

Nanoscale Metal Oxide Particles/Clusters as Chemical Reagents. Adsorption of Hydrogen Halides, Nitric Oxide, and Sulfur Trioxide on Magnesium Oxide Nanocrystals and Compared with Microcrystals

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Adsorption of HCl, HBr, NO and SO₃ on nanoscale MgO (autoclave prepared = AP-MgO) and microscale MgO (conventionally prepared = CP-MgO) has been studied. The higher surface area of AP-MgO allows a higher capacity of these gases to be adsorbed/mol MgO. However, at pressures of 100 Torr or higher, the amounts adsorbed/nm² for HX and SO₃ are larger on the microcrystals. This is explained as due to the formation of ordered multilayers of adsorbate on the more perfect crystals of CP-MgO (adsorption on flatter, more extended planes). In the case of NO, the different surface chemistry of AP-MgO vs CP-MgO is again demonstrated. In this case, AP-MgO adsorbed more NO/nm², and NO₂, N₂, and N₂O were formed on the surface. The high surface area and unusual surface reactivity of nanoscale MgO allows it to be considered as a new type of adsorbent as well as a near-stoichiometric chemical reagent.

Introduction

The surface chemistry of MgO is remarkably diverse involving catalytic processes^{1–8} including the fascinating oxidative methane coupling reaction.^{9–11} The adsorptive properties of MgO are also diverse and studies have been reported on the adsorption of H₂,^{17–20} CO,^{11,21–28}

H₂O,^{29–34} NH₃,^{35,36} pyridine,^{37,38} nitrobenzene,²⁸ and others. There has been much discussion of the type of surface sites necessary for the generation of strong base sites on MgO.^{1,39–44}

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Recently, we have been interested in determining if nanoscale MgO possessed different and unique surface chemistry compared with more conventional samples. Such differences might be expected based on the very different morphologies of nanoscale vs microscale MgO crystallites.^{38,45} Herein we report on further studies of the adsorption properties of AP-MgO (autoclave prepared, nanoscale, 4 nm polyhedral crystallites) compared with CP-MgO (conventionally prepared, microscale, ~100 nm long by 10 nm thick hexagonal platelets).

Experimental Section

The preparation of AP-MgO and CP-MgO has been discussed earlier.⁴⁶

A. Gravimetric Analysis Using a Quartz Spring Balance.⁴⁷ A spring balance was used to measure the amount of physically and chemically adsorbed acid gas adsorbed onto the MgO surface. AP-Mg(OH)₂ and CP-Mg(OH)₂ were pressed into pellets, crushed with a mortar and pestle, and sifted through a mesh to produce uniform size aggregates. Then 100 mg of the Mg(OH)₂ was loaded into the basket of the spring balance and slowly evacuated to 1 mTorr. The initial spring position was then measured with the attached magnifying scope. The sample was heated to 500 °C over 3 h and maintained for either 3 h, forming AP-MgO-3h and CP-MgO-3h, or *overnight*, forming AP-MgO-on and CP-MgO-on. After complete cooling to room temperature for 1 h, the spring position was measured again. The samples were then exposed to 100 Torr of acid gas for 15 min and later evacuated for one hour with spring positions measured before and after adsorption. Samples heated overnight were exposed to 100 Torr of acid gas for 1 h followed by evacuation for 1 h, again measuring spring positions before and after evacuation. Weight calculations were made from the calibrated spring constant. The weight loss was calculated and subtracted from the Mg(OH)₂ weight to find the weight of MgO. Surface area measurements, discussed before,⁴⁵ showed that heating overnight versus 3 h did not appreciably change the surface area. The AP-MgO and CP-MgO used in these experiments had surface areas of 302 and 177 m²/g and surface hydroxyl concentrations of 1.7 and 1.2 OH/nm², respectively. The acid gases used in these experiments were 99% HCl, 99% HBr, and 98.5% NO in lecture bottles purchased from Aldrich. The SO₃ was 99% pure, stabilized, and contained some low-melting solid polymer, the formation of which is unavoidable. The SO₃ was mildly heated to melt it, transferred to a Schlenk tube under inert conditions and freeze-pump-thawed to further purify. For use, the SO₃ was mildly heated to melt it and the vapor pressure produced was used.

