

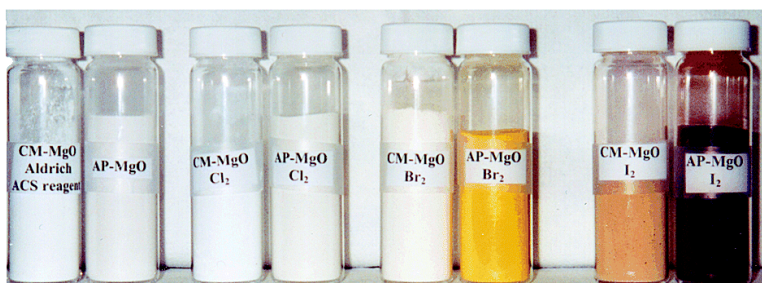
Article

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Novel Halogen and Interhalogen Adducts of Nanoscale Magnesium Oxide

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Abstract: The difference in the adsorption properties of magnesium oxide in two different physical forms—large micron-sized crystals (CM-MgO) and nanoscale crystals (AP-MgO)—is described. The highly energetic surface of the nanoparticles is significantly more active than the bulk surface in adsorption of nonpolar halogens (Cl₂, Br₂, and I₂) and dipole interhalogen molecules (ICl, IBr, and ICl₃). The nanocrystalline and microcrystalline MgO adducts with halogens and interhalogens were characterized by thermogravimetric analysis (TGA), UV–vis and Raman spectroscopies, and transmission electron microscopy (TEM). The bonds of the adsorbates were considerably strained upon adsorption on the nanocrystalline MgO without a molecular dissociation. The results presented in the paper explain the enhanced reactivities of the nanoscale MgO, halogen adducts as halogenating agents of organic molecules and their noticeable biocidal activity.

Introduction

The chemical reactivity of solid-state materials is exclusively determined by their surface. The rate of practically all chemical reactions involving solid substances is dependent on parameters such as surface area, number of active sites such as corners and edges, presence and type of pores, type of surface planes exposed to the reactant, etc. These parameters are dramatically altered when any material is broken down to nanoscale dimensions, causing remarkable change in the chemical behavior, although the chemical composition remains the same. Nanoscale materials are expected to have significant differences from their bulk counterparts in both chemical reactivity and physical properties.

Several theoretical works based on quantum calculations and molecular dynamics simulations are dedicated to the adsorption of interhalogen molecules such as ICl^{1,2} and IBr^{3,4} on MgO. To our knowledge, there is no available experimental work on these systems. The photodissociation of ICl¹ and IBr³, as well as their absorption spectra,⁴ can be significantly changed by adsorption on a magnesium oxide surface. The elucidation of the photochemical behavior of ICl is of interest because of its use as a chemical source of translationally hot chlorine atoms.⁵ Iodine monobromide is expected to have an altered intramolecular potential curve as a result of the adsorption on a MgO surface.³ Halogen adsorption on high surface solids such as

zeolites^{6,7} and porous glass⁸ leads to significant changes in the properties of the adsorbed halogen molecules and can be important for the development and understanding of new catalytic processes.⁷

Halogen adsorption on MgO nanoparticles described earlier⁹ can be used as a very convenient and safe way for storing intact halogen. In fact, our earlier work has demonstrated that the combination of active halogen and sharp edges allowed the nanoparticles to possess excellent antibacterial and sporicidal activities, which surpass those of the free halogens.^{10,11} Compared to other disinfectants, these nanoparticles and halogen adducts are attracted to the microbial cells (because of the opposite charge) and stick to them. Magnesium oxide basicity reduces the spore coat thickness, thus reducing the spore resistance for halogens, facilitating the halogen action. We have determined earlier¹¹ that the combination of the basic character of the particles, their abrasive properties, oxidative action of adsorbed “free” halogens as well as opposite charge attraction are major reasons for their excellent bactericidal and sporicidal activity.

Here, we describe the adsorption of halogen (Cl₂, Br₂, I₂) and interhalogen (ICl, IBr, ICl₃) compounds on two chemically identical, but morphologically very different substances: MgO nanoparticles and micron-sized, commercially available MgO particles (bulk phase). The adducts are characterized by thermogravimetric analysis, UV–vis and Raman spectroscopy, and transmission electron microscopy (TEM). The larger adsorption

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capacity of the nanocrystalline samples compared to that of their bulk counterparts is attributed to the highly energetic surface of the nanoparticles.

Experimental Section

Materials. All halogen and interhalogen compounds (Cl_2 , Br_2 , I_2 , ICl , IBr , and ICl_3) were purchased from Aldrich and used without further purification. Bulk microcrystalline MgO (CM-MgO, CM = commercial), anhydrous MgCl_2 , and MgBr_2 were purchased from Aldrich and used as received. Nanoscale particles of magnesium oxide AP-MgO (AP = aerogel prepared) were prepared as described earlier¹² by an aerogel procedure.

