical warfare agents, and acidic gases.[1–6] In most cases, destructive adsorption takes place on the surface of the nanocrystals, so that the adsorbate is chemically dismantled and thereby made nontoxic. In particular, aerogel-prepared (AP) nanocrystalline MgO has been shown to have a small average particle size ($\sim$4 nm), high surface area ($>$ 500 m^2/g) and high reactivity.[3,7]

The use of these nanocrystalline metal oxides is limited under conditions where liquid water or water vapor is present due to their tendency to adsorb water, and thereby be partially deactivated toward adsorption of the target pollutants. Although the target pollutants are usually subjected to conversion reactions in the presence of water as well, relatively large amounts of water can reduce the amount of adsorption of the target adsorbate decreasing the efficiency of the destructive adsorbent.

Activated carbon is made up of mainly graphitic structures, which exhibit a less polar surface, and the tendency to adsorb water is lower compared with nanocrystalline metal oxide surfaces. Therefore, it was hypothesized that if the metal oxide particles could be coated with a porous carbon, the water problem might be minimized, while still allowing destructive sorption of target pollutants, perhaps, by stepwise adsorption on carbon followed by migration to the nanocrystalline oxide surface.

In the present paper we report two synthetic methods developed for the preparation of carbon-coated MgO nanoparticles and the comparison of the properties of the resulting materials with those of non-coated nanocrystalline MgO.

Experimental

Synthesis of modified $Mg(OH)_2$ aerogels

Magnesium methoxide was prepared by dissolving Mg metal ribbon (Fisher) in methanol. Typically a 1 M solution was prepared by the reaction of 4.86 g (0.20 mol) Mg with 206 ml methanol under a flow of nitrogen at room temperature. After completion of the reaction, the reaction vessel was sealed and stored at room temperature for future use in the synthesis of $Mg(OH)_2$ aerogels.

For the preparation of modified MgO aerogels, the magnesium methoxide solution obtained in the first step was diluted with the desired amount of methanol and/or other solvent (*e.g.*, toluene). Organic modifying agents and water (for hydrolysis) were each dissolved in 10 ml methanol. Then, the solution of the first modifying agent was quickly poured into the reaction vessel with magnesium methoxide and the resulting mixture was stirred for 10 min. If two modifying agents were used, the second one was added following a similar procedure. Finally, a stoichiometric amount of water (for hydrolysis) dissolved in methanol was added. The reaction vessel was continuously maintained under a flow of nitrogen for the whole reaction. The gel formed after adding water was stirred overnight with a magnetic stir bar unless a solid gel was obtained. In the latter case, the gel was aged overnight without stirring. The amount of solvent was adjusted to provide a pressure of about 7000 kPa at the end of the autoclave treatment (see below). The amounts of reagents were adjusted accordingly to provide the desired concentration.

The aerogels were prepared by high temperature supercritical drying of the gels in a standard one liter autoclave (Parr). The autoclave containing the gel was first flushed with nitrogen for 10 minutes. Then it was filled with nitrogen at an initial pressure of about 700 kPa and sealed. The autoclave temperature was slowly increased up to a desired value at a rate of 1 K min^{-1} and maintained at that temperature for 10 minutes. The final pressure was about 7000 kPa. After completion of the procedure, the pressure was quickly reduced by releasing the solvent vapor. The sample was again flushed with nitrogen for 10 minutes and allowed to cool down in nitrogen.

Synthesis of AP-MgO and carbon-coated MgO nanocrystals

AP-$Mg(OH)_2$ was synthesized by a similar procedure without adding any organic modifiers to the magnesium methoxide in a

DOI: 10.1039/b207972k

toluene–methanol solution.[3] The material obtained after supercritical drying at 265 °C was subjected to thermal treatment under vacuum at 500 °C to give AP-MgO. A detailed synthetic procedure can be found elsewhere.[3]

For the synthesis of $Mg(OH)_2$ modified with resorcinol, 20 ml of 1 M $Mg(OCH_3)_2$ solution in methanol was mixed with 60 ml toluene in a 250 ml round-bottom flask maintained under flowing nitrogen. Resorcinol (0.33 g, 0.0030 mol) was dissolved in 10 ml methanol in a beaker. H_2O (0.72 ml, 0.040 mol) was dissolved in 10 ml methanol in another beaker. The total volume of the solvents was 100 ml, with the toluene : methanol ratio equal to 1.5. All solutions were homogenized by stirring with magnetic stir bars for 10 min. Then, the solution containing resorcinol was quickly poured into the flask containing magnesium methoxide. The hydrolysis water was added five minutes later after a dark-brown precipitate had formed. The mixture was stirred overnight resulting in the formation of a dark-green gel. Then the gel was subjected to standard hypercritical drying in the autoclave at 265 °C to yield a fluffy red–brown powder.