B. Fourier Transform Infrared Spectroscopy. Self-supporting pellets of AP-Mg(OH)₂ and CP-Mg(OH)₂ were made using ca. 30 mg of sample in a Spectra-tech Inc. Model 129 die and a Carver Model B laboratory press. The pellets were 13 mm in diameter with an area of 1.3 cm² and were pressed at 7000 psi. The pellets were then transferred to the lower section of an in situ IR⁴⁸ and evacuated to 1 mTorr. Like the spring balance samples, the pellets were heated to 500 °C over 3 h and maintained for 3 h or overnight, cooled to room temperature for 1 h, and, finally, exposed to 100 Torr of acid

Table 1. Amount of HCl and HBr Adsorbed at 100 Torr for 1 h on AP-MgO-on and CP-MgO-on^a

gas	AP-MgO		CP-MgO	
	per nm ²	mmol/mol of MgO	per nm ²	mmol/mol of MgO
HCl	10.9/11.0	221/222	17.9/17.5	212/207
HBr	11.1/11.1	224/224	15.6/15.5	185/183

^a The first number is total adsorption amount, and the second number is the amount after evacuation. All data are averages of two or three trials with <10% error. The term "on" stands for overnight prior evacuation.

Table 2. Amount of HCl and HBr Adsorbed at 100 Torr for 15 min on AP-MgO-3h and CP-MgO-3h^a

gas	AP-MgO		CP-MgO	
	per nm ²	mmol/mol of MgO	per nm ²	mmol/mol of MgO
HCl	12.0	245	16.2	191
HBr	7.88	160	11.9	141

^a All data are averages of two or three trials with <10% error. The term "3h" stands for 3 h prior evacuation.

gas. A Perkin-Elmer 1330 infrared spectrometer with 256 scans, 2 cm⁻¹ resolution and 1.0 cm⁻¹ aperture was used to collect spectra. The pellet was manually transferred to the cell portion of the in situ cell where IR plates of KBr were affixed. Spectra were taken before and after exposure to the acid gas, followed by an extensive multistep evacuation where spectra were collected after evacuation times of 5 min, 4 h, and 18 h. The sample was then heated to temperatures of 100, 150, 300, 500, 600, 700, and 800 °C under dynamic vacuum for 3 h at each temperature with room temperature IR spectra recorded at each step. In some cases, subtractions of MgO spectra were performed where preadsorption spectra were subtracted from adsorption spectra by a factor of 1 to elucidate band shape.

Results

(A) Brønsted Acids: HCl and HBr. (1) *Adsorption Results.* The amount of HCl and HBr adsorbed at 100 Torr for 1 h on AP-MgO-on and CP-MgO-on are shown in Table 1 and at 100 Torr for 15 min on AP-MgO-3h and CP-MgO-3h in Table 2. After evacuation, no appreciable amount of HCl or HBr was desorbed; therefore, nearly all the adsorption is chemisorption. This complete chemical adsorption correlates with the dissociative nature of HCl and HBr chemisorption to metal oxide surfaces. The variation of heat treatment time, as mentioned earlier, does not appreciably change the surface area, but further "cleaning" and possible annealing could occur. It was also found that 80–90% of the adsorption takes place in the first 15 min. Therefore, differences between data in Tables 1 and 2 were most likely due to the heat treatment. AP-MgO adsorbed more HCl and HBr, mmol to mol of MgO, but after surface area effects were corrected for, it can be shown that CP-MgO adsorbs more HCl and HBr/nm². Note, for AP-MgO-on, adsorption of HCl and HBr was identical, whereas CP-MgO-on shows slightly more HCl adsorbed than HBr. Both AP-MgO-3h and CP-MgO-3h showed more adsorption of HCl than HBr with a ca. 50% increase for AP-MgO and a 40% increase for CP-MgO. By comparing heat treatment times to adsorption ability, for AP-MgO, the increase in heat-treatment time increased the adsorption ability for HBr and decreased the adsorption ability for HCl. However, for CP-MgO, the increase in heat treatment time afforded an increase in adsorption for both HCl and HBr.