An activation step was applied prior to halogen adsorption on either CM- or AP-MgO to remove water and carbon dioxide adsorbed on their surface. The activation step was conducted by a gradual heating of the material in a Schlenk tube to 475 °C for 2 h and maintaining this temperature for 2 h under dynamic vacuum. The samples were allowed to cool to room temperature under dynamic vacuum before further manipulation.

Preparation of AP-MgO/ Cl_2 , AP-MgO/ Br_2 , and AP-MgO/ ICl . Approximately 10 g of freshly activated magnesium oxide sample (AP-MgO or CM-MgO) cooled to room temperature was allowed to contact Cl_2 gas or was connected to a Schlenk tube containing either liquid Br_2 or ICl . The outlet to the vacuum line was closed while this step was taking place. The difference in pressure above the magnesium oxide sample ($\sim 5 \times 10^{-3}$ torr) and in the halogen source (approximately 760 torr) allowed the transfer of Cl_2 gas or Br_2 and ICl vapors to the Schlenk tube with the solid MgO material. When the color of the atmosphere above the powder changed to green-yellow (in the case of chlorine) or brown-red (in the case of bromine or iodine monochloride), the connection to the halogen source was disconnected and the powder was well shaken. When the atmosphere above the powder became colorless, the connection was reestablished and another dose of the halogen was allowed to enter. These steps were repeated until halogen gas was clearly visible above the powder even after vigorous agitation. The halogen container was then disconnected, and the Schlenk tube with the magnesium oxide adduct was attached to the vacuum line. A dynamic vacuum was maintained until the pressure reached 50×10^{-3} torr or below. This ensured removal of all free halogen. The as-prepared adducts were transferred to Teflon-sealed glass vials and retained for further experiments.

Preparation of AP-MgO/ I_2 , AP-MgO/ IBr , and AP-MgO/ ICl_3 . Iodine, iodine monobromide, and iodine trichloride are not sufficiently volatile to be transferred as vapors as described in the case with chlorine, bromine, or iodine chloride. It is not recommended to heat iodine monobromide and iodine trichloride, because even gentle heating causes their partial decomposition. Our preparation scheme did not involve heating in the cases of IBr and ICl_3 . In this case, solid material (I_2 , IBr , ICl_3) was added directly to the activated MgO powder. There was an apparent transfer of halogen to the nanoparticles, with color change from white to brownish. The solid mixtures were extensively shaken until no solid halogen was visible within the material. The appearance of vapors above the solid phase or persistency of solid halogen material was considered the saturation point. The Schlenk tubes with the solid material were attached to a vacuum line and kept under dynamic vacuum until the pressure reached 50×10^{-3} torr or below and there was no apparent presence of free halogen or interhalogen. The sample with I_2 was heated to 125 °C to ensure enough volatility of the excess iodine present in the system. To facilitate further discussion, the prepared adducts are described as CM-MgO/ X_2 and AP-MgO/ X_2 ($X_2 = \text{Cl}_2, \text{Br}_2, \text{I}_2, \text{ICl}, \text{IBr}, \text{ICl}_3$).

Bacteriological Experiments. *Escherichia coli* (C3000) and *Bacillus megaterium* (ATCC14581) were purchased from ATCC. *Bacillus*

subtilis spores (ATCC6633) were purchased from Raven Biological Labs. The *E. coli* and *B. megaterium* cultures were freshly prepared in tryptic soy broth for 24 h prior to the experiment. The *B. subtilis* spore cells were used as received. The bacteria cultures were loaded on water membranes (Millipore, 0.45 μm pore size) by filtration. The membranes were dried for 20 min prior to the experiment. The membranes were covered with AP-MgO/ X_2 for 30 min. After the treatment, the membranes were washed with diluted HCl /ascorbic acid solution (0.05 and 0.3 M, respectively) until all the powder was removed, and they were then washed with deionized water. The membranes were deposited on nutrient agar plates and incubated for 24 h at 37 °C. The decrease in the colony count was determined by comparison with controls, which were subjected to all procedures except the nanoparticle powder treatment.

Experimental Techniques. The surface area of the starting solid materials was determined using a Quantachrome NOVA-1200 by the BET method using nitrogen adsorption. Quantitative analysis was conducted by TGA and/or iodometric titration. The samples with adsorbed interhalogen were analyzed only by TGA. Thermogravimetric analysis was conducted on a Shimadzu TGA model TA-50 (under helium atmosphere and heating rate of 5 °C/min).