The resulting material denoted as Re-$Mg(OH)_2$ was subjected to heat treatment under vacuum at variable temperatures to give carbon-coated MgO. Samples obtained after evacuation of Re-$Mg(OH)_2$ at 500 °C and 750 °C for 3 hours, denoted as Re-MgO-500 and Re-MgO-750, respectively, were used in catalytic experiments.

For the synthesis of carbon-coated magnesium oxide from magnesium methoxide, Mg chips (100 g, 4.11 mol) were placed in a stainless steel autoclave, and dry methanol (3168 g, 98 mol) was added. The reaction was allowed to proceed for several hours under a head of nitrogen. Then the hydrogen gas byproduct was released, and the autoclave was purged with nitrogen. The resulting magnesium methoxide product $Mg(OCH_3)_2$ was separated from the excess methanol by spray drying through a 0.5 mm orifice using nitrogen pressure at 150 °C. A portion of this material (0.5 g) was placed on a belt heater system and heat treated for 1.75 minutes at 650 °C under nitrogen which caused the formation of carbon coated magnesium oxide (C/MgO).

Characterization of materials

Textural characterization of the samples was performed on a NOVA 1200 gas sorption analyzer (Quantachrome Corp.). Prior to the analysis the samples were outgassed at 180 °C for 1 hour. Seven point BET surface areas, total pore volumes and pore size distributions (BJH method) were calculated from nitrogen adsorption/desorption isotherms.

X-Ray powder diffraction experiments were conducted on a Scintag-XDS-2000 spectrometer using Cu-Kα radiation. Scans were made in the 2θ range of 20–80° with a scanning rate of 1° min^{-1}. Crystallite sizes were determined from X-ray line broadening using the Scherrer equation.

IR spectra were recorded using a Mattson RS-1 research series FTIR spectrometer with nitrogen purge and a HgCdTe detector. All spectra were obtained as the FT average of 64 scans with a resolution of 1 cm^{-1}.

TEM studies were performed using a Philips CM100 electron microscope operating at 100 kV. The samples were prepared by suspending powders ($\sim$1%) in methanol followed by ultrasound treatment. Holey amorphous carbon grids were used as supports.

Dehydrochlorination of 1-chlorobutane was performed in a flow reactor. 1-Chlorobutane (99%, Aldrich) used in the experiments was introduced into the reactor by saturation of the argon flow with C_4H_9Cl vapor at room temperature. 10 µl injections of C_4H_9Cl were used. The experiments were performed at 380 °C, the volume flow rate was about 2 l h^{-1}, and the catalyst loading was equal to 0.02 g. The product composition after the reaction was analyzed by gas chromatography. Prior to each experiment the catalyst was activated in an argon flow at 500 °C for 1 h to remove adsorbed water.

The destructive adsorption of 2-CEES on nanocrystalline MgO has been described previously.[8] In short, dry MgO nanocrystals were treated with liquid 2-CEES in an evacuated chamber at room temperature. The major product was the dehydrohalogenated vinyl compound ethyl vinyl sulfide ($CH_3CH_2SCH{=}CH_2$), which is volatile and under reduced pressure enters into the gas phase above the MgO sample where it was detected by infrared spectroscopy.

Results and discussion

Modification of $Mg(OH)_2$ aerogels

One of the most versatile modern methods for preparing inorganic materials from molecular precursors is the sol–gel process. Organic groups used for modification of typical metal alkoxide precursors in the sol–gel process can serve two different purposes: i) to control the reaction rates of the reactants as well as the homogeneity and microstructure of derived gels being degraded during subsequent calcination to give purely inorganic materials; or ii) to modify or functionalize the oxide material.

The latter approach could be applied to the synthesis of oxide nanocrystals coated with carbonaceous structures. Nanostructures of this type can be created very effectively by controlled pyrolysis of organically modified aerogels. In this case organic groups are already located at the surface of the oxide, and their relatively homogeneous distribution can result in a higher number of well-distributed nucleation centers during pyrolysis leading to smaller carbon particles. To achieve a high carbon content in the pyrolysed sample and to retain a large percentage of carbon during pyrolysis aerogels substituted with large, preferably aromatic, organic groups are particularly well suited.[9] Owing to the arrangement of the carbon structures generated during pyrolysis, a relatively small amount of carbon could give efficient coating of the oxide skeleton.