(2) *Fourier Transform Infrared Results.* Before adsorption of HX, AP-MgO had a sharp band at 3750 cm⁻¹

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Table 3. IR Bands and Assignments for AP-MgO-3h and CP-MgO-3h Produced upon HCl and HBr Adsorption^a

HX	band position and strength (cm ⁻¹)	effect of 5 min evacuation ^a	assignment
AP-MgO-3h			
none	3750 (vs)		isolated -OH (residual)
HCl	3750 (vs) remains	3745	isolated -OH
	3300–3640 (s, broad)	no change	hydrogen bonded -OH
	1708 (s)	no change	
	1605 (s, broad)	no change	
none	3738 (vs)	3738 partially restored	adsorbed water
HBr	(3738 removed)	no change	isolated -OH (residual)
	2950–3665 (s, very broad)		isolated -OH
	1702 (w)		hydrogen-bonded -OH
	1614 (vs)	no change	
CP-MgO-3h			
none	3745 (s)		isolated -OH (residual)
HCl	(3745 removed) ^b		isolated -OH
	3000–3700 (s, very broad)	no change	hydrogen-bonded -OH
	1705 (vs)	no change	
	1619 (vs)	no change	
none	3745 (s)	no change	adsorbed water
HBr	3745 (m)	no change	isolated -OH (residual)
	3200–3600 (s, very broad)	further broadened	isolated -OH
	1705 (m)	no change	hydrogen-bonded -OH
	1618 (vs)	no change	

^a The term "3h" stands for 3 h prior evacuation.

Table 4. Amount of NO and SO₃ Adsorbed at 100 Torr for 1 h on AP-MgO-on and CP-MgO-on^a

	AP-MgO		CP-MgO	
gas	per nm ²	mmol/mol of MgO	per nm ²	mmol/mol of MgO
NO	5.0	100	2.8	33
SO ₃	14.8	300	22.3	264

^a All results are averages of two or three trials with <10% error.

due to residual isolated -OH after the 500 °C preheat treatment. Upon HCl or HBr adsorption a broad band centered at 3525 cm⁻¹ (due to hydrogen-bonded surface -OH) was produced (Table 3). However, the isolated -OH band remained. Evacuation for 5 min caused no change.

(B) Lewis Acids: NO and SO₃. (1) *Adsorption Results.* The amounts of NO and SO₃ adsorbed at 100 Torr for 1 h on AP-MgO-on and CP-MgO-on are shown in Table 4. CP-MgO clearly adsorbed more SO₃/nm² while AP-MgO adsorbed more NO. By comparing heat treatment times, both AP-MgO and CP-MgO for longer heat treatment times showed increased adsorption ability toward these adsorbates, with an exception for SO₃ on CP-MgO, where the adsorption was nearly the same for both heat treatments.

(2) *Fourier Transform Infrared Results.* Tables 5 and 6 summarize the IR bands generated upon adsorption of NO and SO₃ on AP-MgO and CP-MgO.

Discussion

A. Hydrogen Halides. The chemisorption of HCl and HBr proceeded dissociatively as expected. Although Mg-Cl vibrations could not be detected in the IR due to masking by MgO lattice vibrations, newly formed surface -OH groups were readily observed. Isolated residual -OH groups (3750 cm⁻¹) were retained on AP-MgO even after HCl adsorption, although upon HBr adsorption, this band disappeared. In all cases, broad bands for hydrogen-bonded -OH were formed (about 3000–3600 cm⁻¹), although the narrowest band (3300–

Table 5. IR Bands and Assignments for NO Adsorbed on AP-MgO-3h and CP-MgO-3h^a

band position and strength	effect of 4 h evacuation	band assignment
AP-MgO-3h		
2245 (w)		N ₂ O weakly adsorbed
1650 (w)	same	bidentate carbonate
1415 (m)	same	Mg-O-N-O plus bidentate carbonate
1380 (m)	same	bidentate carbonate
1265 (w)	increased	methoxy
1240 (m)	same	
1212 (s)	decreased	bidentate NO ₂
1168 (vs)	decreased	Mg-N-O
1070 (m)	no change	
CP-MgO-3h		
1510 (m)	same	Mg-O-N-O
1415 (s)	same	Mg-O-N-O plus monodentate carbonate
1380 (sh)	same	bidentate carbonate
1265 (sh)	increased	methoxy
1238 (w)	same	
1212 (s)	decreased	bidentate NO ₂
1170 (vs)	same	Mg-NO

^a The term "3 h" stands for 3 h prior evacuation.