FT-Raman spectra of the halogen, interhalogen, and magnesium oxide adducts were collected on a Nicolet Nexus 670 with a Raman module. The system works with a continuous Nd:YAG laser (1064 nm) and liquid nitrogen-cooled germanium detector within the 4000–100 cm^{-1} range. The laser power was in the range of 0.2–0.6 W, with a data point spacing of 3.5 cm^{-1} . The sample was placed in a static glass cylindrical Raman cuvette (Nicolet).

Diffuse reflectance and UV–vis spectra were collected on a Varian UV–vis–NIR spectrophotometer Cary 500 Scan. Teflon powder was used as a diffuse reflectance reference.

Low-magnification TEM experiments were conducted with Philips CM 100 operating at 100 kV. High-resolution TEM (HRTEM) was performed with JEM-2010 (JEOL, Japan) with 1.4 Å lattice resolution at a 200 kV accelerating potential.

Results and Discussion

Several techniques were used to elucidate the structure of the halogen and interhalogen adducts. The results from the different techniques are presented in separate sections together with the conclusions drawn from them.

A. Specific Surface Area, TGA, and Quantitative Analysis. Specific surface area measurements for the starting AP-MgO and CM-MgO were determined to be $\sim 550 \text{ m}^2/\text{g}$ and $\sim 10 \text{ m}^2/\text{g}$, respectively. The much larger surface area and the presence of numerous corners, edges, and defects significantly enhance the adsorption capabilities of the nanoscale material.⁹ Moreover, electron microscopy studies indicate that morphology changes do not occur upon halogen adsorption. Table 1 summarizes the quantitative results for the TGA-determined halogen content and the calculated surface concentration for AP-MgO adducts. The amount of halogen released in the TGA experiment represents only adsorbed halogen on the MgO surface and shows no presence of free halogen physically retained in the pore structure. An indication for this is the fact that a maximum loss (determined by the first derivative of the TGA trace) for all compositions occurs at temperatures well above those at which boiling or sublimation of the free compounds take place.

As determined by TGA, the amounts of halogens adsorbed on the nanoparticles can be as high as 43 wt % (Table 1). The CM-MgO is considerably less capable of adsorption, and the amount of adsorbed halogen is much lower than that for the AP-MgO nanoparticles. Another important point is the strength

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Table 1. Quantitative Results from Analysis of AP-MgO and CM-MgO Adducts^a

material	halogen content wt %, (TGA)	surface concn molecules/nm ²	color
AP-MgO/Cl ₂	6.6	1.03	white
AP-MgO/Br ₂	16.3	1.12	yellow
AP-MgO/I ₂	20.6	0.89	brown
AP-MgO/ICl	22.3	1.50	brown-red
AP-MgO/IBr	43.5	2.30	red-brown
AP-MgO/ICl ₃	37.1	1.74	yellow-brown
CM-MgO/Cl ₂	~1	N/A	white
CM-MgO/Br ₂	~1	N/A	pale yellow
CM-MgO/I ₂	1.5	N/A	light brown
CM-MgO/ICl	<1	N/A	red shade
CM-MgO/IBr	<1	N/A	red shade
CM-MgO/ICl ₃	<1	N/A	red shade

^a Error for the TGA determination is within 2–3 wt %. Surface concentration for the CM-MgO adducts is not included because the measured values are smaller than the experimental error.

of adsorption: while the nanoparticle adducts are stable for weeks and have weak smells of halogens, their bulk counterparts release the adsorbate rather easily and have strong smells. For example, if CM-MgO/X₂ adduct is left under dynamic vacuum for 15 min or more and then examined by TGA, practically no weight loss is found corresponding to a complete loss of the adsorbate under the vacuum conditions. Similar treatment of the AP-MgO adducts does not lead to any significant adsorbate release under dynamic vacuum. Furthermore, the CM-MgO/I₂ adduct segregates with time, and the initially homogeneous adduct separates iodine crystals after about a week, within the volume of the powder. Contrarily, the AP-MgO/I₂ adduct with iodine is stable even after several months without notable iodine crystal formation. The surface concentration for AP-MgO hovers in the range 0.9–2.3 molecules/nm², which corresponds to less than one monolayer. The values for the CM-MgO/X₂ are not reported because the systematic errors in TGA are large due to the low surface areas and small amounts of adsorbed halogens.

Temperature effects are important when considering the strength of an adsorption process. As mentioned in the Experimental Section, all starting magnesium oxide samples were at room temperature when allowed to contact with the halogen and interhalogen compounds. Heat release took place in all cases upon contact of the adsorbates, and the solid nanoscale samples decreased in the following sequence: ICl₃ > Cl₂ > Br₂ ≈ ICl > IBr > I₂. The heat release was not precisely quantified, but in the case of ICl₃ the temperature of the Schlenk tube rose to 60–70 °C, while with IBr it was just warm to the touch. In the case of CM-MgO, the heat effects were present to a significantly smaller extent. In all CM-MgO experiments, the adducts lost their adsorbed halogen earlier compared to the AP-MgO adducts. These results yield the conclusion that the strength of adsorption is considerably larger on the nanoparticles surface compared to that of the bulk phase material.

