

## Nanocrystal Metal Oxide–Chlorine Adducts: Selective Catalysts for Chlorination of Alkanes

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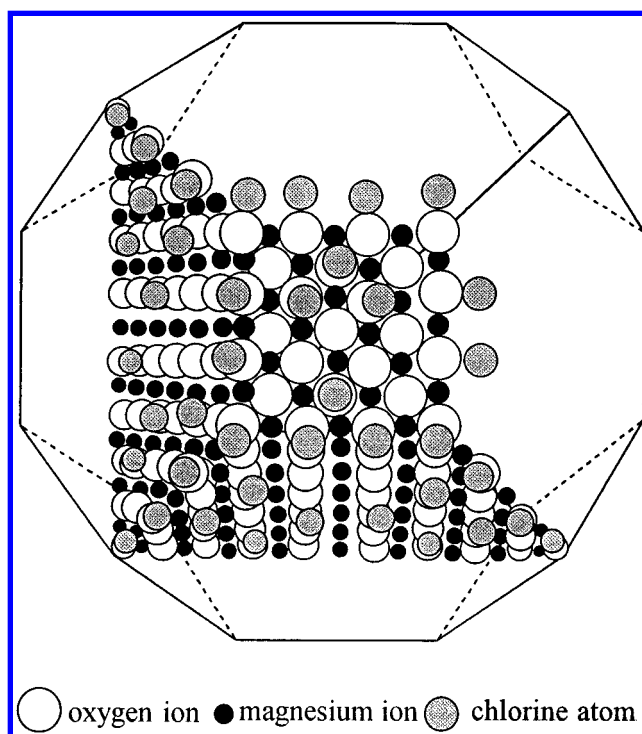
In recent reports the authors have described the preparation of MgO and CaO ultrafine powders in nanocrystalline form, and the smallest crystallite materials have been labeled AP–MgO and AP–CaO (4- and 7-nm average crystallite sizes, respectively) as designated by their *aerogel* preparation method.<sup>1</sup> Somewhat larger crystallites, but still in the nanometer size range have also been prepared, and labeled CP–MgO and CP–CaO (7- and 15-nm average crystallite sizes, respectively) designated “conventional prepared”.

The surface reactivities and adsorption powers of these samples are considerably higher than normal, commercially available (CM–MgO and CM–CaO) samples. Furthermore, we have disclosed further reactivity enhancements of these materials by depositing very thin layers of transition-metal oxides on the crystallites of these MgO and CaO samples.<sup>2</sup>

It is believed that the enhanced surface reactivities of these samples of MgO and CaO are due to the morphological features of the small crystallites and, more specifically, are due to a relatively higher population of reactive surface sites, for example, edges, corners, and ion vacancies. The “smallness” and the shapes of the crystallites allow much higher ratios of edge-corner ions to total surface ions.<sup>3a,3b</sup>

The presence of these edge-corner sites and other reactive defect sites (such as vacancies) allow these materials to possess surprisingly high surface concentrations of reactive surface ions. For example, an edge, or even more so, a corner  $O^{2-}$  anion is coordinately unsaturated and is “seeking” Lewis acids (electron-deficient species) to help stabilize and delocalize its negative charge. Conversely, a  $Mg^{2+}$  ion on an edge or corner is “seeking” Lewis bases (electron-rich species) to stabilize and delocalize its positive charge. Therefore, these coordinately unsaturated  $O^{2-}$  and  $Mg^{2+}$  ions readily accept incoming reagents with Lewis acid or Lewis base character.

This situation presents an opportunity to prepare new and unusual materials where highly reactive Lewis base or Lewis acid adsorbents could be stabilized by forming adducts with the reactive-accepting surface sites on the MgO or CaO samples. In the current context, nanocrystalline MgO and CaO were exposed to chlorine gas at room temperature. During the adsorption, a great deal of heat was generated, and the white powder samples turned light yellow. Excess  $Cl_2$  gas was allowed to stand over the powder for 30 min, followed by evacuation for 0.5 h. A light yellow sample was transferred to a TGA instrument and heated at 10 °C/minute under  $N_2$ . Chlorine gas and a trace of  $O_2$  were released over a broad temperature range 100–700 °C, and it was determined that 13 wt % of  $Cl_2$  was released. In the case of AP–MgO, the surface area was 383  $m^2/g$  (which decreased consider-