In an attempt to find a modifying agent suitable for our purposes and optimum reaction conditions, we have studied the effect of the addition of several acids, β-diketones and aromatic alcohols as well as the effect of toluene in the magnesium methoxide solution on the gelation behavior and properties of the resulting MgO aerogels. Strong complexing agents, such as β-diketones, polyhydroxylated ligands and hydroxyacids have been successfully used for the synthesis of modified zirconia and titania gels[10,11] as they are more stable towards hydrolysis than alkoxy groups. Therefore, upon hydrolysis many of these groups remain bound to metal atoms while alkoxy groups are quickly removed. Thus, they play a key role during condensation acting as termination sites. Usually, such ligands end up on the surface of resulting hydroxide or oxide nanoparticles, and it is often possible to control the size of the nanoparticles by varying the relative concentration of the ligands. One of the goals of the present study was to find which of such ligands, if any, would have a similar effect on the properties of $Mg(OH)_2$ gels.

Similar to zirconia and titania gels, addition of acetylacetone, acetic acid and HNO_3 to $Mg(OH)_2$ gels prevented precipitation and resulted in a noticeable increase of the gel time and often the formation of nice clear gels. Hard clear gels, which are often desirable during the synthesis of other metal oxide aerogels,[12,13] could be easily obtained at a $Mg(OCH_3)_2$ concentration of 0.5 M after addition of acid. Still, however promising it looked at first glance, our initial attempts to apply such a modification to the synthesis of $Mg(OH)_2$ always yielded materials with very low surface areas. Addition of modifiers such as acetic acid, benzoic acid, nitric acid, acetylacetone or benzoylacetone resulted in a decrease in surface area from about 300 m^2 g^{-1} to 50–75 m^2 g^{-1}.

The use of toluene and other aromatic compounds such as benzene and mesitylene as co-solvents resulted in the formation of clear gels, eliminating the need for the addition of acids, and a noticeable increase in the surface area of the resulting aerogels (up to 1150 m^2 g^{-1} with a toluene : methanol ratio equal to 5). These data are in good agreement with the reported favorable effect of toluene on the textural properties of MgO aerogels.[3,7] Its presence is believed to accelerate both the hydrolysis and the gelation processes.[14]

The preparation procedure developed previously for the synthesis of high-surface area AP-MgO nanocrystals[3] involves the addition of toluene as a second solvent and results in the rapid formation of a soft nearly liquid gel. Meanwhile, in the absence of any modifiers, the addition of water to $Mg(OCH_3)_2$ in a methanol solution brings about slow gelation with visible formation of a precipitate so that the resulting solid does not possess as high a surface area or desirable porous structure after supercritical drying. In other words, the use of toluene as a cosolvent has an obvious beneficial effect.[7,14]

Although toluene appears to be not the only compound to exert such an effect, it is the most convenient for practical use being less toxic than benzene and more volatile than heavier organic solvents. The autoclave temperature of 265 °C employed in the standard procedure for the preparation of AP-MgO is above critical for methanol, but not for toluene. Still, the incomplete elimination of surface tension under these conditions does not seem to have a significant detrimental effect on the properties of the aerogels. The use of benzene as a co-solvent and a drying temperature of 295 °C that is above critical for benzene did not give a higher surface area of the dried material.

While our attempts using acids and acetylacetone proved to be unsuccessful, very promising results were obtained with bidentate compounds of another type, *i.e.* hydroxyphenols. The addition of resorcinol and hydroquinone led to a gradual formation of intensely colored precipitates, which were dark brown in the case of resorcinol and bright green in the case of hydroquinone. Reactions taking place at this stage involve alcohol exchange [reactions (1)–(3), (shown for resorcinol)] . Obviously, the product formed in reaction (3) can participate in further alcohol exchange reactions that can eventually lead to relatively large oligomers precipitating out of the solution. The average size of these oligomeric species must depend on the absolute and relative concentrations of magnesium methoxide and resorcinol. The use of a higher relative resorcinol concentration results in the formation of larger oligomers.