B. UV–Vis Spectra Analysis. All halogen and interhalogens involved in this study exhibit significant absorption in the UV–vis region of the spectrum. Upon absorption they undergo several electron transitions from the ground state to the lowest excited states,¹³ giving rise to several broad bands.^{13,14} UV–



Figure 1. Photographs of (a) nanoscale AP-MgO/X₂ and (b) AP-MgO/X₂ and their bulk counterparts (CM-MgO/X₂) synthesized at identical experimental conditions.

vis spectra can be used to judge to what extent the adsorption influences the electronic structure of the molecule. There are theoretical results^{1,3,4} suggesting that the adsorption should cause a significant change in their electronic structure and, hence, in their absorption spectra. All known works^{1,3,4} predict that the UV–vis spectra at low temperature can be used for understanding the orientation of the interhalogen relative to the surface.

Photographs of the synthesized compositions are shown in Figure 1. AP-MgO and CM-MgO are white powders with no absorbance in the range 200–1000 nm, and their diffuse reflectance spectra match that of the reference substance. Similarly, AP-MgO/Cl₂ and CM-MgO/Cl₂ adducts have no absorbance in this range and their spectra practically coincide with the starting materials.

The case with bromine adsorption is different: AP-MgO/Br₂ is a bright yellow powder while CM-MgO/Br₂ is light yellow and loses color with time. The powders have absorption bands with different intensities and locations of the peak position. According to literature,¹³ bromine gas and bromine dissolved in “nonreacting” solvents have very similar absorption spectra with peaks at 415 nm and a shoulder at 475 nm. Upon adsorption on the nanomaterial, bromine gives the adduct an intense yellow color (Figure 1), and there is a broad band in the range of 230–600 nm (Figure 2a) with distinguishable peaks at 280 and 340 nm. In the case of the commercial oxide, the absorbance is considerably less intensive (Figure 2a) and it disappears in several days.

Iodine vapor has a simple spectrum composed of a relatively wide band¹³ (400–620 nm), with a peak position at 516 nm. The iodine adducts of the magnesium oxide have spectra which are distinctively different from the spectrum of iodine dissolved in tetrachloromethane (Figure 2b). The nanoscale particle adduct has a deep brown color (Figure 1) with a broad absorbance in the range 200–760 nm (Figure 2b). Similar behaviors are exhibited by the iodine monochloride, iodine monobromide, and iodine trichloride adducts, which exhibit very broad absorbance bands compared to their spectra in CCl₄ (Figure 2, parts c, d, and e). The diffuse reflectance spectra for CM-MgO/(X₂) (X₂ = IBr, ICl, ICl₃) are very similar to the spectrum of the starting CM-MgO because of the very low concentration of the interhalogens at the microcrystalline surface.

C. Raman Spectra Analysis. Raman spectroscopy can be of significant assistance for the elucidation of how the halogen

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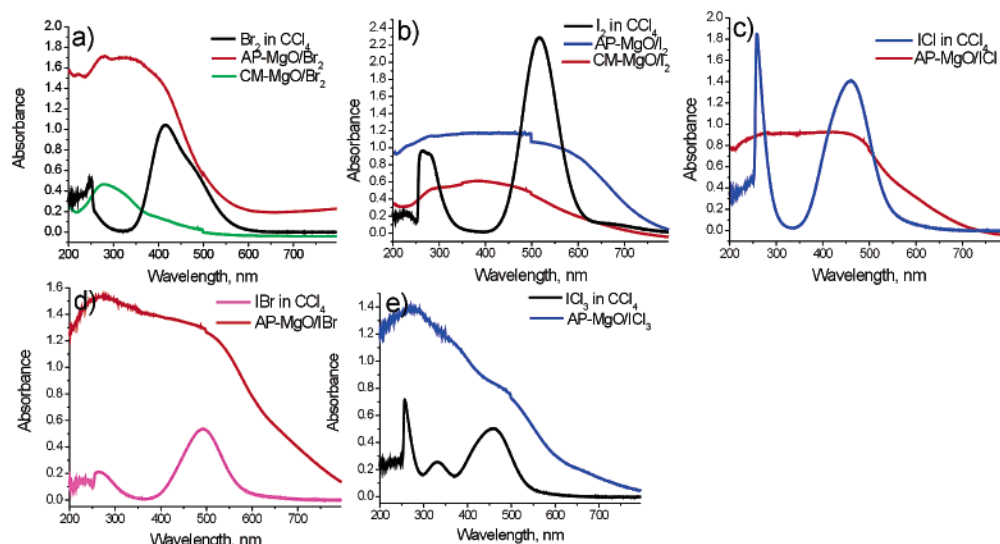


Figure 2. UV-vis spectra of (a) AP-MgO/Br₂, CM-MgO/Br₂, and Br₂ in CCl₄; (b) AP-MgO/I₂, CM-MgO/I₂, and I₂ in CCl₄; (c) AP-MgO/ICl and ICl in CCl₄; (d) AP-MgO/IBr and IBr in CCl₄; and (e) AP-MgO/ICl₃ and ICl₃ in CCl₄.