**Figure 1.** Schematic drawing of an AP–MgO nanocrystal doped with chlorine, which dissociative chemisorbs (exothermally) on strongly basic surface sites. The Cl atoms are probably located at the most basic/reactive edge/corner  $O^{2-}$  sites.

ably during this heating cycle). Knowing the surface area and the amount of  $Cl_2$  released, the number of Cl atoms adsorbed per  $nm^2$  could be calculated, and this ranges from 5 to 7 atoms. By using a polyhedral nanocrystal model and filling in the necessary chlorine atoms required for a 4-nm particle, it is evident that this amount of chlorine adsorbed exceeds the number of edge/corner sites available, and an illustration is shown in Figure 1.<sup>3b,c</sup> Thus, chlorine atoms are located at not only the edge/corner sites but also some adjacent face sites.<sup>4</sup>

Similar studies of normal MgO crystals have been carried out. With common, commercially available MgO powder, less than 5 wt %  $Cl_2$  was adsorbed, and the process was not nearly as exothermic.

This nanoparticle MgO– $Cl_2$  adduct is extremely reactive. To our surprise when 2,3-dimethylbutane came into contact with the adduct in the presence of excess  $Cl_2$  at room temperature, an explosion took place. However, by carrying out the adduct–2,3-dimethylbutane contact at  $-78$  °C followed by slow warming up to room temperature in the dark, a smooth chlorination took place to form mainly a monochlorinated product  $(CH_3)_2CClCH(CH_3)_2$ , and smaller amounts of dichloro isomers. Control experiments with  $Cl_2$  gas–2,3-dimethylbutane in the dark gave practically no reaction, while photolysis for 1 h with a 450-W UV lamp (quartz reactor) yielded about 95% of chlorinated organics with a large

(1) Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1991**, 3, 175.

(2) Klabunde, K. J.; Khaleel, A.; Park, D. *High Temp. Mater. Sci.* **1995**, 33, 99.

(3) (a) Klabunde, K. J.; Stark, J.; Koper, O.; Mohs, C.; Park, D. G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *J. Phys. Chem.* **1996**, 100, 12142. (b) Koper, O.; Lagadic, I.; Klabunde, K. J. *Chem. Mater.* **1997**, 9, 838. (c) The polyhedral structure is supported by high-resolution TEM (ref 3b), and this crystal shape is very different from microcrystals. However, the polyhedral structure can only be considered an “average” since not all of the crystallites are the same.

(4) A 4-nm polyhedral AP–MgO particle contains totally 4500  $Mg^{2+}$  and 4500  $O^{2-}$ . The total number of edge and corner ions is about 6% of the total number of ions. Thus, there are 270  $Mg^{2+}$  and 270  $O^{2-}$  on a 4-nm AP–MgO particle. From the mass of the particle, we can calculate that there are  $3.47 \times 10^{18}$  particles in 1 g AP–MgO. We also know the surface area of AP–MgO is about 380  $m^2/g$ , and thus the surface area of one particle is 110  $nm^2$ . There are 5.8 Cl atoms per  $nm^2$  on the surface; thus, there are  $5.8 \times 110 = 638$  Cl per particle. The number of Cl atoms adsorbed is larger than the number of edge/corner  $O^{2-}$  of a particle; therefore, some Cl atoms are located at the edge and corner sites, and the others are located at the adjacent face sites.

**Table 1.** Chlorination of Methane over Different Oxides at Room Temperature in the Dark<sup>a</sup>

products	CH <sub>4</sub> %	CH <sub>3</sub> Cl%	CH <sub>2</sub> Cl <sub>2</sub> %	CHCl <sub>3</sub> %	CCl <sub>4</sub> %	other heavier products %	Cl <sub>2</sub> reacted %
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.14 g AP-MgO, 4 h	61	6.5	15	14	4.8	0	98
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.14 g CP-MgO, 4 h	64	13	14	8.5	0.99	0	71
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.20 g AP-CaO, 4 h	48	3.8	18	9.6	8.8	12.2	
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.20 g CP-CaO, 4 h	60	12	14	9.7	1.5	3.3	
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.07 g AP-MgO, 4 h	59	13	15	10	2.1		81
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.14 g CM-MgO, 4 h	81	1.4	4.3	9.1	4.2	0	54
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 0.20 g CM-CaO, 4 h	77	4.8	7.5	5.7	3.2	1.1	
0.007 mol Cl <sub>2</sub> , 0.007 mol CH <sub>4</sub> , 450 W UV light for 4 h	55	1.5	4.2	10	7.0	22% total, 5 compounds	

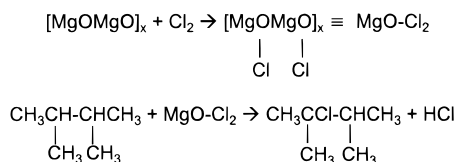
<sup>a</sup> Reactions were carried out by inletting Cl<sub>2</sub> gas into a Schlenk tube containing 380 torr of CH<sub>4</sub> at room temperature.