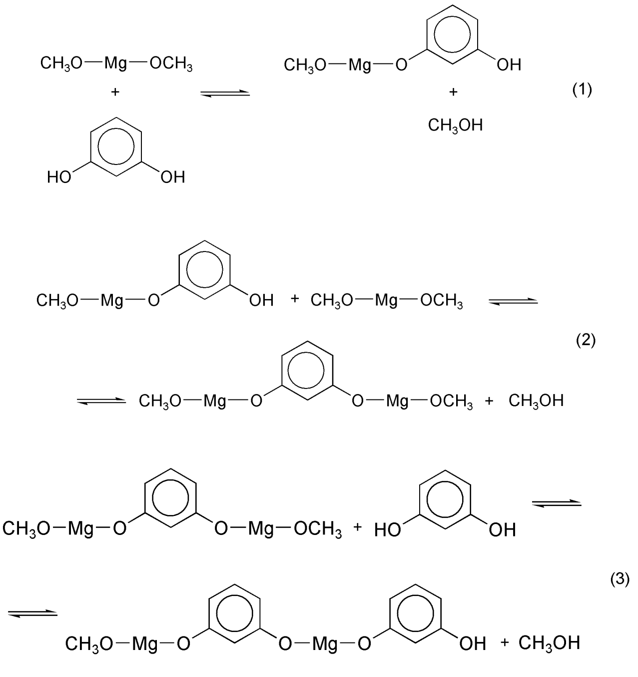

Table 1 Properties of $Mg(OH)_2$ aerogels modified with resorcinol (MeOH : toluene = 2 : 3)

Resorcinol : Mg ratio	Surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Average pore radius/Å	BET C	Density/ g cm^{-3}
0	681	3.49	102	79	2.55
0.02	888	4.13	93	56	2.27
0.05	1019	1.77	35	37	2.63
0.1	1198	1.48	25	39	2.71
0.15	1095	1.26	23	46	2.91
0.2	1057	1.29	24	47	2.82

After the hydrolysis step, the solutions were transformed into gels that are an intense green color. Materials prepared with resorcinol as the only modifier with a methanol–toluene mixture used as a solvent preserved high surface areas (>1000 m^2 g^{-1}) up to resorcinol concentrations of 0.2 mol per mol $Mg(OH)_2$ (Table 1). The introduction of resorcinol and increase in its concentration to 0.1 mol per mol $Mg(OH)_2$ resulted in a significant increase in the surface area of the aerogels accompanied by a decrease in the pore volume and a corresponding decrease in the average pore size. Further increases in the resorcinol concentration brought lower surface areas and pore volumes without any significant alteration in the average pore size. At higher resorcinol concentrations (>0.2 mol per mol $Mg(OH)_2$) precipitation becomes very significant, and the gels become very inhomogeneous.

Hydroquinone addition had a similar effect on the properties of the aerogels, but the maximum surface areas in this case did not exceed 750 m^2 g^{-1}. We believe that the favorable effect of both compounds on the properties of the aerogels is due to their coordination to two different Mg atoms of the same nanoparticle. In this case, it would be much more difficult to remove them during the hydrolysis step than monodentate alkoxy ligands. Thus, if no excess water is used for hydrolysis, they will stay on the surface of the nanoparticles and contribute to other factors limiting their growth, acting in a similar way to strong complexing ligands in zirconia and titania gels. The superior effect of resorcinol in comparison with hydroquinone can be naturally explained by the fact that its geometry should favor bonding to the Mg atoms of the same nanoparticle rather than of two different ones.

Based on these results, resorcinol was chosen as the most promising modifying agent, and materials modified with it were studied in more detail. A larger sample with a resorcinol concentration 0.15 mol per mol $Mg(OH)_2$ was synthesized and was used for further thermal treatment to form carbon-coated MgO.

Carbon-coated MgO prepared from modified aerogel

Resorcinol-modified aerogels proved to have significantly higher thermal stability than typical AP-MgO. For example, the surface area of the carbon-coated gel after thermal treatment at 600 °C under vacuum is as high as 670 m^2/g, exceeding that of AP-MgO by a factor of 2.5 (Fig. 1).

After autoclave drying, resorcinol-modified aerogels do not exhibit any crystalline pattern. Samples subjected to heat treatment at 500 °C or above show a pattern typical for magnesium oxide. The average crystalline size increases from 1.4 nm for the sample evacuated at 500 °C to 2.8 nm for the sample treated at 750 °C. Both are significantly lower than the value of 3.8 nm obtained for AP-MgO after treatment at 500 °C. It is clear that the formation of carbon nanoparticles on the surface of MgO nanoparticles significantly retards sintering of the latter up to very high temperatures if heated under vacuum, although it does not eliminate it completely.