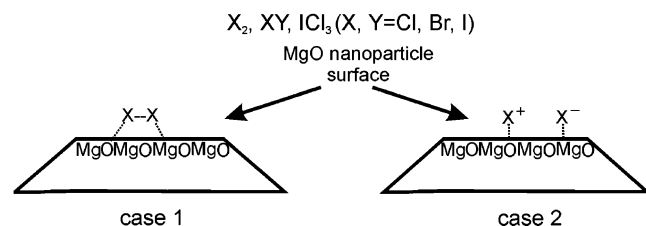


Figure 3. A scheme of the possible interactions that take place upon adsorption. Case 1 is supported by the spectral data. The hydroxyl groups present on the surface are omitted for clarity.

and interhalogen molecules interact with the MgO surface. The nonpolar halogen molecules have stretching vibrations forbidden in IR (the dipole moment does not change upon stretching), while they are allowed in a Raman experiment (only polarizability changes upon stretching). On the other hand, the vibration of a heavy pair of atoms usually has a frequency below 600 cm⁻¹, requiring an IR instrument capable of scanning in this region, which is not trivial. Raman spectra can be easily collected down to 100 cm⁻¹ with simple sample preparation.

There are two possibilities how the halogens or interhalogens could interact with the MgO surface upon adsorption (Figure 3). The first scenario corresponds to chemisorption without polarization (Figure 3, case 1). In this case, the molecule vibration will be altered to some extent depending to what degree the adsorption influences the adsorbate molecule entity. There are reports in the literature⁷ discussing that the vibration frequency can vary to a certain extent depending on the strength of adsorption. In case 1, one should observe in the Raman spectrum the vibration corresponding to the halogen moiety, as well as the MgO inherent lattice vibrations.

The second possibility involves the polarization of the halogen or interhalogen molecule, which is stabilized by the dipoles of the surface (Mg²⁺ and O²⁻ sites).⁷ This case can be extended further to bond rupture (case 2) and the formation of surface halogenides and hypohalogenites (disproportionation). Either of the two possibilities will lead to the formation of new bonds, Mg–X(Y) and/or O–X(Y), leading to bands in the Raman spectra that are allowed.

Halogen Adducts. The halogen vibrations in gas and condensed phases have been described in the literature.^{15–19} Their frequencies in gas phases are as follows: Cl₂, 557.0 cm⁻¹; Br₂, 313.9 cm⁻¹; and I₂, 213.1 cm⁻¹. The Raman spectrum of freshly activated AP-MgO yielded very low intensity bands without specific features (Figure 4a). This is attributed to the fact that the intensity of a Raman spectrum depends on the average particle size. If the average particle size is below 3 λ₀ (λ₀ is the wavelength of the laser source), the intensity declines as the size becomes smaller.²⁰ Because the magnesium oxide nanocrystals have an average diameter of ~4 nm, they are below this critical size and they do not have an intense Raman spectrum. In contrast, CM-MgO, which is composed of large micrometer size particles, has an intense spectrum with wide bands (Figure 4a). The two spectra are very similar in shape in the 4000–1250 cm⁻¹ region, and the nanoparticles have stronger relative absorption in the 1250–100 cm⁻¹ region.

The Raman spectra of AP-MgO/X₂ (X = Cl, Br, I) halogen adducts were collected immediately after their synthesis (Figure 4, parts b–d). The spectra are reproducible with time (even after several months), which confirms the adducts' stability. In all three cases, one strong peak is present and there is an additional small peak at lower wavenumber in the cases of bromine and iodine.

