

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.¹ 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.²

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.^{3a,3b}

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 O²⁻ anion is coordinately unsaturated and is “seeking” Lewis acids (electron-deficient species) to help stabilize and delocalize its negative charge. Conversely, a Mg²⁺ ion on an edge or corner is “seeking” Lewis bases (electron-rich species) to stabilize and delocalize its positive charge. Therefore, these coordinately unsaturated O²⁻ and Mg²⁺ 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 Cl₂ 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 N₂. Chlorine gas and a trace of O₂ were released over a broad temperature range 100–700 °C, and it was determined that 13 wt % of Cl₂ was released. In the case of AP–MgO, the surface area was 383 m²/g (which decreased consider-

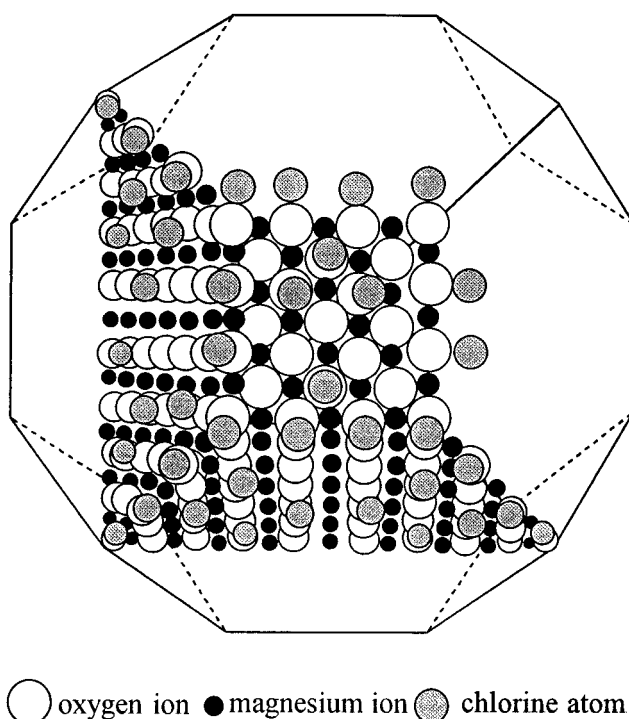


Figure 1. Schematic drawing of an AP–MgO nanocrystal doped with chlorine, which dissociative chemisorbs (exothermally) on strongly basic surface sites. The Cl atoms are probably located at the most basic/reactive edge/corner O²⁻ sites.

ably during this heating cycle). Knowing the surface area and the amount of Cl₂ released, the number of Cl atoms adsorbed per nm² 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.^{3b,c} Thus, chlorine atoms are located at not only the edge/corner sites but also some adjacent face sites.⁴

Similar studies of normal MgO crystals have been carried out. With common, commercially available MgO powder, less than 5 wt % Cl₂ was adsorbed, and the process was not nearly as exothermic.

This nanoparticle MgO–Cl₂ adduct is extremely reactive. To our surprise when 2,3-dimethylbutane came into contact with the adduct in the presence of excess Cl₂ 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 (CH₃)₂CClCH(CH₃)₂, and smaller amounts of dichloro isomers. Control experiments with Cl₂ 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 Mg²⁺ and 4500 O²⁻. The total number of edge and corner ions is about 6% of the total number of ions. Thus, there are 270 Mg²⁺ and 270 O²⁻ on a 4-nm AP–MgO particle. From the mass of the particle, we can calculate that there are 3.47 × 10¹⁸ particles in 1 g AP–MgO. We also know the surface area of AP–MgO is about 380m²/g, and thus the surface area of one particle is 110 nm². There are 5.8 Cl atoms per nm² on the surface; thus, there are 5.8 × 110 = 638 Cl per particle. The number of Cl atoms adsorbed is larger than the number of edge/corner O²⁻ 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.