Nitrogen adsorption/desorption isotherms measured at 77 K for the resorcinol-modified sample heat treated at 1023 K in a

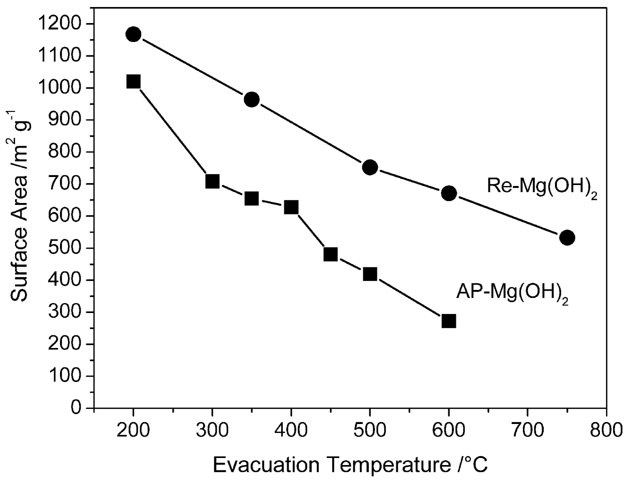

Fig. 1 Effect of evacuation temperature on the surface area of AP-MgO and resorcinol-modified MgO.

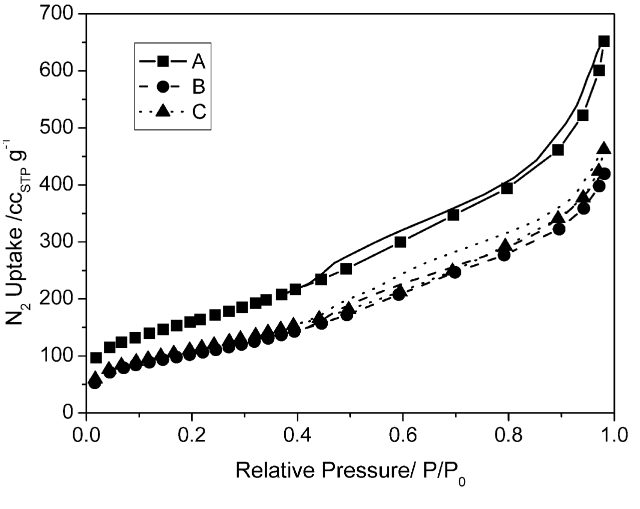

Fig. 2 Nitrogen adsorption/desorption isotherms for Re-MgO-750 (A), Re-MgO-750 after additional calcination at 450 °C under a flow of dry air (B), and AP-MgO (C).

dynamic vacuum, and in a flow of dry air at 723 K, are shown in Fig. 2. Data for regular AP-MgO are presented for comparison. Pore volume–size distributions (PVSD) calculated from desorption branches of the adsorption isotherms by the BJH method are shown in Fig. 3.

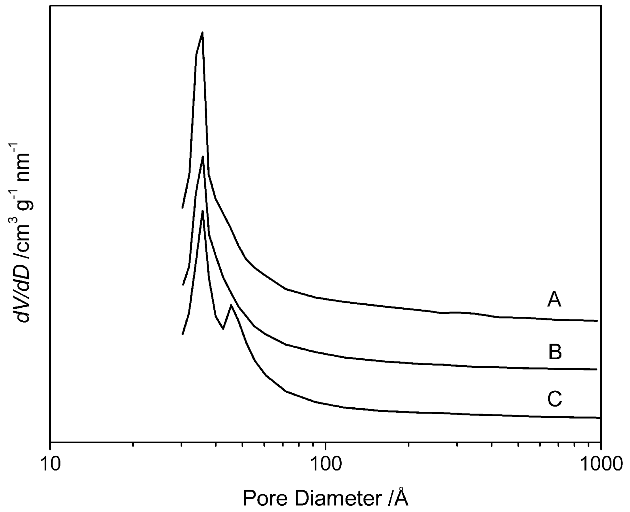

Fig. 3 Pore volume–size distributions for Re-MgO-750 (A), Re-MgO-750 after additional calcination at 450 °C under a flow of dry air (B), and AP-MgO (C).

The specific surface area of the initial carbon-coated sample Re-MgO-750 is very high (593 m^2 g^{-1}). As one can see, burning carbon off results in some decrease in the specific surface area, but does not affect the shape of PVSD considerably. The peak at 3.5 nm is observed in all PVSDs including AP-MgO. Nitrogen adsorption isotherms for the sample with carbon burnt off and AP-MgO are similar, except for some deviations in the shape of the hystersis loops, which are observed more clearly for AP-MgO. The similarity of these N_2 adsorption isotherms is evidence that both samples have similar textures. The specific surface areas for Re-MgO-750 with carbon burnt off and AP-MgO are of 429 and 463 m^2 g^{-1}, respectively. The mean sizes of the nanoparticles can be estimated to be 4.5 and 4.2 nm, respectively, assuming the true density of the MgO phase is 3.1 g cm^{-3}.[15]