If we assume that chemical interaction takes place, a new species should form on the surface, which contains Mg–X and O–X bonds. The recorded Raman spectra of anhydrous MgCl₂ and MgBr₂ are presented in Figure 4e. Both compounds exhibit single intense sharp peaks in the Raman spectra, neither of which is present in the nanoscale AP-MgO/X₂. Thus, we conclude that Mg–X bond formation does not take place upon adsorption or it takes place to a negligible extent. On the other hand, there are many reports in the literature on different oxygen-containing

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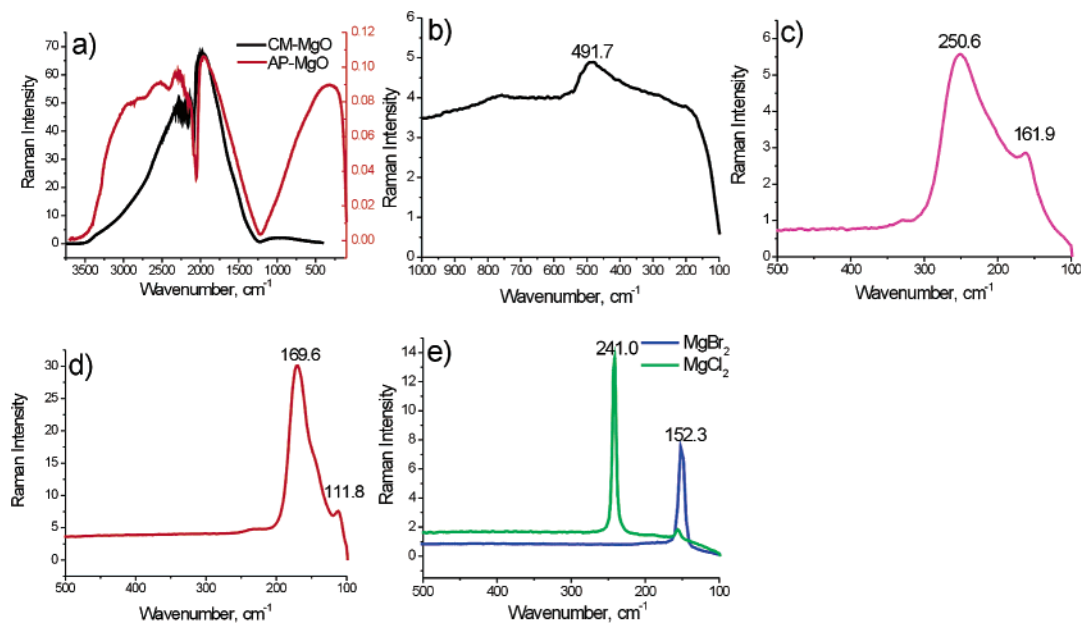


Figure 4. Raman spectra of (a) AP-MgO and CM-MgO, (b) AP-MgO/Cl₂, (c) AP-MgO/Br₂, (d) AP-MgO/I₂, and (e) anhydrous MgCl₂ and anhydrous MgBr₂.

halogen molecules and ions such as hypochlorite and hypobromite,²¹ hypiodite,²² as well as XO₂⁻, XO₃⁻, XO₄⁻,^{22–27} and Br₂O,²⁶ and all the observed frequencies are at considerably higher wavenumbers than those observed in the case of the adducts. The results support the hypothesis of a strained halogen–halogen bond. Previous studies with halogens adsorbed on zeolites and porous glass clearly demonstrated^{6–8} that the original vibration frequency can significantly downshift depending on the strength of interaction with the surface. In the current work, the downshift with respect to the gaseous halogen is 66.0 cm⁻¹ for chlorine, 63.3 cm⁻¹ for bromine, and 43.5 cm⁻¹ for iodine. These results infer that the adsorption of halogen molecules on the nanoscale magnesium oxide is relatively strong and causes a reduction in the molecular force constant. Therefore, the halogen molecules adsorbed on the nanoparticle surface are in a more chemically active state than the corresponding gas-phase halogen molecules.⁷

There is no clear evidence that can conclusively elucidate the species causing the appearance of the small peaks at lower wavenumbers observable only in the cases of the bromine (161.9 cm⁻¹) and iodine adducts (111.8 cm⁻¹). We expect that minor amounts of X₃⁻ (X = Br, I) could account for these peaks, as the literature data suggest that low wavenumber peaks can appear for Br₃⁻ (163 cm⁻¹ for Br₃⁻ in acetonitrile solution²⁵) and I₃⁻ (111 cm⁻¹ for (CH₃)₄NI₃⁻,²⁸ 107 cm⁻¹ in complexes containing I₃⁻²⁹). This hypothesis is supported by the absence of a similar peak in the AP-MgO/Cl₂ Raman spectrum because Cl₃⁻ is very unstable and cannot exist at ambient conditions.

Raman spectra of CM-MgO/X₂ were collected, but because of the low surface concentration of the halogens and the intense

scattering by the microcrystalline oxide, no changes in the spectra were recorded.

Interhalogen Adducts. Interhalogen molecules such as ICl, IBr, and ICl₃ are expected to interact more strongly with the ionic surface of nanoscale magnesium oxide because all of them are permanent dipoles. This is expected to lead to a more significant dipole–ion interaction compared to the induced dipole–ion interaction in the case of pure halogens Cl₂, Br₂, and I₂.