Table 6. IR Bands and Assignments for SO₃ Adsorbed on AP-MgO-3h and CP-MgO-3h

band position and strength	effect of evacuation	band assignment
AP-MgO-3h		
1260 (vs)	increased	sulfate
1105 (vs)	increased	sulfate
CP-MgO-3h		
1630 9s)	reduced	bidentate carbonate
1290 (s)	reduced	sulfate
1220 (s)	no change	sulfate
1140 (s, broad)	no change	sulfate
990	no change	probably sulfate

^a The term "3 h" stands for 3 h prior evacuation.

3640 cm⁻¹) was observed on AP-MgO. Peaks for adsorbed water were also observed after HCl or HBr adsorption (1600–1620 cm⁻¹), and this adsorbed water could be removed by evacuation at 150 °C for all samples (Figures 1 and 2).

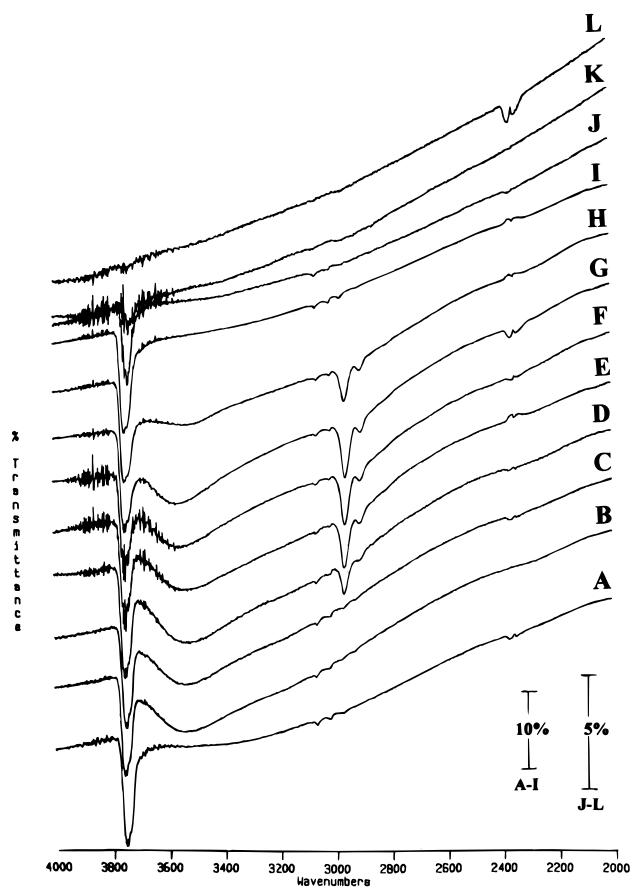
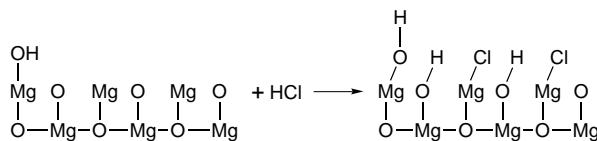


Figure 1. IR spectra 4000–2000 cm^{-1} of HCl on AP-MgO-3h: (A) before adsorption; (B) after 100 Torr of HCl for 15 min; (C) after 5 min evacuation; (D) 4 h evacuation; (E) 18 h evacuation; (F) 100 °C evacuation, (G) 150 °C, (H) 300 °C, (I) 500 °C, (J) 600 °C, (K) 700 °C, (L) 800 °C.