These data seem to indicate that the introduction of the carbon precursor at the preparation stage does not affect considerably the texture of the MgO phase. The main distinction here is in the organization of MgO nanoparticles in aggregates, as shown in the TEM images presented in Fig. 4. One can see that carbon-coated samples (left) consist of many tiny spherical particles assembled into larger spheres. Meanwhile, AP-MgO (right) has a distinctly different, much more complex structure, as discussed in detail previously.[16]

The catalytic properties of carbon-coated MgO aerogels were compared to those of AP-MgO using dehydrochlorination of 1-chlorobutane as a model reaction. Recently, we have shown AP-MgO to be active in this reaction, yielding HCl and butene isomers as the reaction products.[17,18] As the reaction

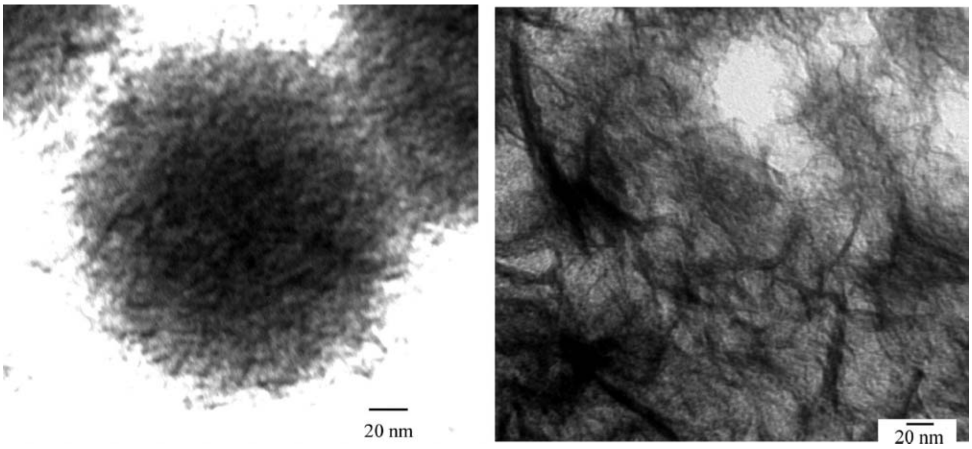

Fig. 4 TEM images of Re-MgO-750 (left) and AP-MgO (right).

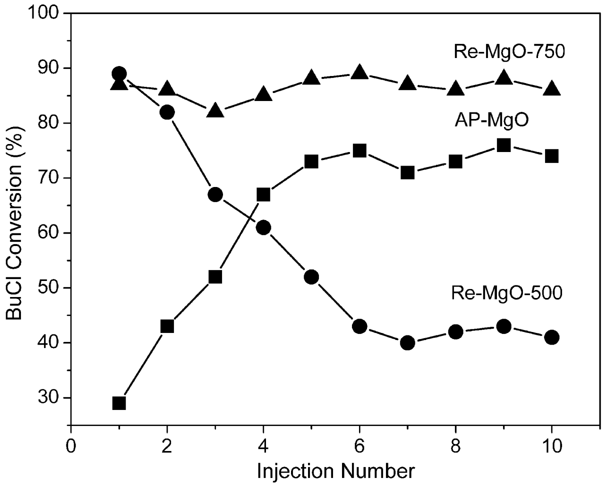

Fig. 5 Activity of carbon-coated MgO and AP-MgO in dehydrochlorination of 1-chlorobutane at 380 °C.

proceeds, MgO is partially converted to $MgCl_2$, and the resulting material appears to be a very active and stable catalyst. Unfortunately, this process is accompanied by a significant drop in the surface area. The application of carbon-coated MgO in this reaction had two main goals—to find out if the MgO was still accessible for the catalytic reaction to take place and if the carbon-coated material had any advantages in stability in comparison with the non-coated one.

Fig. 5 illustrates typical changes in 1-chlorobutane conversion with the injection number. The total of 10 injections corresponds to a molar amount of 1-chlorobutane exceeding that of the MgO in the catalyst by a factor of 2.5–4 depending on the amount of carbonaceous residues in the latter. One can see that the activity of a typical AP-MgO sample is initially relatively low and grows during the first 4–5 injections in agreement with the fact that it undergoes partial conversion to $MgCl_2$, the latter being a better catalyst.