**Table 2.** Activity of AP-MgO for Chlorination of Methane over AP-MgO at Room Temperature<sup>a</sup>

reaction time (min)	CH <sub>4</sub> %	CH <sub>3</sub> Cl %	CH <sub>2</sub> Cl <sub>2</sub> %	CHCl <sub>3</sub> %	CCl <sub>4</sub> %	reacted Cl <sub>2</sub> percentage
10	80	11	6.4	3.0	0	33
25	68	10	16	6.1	0.12	61
45	66	10	15	8.4	1.8	73
60	64	9.4	14	11	2.2	79
80	63	10	14	11	3.9	85
95	62	7.2	13	13	5.3	94
240	61	6.5	15	14	4.8	99

<sup>a</sup> CH<sub>4</sub>/Cl<sub>2</sub> ratio = 1:1, 0.007 mol CH<sub>4</sub>, 0.007 mol Cl<sub>2</sub>, 0.14 g AP-MgO.

portion of products. Likewise, a commercial CM-MgO-Cl<sub>2</sub> adduct was much less reactive (longer times, less CH<sub>4</sub> and Cl<sub>2</sub> consumption). These results show that the nanocrystalline MgO-Cl<sub>2</sub> adduct was more reactive than Cl<sub>2</sub> gas in the dark and more selective than gaseous Cl atoms formed by a classic photochemical initiation process.



In similar experiments with methane, exposure of the MgO-Cl<sub>2</sub> adduct to CH<sub>4</sub> at room temperature did not cause an explosion, but chlorination took place rapidly to give a mixture of halides (Table 1). Many experiments have repeatedly shown that no light is required. Also, when excess Cl<sub>2</sub> gas above the MgO powder is available, the reaction is catalytic, and the initial turnover number

is about  $1.8 \times 10^{-2} \text{ s}^{-1}$  (assume edge/corner sites are active sites). The reaction gives 99% yield in 4 h (based on Cl) with 61% CH<sub>4</sub> unreacted. The major products are CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. The activity data of AP-MgO are shown in Table 2.

Similar results with CaO samples have been observed. In the case of AP-CaO-Cl<sub>2</sub>, about 12 wt % chlorine was adsorbed. Reactivity of the AP-CaO-Cl<sub>2</sub> adduct with 2,3-dimethylbutane gave 93% monochlorinated product and 41% total yield of products over a 6 h period warming up from -78 °C. In the case of CH<sub>4</sub>, the presence of AP-CaO produced 12% oligomers with 48% CH<sub>4</sub> unreacted, while AP-MgO generates no oligomers.

These results point out several interesting things. First, the fact that MgO and CaO nanocrystals have high surface area allows them to behave as "chemical reagents". That is, large amounts of Cl<sub>2</sub> can be adsorbed per gram of oxide. Second, the nanocrystals have high surface reactivities, allowing for the favorable dissociative chemisorption of many molecules, including the halogens. Actually, a different mode of adsorption apparently takes place, compared with "normal" crystals. For example, an earlier report of the adsorption of halogen on MgO indicates that (we calculate) six Cl species/nm<sup>2</sup> were adsorbed, and Kibblewhite et al. indicated that the adduct yielded oxygen upon heating.<sup>5</sup> This is not the case in the present study. The oxygen released in our study was only about 0.4%. Third, we have shown for the first time that nanocrystalline MgO(CaO)-Cl<sub>2</sub> adducts can serve as rather selective, catalytic alkane chlorination reagents. This suggests that Cl atoms were trapped. Thus, these adducts behave as solid-state warehouses for the storage of reactive atoms in large amounts.

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(5) Kibblewhite, J. F. J.; Tench, A. J. *J. Chem. Soc., Faraday Trans. 1* 1974, 70, 72.