The differences in the isolated $-\text{OH}$ band is of particular interest. This band was present on the starting AP-MgO and was retained upon HCl adsorption. However, for CP-MgO, this band disappeared upon HCl addition, and upon heating and evacuation, it reappeared shifted to 3723 cm^{-1} (from 3745 cm^{-1} initially), suggesting a transfer of surface $-\text{OH}$ groups from lower coordination to higher coordination.⁴⁹

In comparing the spectra of HX adsorbed on AP-MgO and CP-MgO, the differences are only minor. Perhaps the only significant difference is the tendency of AP-MgO to preserve its isolated $-\text{OH}$ groups even after HCl adsorption and the fact that the band is highest (3750 cm^{-1}) on the AP-MgO sample. This would suggest that these isolated $-\text{OH}$ groups are located on lower coordination sites:



The amounts of HCl and HBr adsorbed are consistently higher on AP-MgO on a mmol/mol basis. This is as expected based on the higher surface areas. However, note that on the basis of per nm^2 and at relatively high pressures of HX (>100 Torr), the CP-MgO sample is

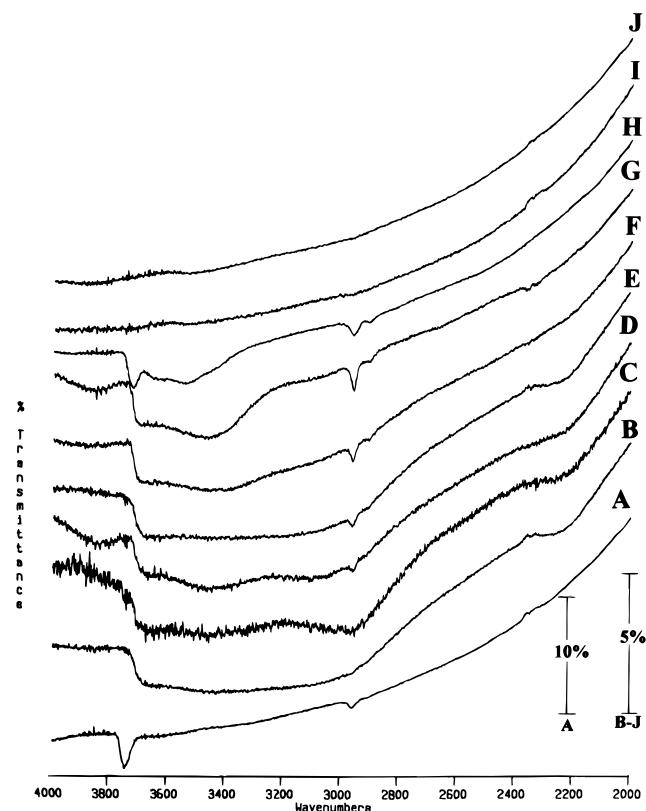


Figure 2. IR spectra 4000–2000 cm^{-1} of HCl adsorbed on CP-MgO-3h: (A) before adsorption; (B) after 100 Torr of HCl for 15 min; (C) after 5 min evacuation; (D) 4 h evacuation; (E) 18 h evacuation, (F) 100 °C evacuation; (G) 150 °C, (H) 300 °C, (I) 500 °C, (J) 600 °C.

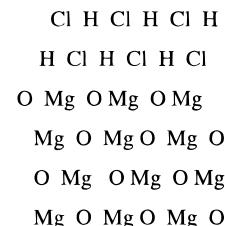


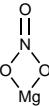
Figure 3. Illustration of how the (100) face of CP-MgO could adsorb ordered multilayers of HCl.

superior. Initially, this was surprising, until a study of pressure effects on adsorbed amounts of SO_2 was completed, where it was shown that at low pressures, where monolayer (or less) coverage was expected, the greater surface reactivity of AP-MgO allowed more adsorption/ nm^2 . It was found that as the pressure of adsorbate went up, multilayer adsorption took place. It was rationalized that the formation of multilayers on CP-MgO was more favorable based on its more ordered morphology.⁴⁵

Calculations based on MgO crystal surfaces show that a monolayer of HCl should be 12 HCl/nm^2 MgO. For AP-MgO essentially a monolayer was adsorbed (1:1 ratio of HCl:MgO surface). However, for CP-MgO clearly a second layer, actually about 1.5 layers, formed at greater than 100 Torr. This multilayer is apparently more favored on the microcrystalline CP-MgO, as shown by the increased adsorption amount and by the increased broadness of the IR band for hydrogen-bonded HCl. Figure 3 attempts to depict how this additional adsorption might be favored on the flatter (100) face of MgO. It is also noted from Table 1 that sample evacuation