Resorcinol-modified samples evacuated at 500 °C show an opposite behavior; the activity is initially much higher due to their higher surface area and then decreases. Despite differences in the starting and final activities, this trend was the same for all resorcinol-modified samples activated at 500 °C. Apparently, this temperature was not sufficient for complete conversion of organic groups on the MgO surface to carbon. This is evidenced by the dark-brown color of the samples, elemental analysis data and typical C–H stretches observed in the IR spectra. According to the elemental analysis, Re-MgO-500 had 13.7 wt% carbon and 1.8 wt% hydrogen, the latter value being well above the amount typical for pure MgO nanoparticles. It appears that these carbonaceous residues block an increasingly significant portion of the surface as the reaction proceeds, thus, limiting access to the catalytically active surface sites.

Heat treatment at a higher temperature (750 °C) eliminated this drop in activity and preserved it at the high starting value. According to the elemental analysis, Re-MgO-750 had 10.2 wt% carbon and 0.5 wt% hydrogen. As evidenced by the FTIR data, the latter was mostly present in the form of OH groups, with no C–H stretches observed. The sample was black in color, and, evidently, most of the surface organic groups had been converted to carbon.

The carbon coating had no apparent effect on the catalytic selectivity. The conversion to butene was close to 100%, with 2-chlorobutane being formed in very small amounts as the only by-product. Three butene isomers—but-1-ene, (*Z*)-but-2-ene and (*E*)-but-2-ene—were formed in significant and comparable amounts with all the catalysts studied.

Fig. 6 illustrates the effect of water poisoning on the activity of the same AP-MgO and carbon-coated samples reported above. The experiments were performed as follows. 50 µl of water were injected into the saturator after catalyst activation. The first chlorobutane injection was made approximately 15 minutes after the water injection, so that water was still present in the gas flow during the first injection but not during injections 2 through to 7. Then, 50 µl of water was injected again immediately followed by the chlorobutane injections made every 5 minutes. In this case water was present in the gas flow during injections 8 through to 11. The results indicate that although water does have a significant detrimental effect on the performance of both catalysts, the carbon-coated sample is much more stable than standard AP-MgO.

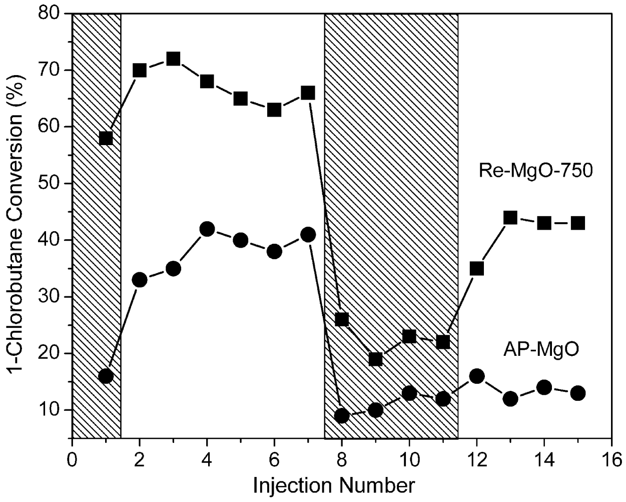

Fig. 6 Effect of water vapor on the performance of carbon-coated MgO and AP-MgO in dehydrochlorination of 1-chlorobutane at 380 °C. Shaded regions correspond to periods when water was present in the gas flow.

Pyrolysis route for synthesis of carbon-coated MgO

Another technique used for the preparation of carbon-coated MgO nanoparticles involved direct decomposition of magnesium methoxide. Magnesium methoxide separated by spray drying from excess methanol was decomposed at 650 °C under nitrogen. The thermal driven chemical reaction is assumed to have the following stoichiometry:

$$(CH_3O)_2Mg \xrightarrow{650^{\circ}C} C/MgO+CH_4+H_2O \qquad (4)$$

In this way 0.5g $(CH_3O)_2Mg$ yielded 0.21 g C/MgO product, or 69% based on reaction (4), which had a surface area of 260 m^2 g^{-1}. Although the surface area of this sample is significantly lower than that of the material prepared from resorcinol-modified $Mg(OH)_2$ aerogel, this method is much more economical as it avoids the use of a large amounts of toluene and the supercritical drying procedure.

Powder X-ray diffraction (XRD) showed peaks indicative of nanocrystalline MgO (Fig. 7, spectrum A). No peaks were observed for carbon, indicating that the graphitic portion is noncrystalline as is commonly the case with graphitic activated carbon.