The interhalogen compounds used for this study are described in the literature, and their vibration frequencies have been determined.^{30–33} Because of the present dipole moment and positively charged iodine atom, interhalogens are better Lewis acids compared to halogens.^{30,34,35} The values for gaseous ICl is determined to be 381.5 cm⁻¹,^{30,31} and 247.0 cm⁻¹³⁵ for IBr in dioxane. Indeed, ICl and IBr interacted relatively strongly with the surface, resulting in adducts with a large surface coverage in the case of the nanoparticles (Table 1).

The Raman spectra of the nanoscale MgO adducts with ICl and IBr (Figure 5, parts a and b) show very similar behavior compared to the halogens; significant downshifts were detected in both cases. In the case of ICl, the change is 198.4 cm⁻¹, while for IBr it is 53 cm⁻¹. The ICl dipole moment is considerably larger than that of IBr. The interaction with the surface enhances the polarization even further, causing a very significant downshift in the vibration frequency. Iodine bromide has a smaller dipole moment compared to that of ICl, and the downshift of the stretching frequency is comparable to the one

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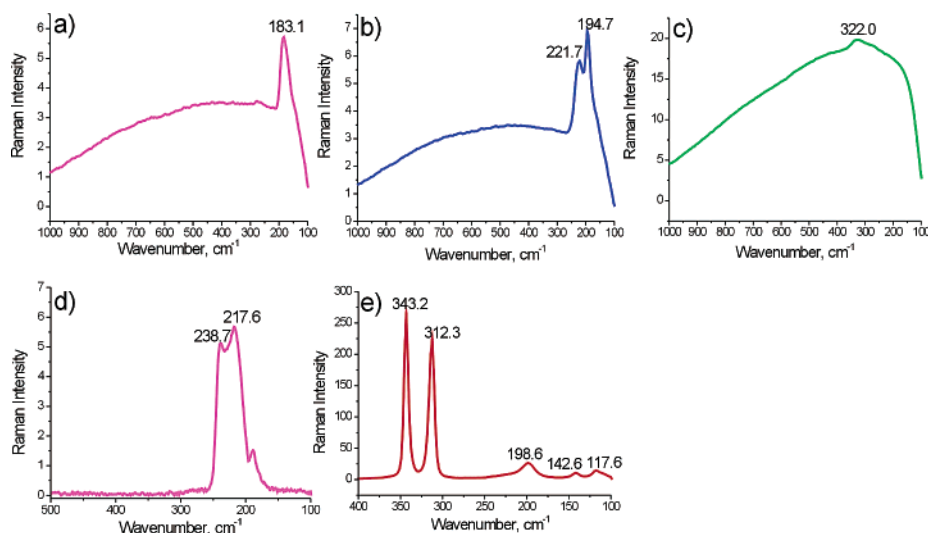


Figure 5. Raman spectra of (a) AP-MgO/ICl₃, (b) AP-MgO/IBr, (c) AP-MgO/ICl₃, (d) solid IBr, and (e) solid ICl₃.

found for Br₂ and I₂ adsorption of AP-MgO. The Raman spectrum of the AP-MgO/IBr adduct is composed of an additional smaller peak at 221.7 cm⁻¹. This peak is most probably due to the presence of impurities in the starting material, since its Raman spectrum (Figure 5d) also contains two peaks (it is very difficult to prepare chemically pure IBr).

As mentioned earlier, iodine trichloride adsorption was the most exothermic interaction with the nanoparticles increasing significantly the temperature of the mixture. The Raman spectrum shows only a single broad peak (Figure 5c), which is very different compared to the spectrum of solid ICl₃ (Figure 5e). A chemical reaction cannot be completely ruled out, but it is a fact that ICl₃ is released upon heating, which means that ICl₃ has not been converted to nonvolatile products such as MgCl₂ or MgI₂. Determination of the ICl₃ outcome upon adsorption will be addressed in future work.

Commercial magnesium oxide adducts were prepared under identical synthetic conditions. As shown earlier (Table 1) the CM-MgO did not adsorb significant amounts of the interhalogen compounds. The only compound which yielded a spectrum different than the typical magnesium oxide Raman spectrum is the iodine trichloride adduct. However, contrary to the considerable interaction in the case of AP-MgO, a very weak interaction was observed with CM-MgO. The Raman spectrum completely coincided with the spectrum of the solid ICl₃, which shows that the interhalogen is retained in the pore structure rather than physisorption or chemisorption on the surface.