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Table 7. IR Bands for N₂, N₂O, NO, and NO₂ Adsorbed on MgO^{52,53}

nitrogen species	IR bands (cm ⁻¹)			
	ref 52	ref 53	AP-MgO	CP-MgO
	1160	1171 1161	1168	1170
		1435 1342		
	1222/1208 1190/1168 850/850	1213 1126	1212	1212
	1416/1404 1145/1120		1415	1415
		1309 1232		
NO gas	1870			
N ₂ O weakly adsorbed	2245			
N ₂ adsorbed		2210 2200 2193	2245 2200	

did not remove the adsorbed HCl or HBr; therefore, even the second layer was strongly chemisorbed (possibly dissociatively). An explanation for CP-MgO adsorbing a second layer, while AP-MgO does not, may lie in the fact that the flat planes on CP-MgO are able to accommodate more ordered self-association of HCl or HBr (as previously proposed for SO₂ adsorption).⁴⁵ However, another rationale also needs to be considered. Earlier work showed that CP-MgO exhibited enhanced basicity and it was proposed that basic/reducing character depends on more long-range order (existence of domains).⁵⁰ Thus, it may be that a combination of "electronic" and "morphological" effects are working together to allow the larger crystallites to adsorb more than a monolayer of HCl (or HBr) under the conditions employed.

B. Nitrogen Monoxide. Nitrogen monoxide adsorbs as a Lewis base donating electron density to Mg²⁺ either through its nitrogen or oxygen atoms. Table 7 summarizes IR data in the literature for the N₂, N₂O, NO, and NO₂-MgO systems. We considered that NO would be a good probe of Mg²⁺ coordination on the surfaces of AP-MgO and CP-MgO. On both MgO samples very strong absorptions (1168 and 1170 cm⁻¹) for Mg-N-O were observed. However, bands at 1415 cm⁻¹ on both samples were also observed and are probably due to O-N-O, where NO has adsorbed on a O²⁻ site as well. A peak at 1212 cm⁻¹ was observed on both samples and is attributed to bidentate NO₂ (see Figure 4). Also observed was a small peak at 2200 cm⁻¹ due to adsorbed N₂ which was quickly lost upon evacuation.

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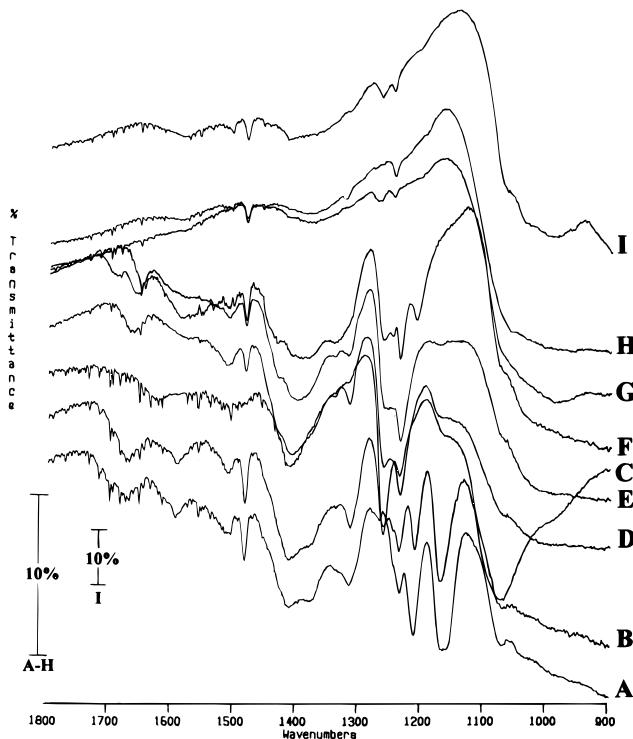


Figure 4. IR spectra 1800–900 cm⁻¹ of NO adsorbed on AP-MgO-3h: (A) after 100 Torr of NO for 15 min; (B) after 4 h evacuation at 25 °C; (C) 18 h; (D) 100 °C; evacuation, (E) 150 °C, (F) 300 °C, (G) 600 °C, (H) 700 °C, (I) prior to NO adsorption, 25 °C.