The effect of humidity on the crystalline structure of C/MgO was studied by placing the sample into a humidity cabinet at 62% humidity for 24 hours. According to XRD, such humidity treatment caused no change in the composition or crystallite size of C/MgO (Fig. 7, see spectra A and B). However, a MgO sample of the same crystallite size, but not coated with carbon underwent substantial conversion to $Mg(OH)_2$ crystallites by the same humidity treatment (Fig. 7, spectra C and D). These results clearly show that the carbon coating does protect the

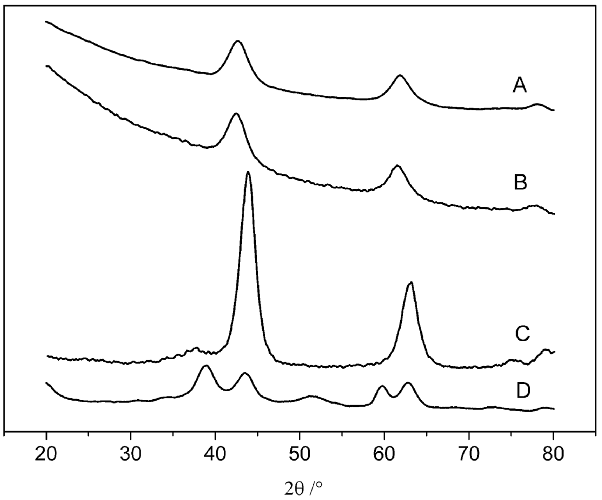

Fig. 7 XRD spectra of C/MgO after treatment in humidity cabinet (A), C/MgO before the treatment (B), AP-MgO (C), and AP-MgO after treatment in humidity cabinet (D).

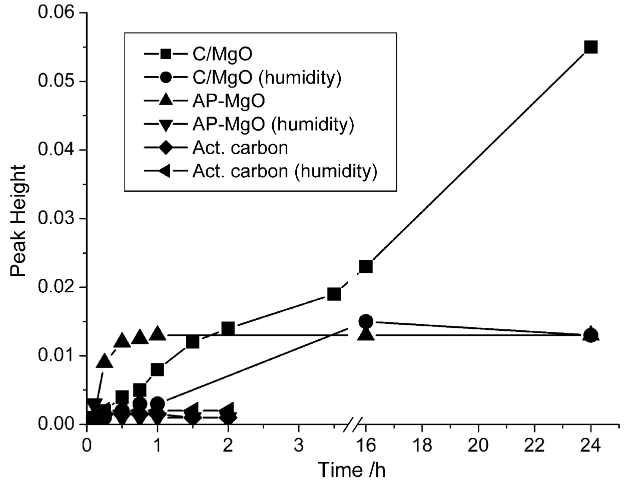

Fig. 8 Kinetics of ethyl vinyl sulfide formation from 2-CEES at room temperature.

MgO crystallites substantially from conversion to hydroxide under the action of water vapor.

2-Chloroethyl ethyl sulfide (2-CEES) is a mimic of mustard gas, which is a warfare agent. Destructive adsorption of 2-CEES has previously been shown to take place on nanocrystalline MgO at room temperature, the main reaction product being the dehydrohalogenated vinyl compound ethyl vinyl sulfide ($CH_3CH_2SCH{=}CH_2$).

When a C/MgO sample was treated in the same way, ethyl vinyl sulfide was formed as well. Fig. 8 illustrates the formation of this product *vs.* time using a variety of adsorbents. Note that activated carbon gives no vinyl product, while the rates of its generation over MgO and C/MgO are comparable. These results indicate that the structure of C/MgO allows 2-CEES to interact with the MgO core, so that the reaction takes place and the vinyl product is released into the gas phase.

An identical test was carried out with C/MgO treated for 24 hours under 62% humidity. 2-CEES again reacted and the vinyl product was released, although more slowly (Fig. 8). The humidity treated uncoated MgO reacted much more slowly. So, once again, although water has a detrimental effect on the performance of the destructive adsorbent in this reaction, the carbon coating is effective in providing significant protection to the MgO core.

Conclusions

The above examples prove that we have achieved success in preparing carbon-coated nanocrystalline MgO by two different methods. The samples have small particle size and high reactivity comparable to those of AP-MgO, while their stability with respect to water is significantly improved. Direct pyrolysis of magnesium methoxide appears to be a cheap and efficient pathway to the synthesis of nanocrystalline carbon-coated MgO. Modification of the gel with resorcinol proved to be a convenient way to prepare carbon-coated nanocrystalline MgO with higher surface area, smaller crystallite size and better stability than traditional nanocrystalline AP-MgO. With minor modification these methods should be applicable to the preparation of a wide variety of carbon coated metal oxides (MgO, CaO, SrO, BaO, Al_2O_3, ZnO, TiO_2, ZrO_2, NiO, Fe_2O_3, and others) of different particulate sizes.

Acknowledgements

Financial support from the U.S. Army Research Office is acknowledged with gratitude.

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