D. Transmission Electron Microscopy. Transmission electron microscopy was used to determine if the morphology of the nanoparticles changes upon adsorption of halogens and interhalogens. All nanoparticulate compositions were imaged by low-magnification TEM and HRTEM and compared to the images of AP-MgO nanoparticles. Figure 6, parts a and b, illustrates low-magnification TEM micrographs of AP-MgO nanoparticles and nanoparticles after adsorption of bromine. The highly porous weblike structure of the nanomaterials is preserved upon halogen and interhalogen adsorption, and no change in the morphology of the nanoparticulate aggregates occurs upon adsorption. The TEM image of the AP-MgO/Br₂ (Figure 6b) is representative of all halogen and interhalogen adducts. The HRTEM micrograph of AP-MgO/Br₂ (Figure 6c) reveals that

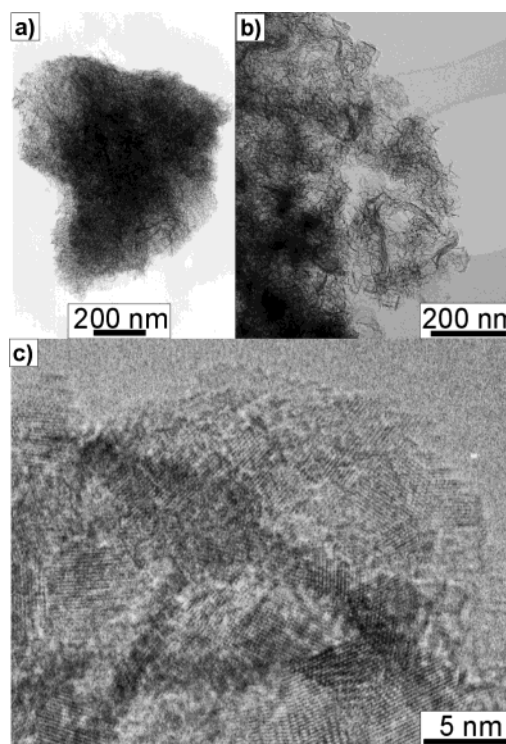


Figure 6. TEM images of (a) AP-MgO, (b) AP-MgO/Br₂, and (c) AP-MgO/Br₂. No change in the MgO nanoparticles morphology occurs upon adsorption.

the intact structure of the separate AP-MgO nanoparticles is preserved. The image in Figure 6c is also representative for all adducts. Energy-dispersive X-ray (EDX) analysis of the samples confirmed the presence of halogens on the nanoparticles surface.

E. Antimicrobial Activity of the Halogen- and Interhalogen-Loaded MgO Nanoparticles. The prepared interhalogen and halogen adducts with MgO nanoparticles were tested for their bactericidal and sporicidal activity. All halogen and interhalogen adducts were found to have excellent activity against *E. coli* (Gram-negative) and *B. megaterium* (Gram-positive) bacteria: more than 99.99% of the bacteria were killed in 20 min or less. When tested against spore cells (*B. subtilis*), a significant differentiation was observed: AP-MgO/IBr and

AP-MgO/ICl₃ exhibited excellent performance, killing more than 99.9% of the spore cells in 30 min. This activity is higher than the sporicidal activity found for AP-MgO/Cl₂ and AP-MgO/Br₂.^{10,11} On the other hand, AP-MgO/ICl and AP-MgO/I₂ did not perform as well, and the efficiency was lower. We associate this lower activity with the inability of iodine to effectively kill spores.^{36,37} In the case of AP-MgO/ICl, we suspect that the adsorbed molecules interact very strongly (perhaps too strongly) with the AP-MgO nanoparticle surface and they cannot be easily released. This is in an excellent agreement with the TGA data, which show that ICl is released mostly at high temperatures.

Conclusions

The present paper describes the difference in the adsorption properties of magnesium oxide in two different physical forms: large micron-sized crystals (CM-MgO) and nanoscale-sized crystals (AP-MgO). We have observed that the surface of the nanoparticles is significantly more active than the bulk surface in adsorption of nonpolar halogen (Cl₂, Br₂, and I₂) and dipole

interhalogen molecules (ICl, IBr, and ICl₃). In all adducts based on nanomaterials, considerable changes were observed in vibrational frequency of the adsorbed molecules and in their electronic transitions (UV-vis spectra). These changes are expected to affect the chemical properties of the halogen species. All the prepared nanocrystalline adducts could be used as halogenating agents in organic/inorganic synthetic schemes and have the potential of being excellent bactericides and sporicides. The capability of the solid nanomaterial to immobilize the bactericides, while at the same time enhancing their chemical activity, could lead to a new class of effective and easy-to-use bactericidal compositions. The preliminary results show that all adducts are excellent bactericides. AP-MgO/IBr and AP-MgO/ICl₃ were found to be very good sporicides, similar to the already described AP-MgO/Cl₂ and AP-MgO/Br₂.^{10,11}

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