The only differences that were ascertained are as follows:

A band at 2245 cm⁻¹ for adsorbed N₂O was observed only on AP-MgO. Perhaps the only conclusion is that the AP-MgO enabled some chemistry to occur under mild conditions, namely, NO disproportionation to yield adsorbed N₂O and NO₂. The N₂O product was not observed on CP-MgO. The amounts of NO adsorbed (Table 4) show that over a 1 h period AP-MgO is a superior agent for adsorbing NO, both on a mmol/mol basis and on per nm² basis. The NO molecule should take up a cross-sectional area of 0.072 nm², so that 14 would be the number of NO molecules (linear adsorption structure) on 1 nm² of MgO (100 plane). Our data for the amount of NO adsorbed clearly indicates that less than one monolayer adheres to the AP- or CP-MgO. Thus, once again we see that when either low pressures are employed or adsorbates with relatively low heats of adsorption are employed, AP-MgO exhibits superior behavior. It is only when multilayer coverage occurs that CP-MgO is generally superior.

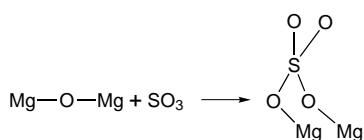
C. Sulfur Trioxide. In the case of SO₃ adsorption, both AP-MgO and CP-MgO showed strong IR bands for sulfate species (1260 and 1105 cm⁻¹ on AP-MgO and 1290, 1220, and 1140 cm⁻¹ for CP-MgO). The spectra were more complex in the case of CP-MgO, indicating multiple sulfate species (which have been observed by Schoonheydt and Lunsford).⁵¹

The SO₃ adsorbed was obviously in multilayers and, as expected, on a mmol/mol basis, AP-MgO was superior, but on a per nm² basis, CP-MgO prevailed:

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(52) Cerruti, L.; Modone, E.; Guglielminotti, E.; Borello, E. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 729.

(53) Wakabayashi, F.; Naito, S.; Onishi, T.; Tamaru, K. *Bull. Natl. Sci. Mus. (Tokyo, Ser. E)* **1982**, *5*, 21.



In the case of SO_3 , using 0.27 nm^2 as its cross-sectional area, the number of SO_3 molecules that would be adsorbed on 1 nm^2 of MgO (100 plane) would be 3.7. The data show that 4 monolayers on AP- MgO and 6 monolayers on CP- MgO are adsorbed (Table 4). This is the largest amount/ nm^2 for the molecules reported in this study. In this case, CP- MgO clearly shows its superior property for multilayer adsorption, apparently due to the more highly ordered nature of the micro-crystals in CP- MgO compared with the nanocrystalline AP- MgO , both on per nm^2 and mmol/mol basis. It should also be noted that SO_3 , in particular, easily forms polymers, which may be what is affording the higher adsorption amounts. Since sample evacuation does not remove these multilayers, it is very likely that such polymers are formed (on top of a monolayer of sulfate).

Conclusions

On a mmol/mol basis, nanoscale MgO (AP- MgO) adsorbs more HCl , HBr , and SO_3 than microscale MgO (CP- MgO). However, on a per nm^2 basis the larger, more crystalline CP- MgO is superior, and this appears

to be due to the formation of more ordered multilayers, apparently allowing more adsorbate molecules to adsorb/ nm^2 .

For NO , which at 100 Torr adsorbs less than a monolayer, the nanocrystalline MgO is superior as an adsorbent on both the per nm^2 and mmol/mol basis.

In general, the nanoscale MgO crystallites possess a more reactive surface. However, when multilayer adsorption occurs, the more ordered surfaces on larger crystallites became more important. This multilayer adsorption is encouraged by higher adsorption pressures (>100 Torr, and, of course, by the strength of interaction of the surface–adsorbate pair in question.

It is possible that both “electronic” effects and “morphological” effects combine to allow the microcrystalline CP- MgO to adsorb multilayers of HX and SO_3 (as well as SO_2 reported earlier).⁴⁵ However, in order for CP- MgO to exhibit this behavior, relatively high pressures of adsorbate must be employed.

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