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Enhancing Effect of Fe_2O_3 on the Ability of Nanocrystalline Calcium Oxide to Adsorb SO_2

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Calcium oxide is of great utility as a scrubber for SO_2 and NO_x gases in the flue exhaust of fossil fuel power plants. The purpose of this communication is to disclose the striking effect that a small amount of surface iron oxide can have on the effectiveness of nanocrystalline calcium oxide as an adsorbent for sulfur dioxide.

For some time we have been investigating the application of nanocrystalline calcium and magnesium oxides as destructive adsorbents for environmental toxins. Such toxins include chlorinated hydrocarbons (CCl_4, C_2Cl_4, C_2HCl_3, $CHCl_3$, chlorinated benzene),[1,2] acid gases (SO_2, CO_2, HCl, HBr, SO_3),[3,4] and organophosphors (DMMP).[5] The small particles often exhibit a striking reactivity toward these toxins which is due to several factors that can be attributed to the small size and shape of the particles. These factors include a high surface area (∼100 m^2/g) which exposes a large fraction of the CaO or MgO moieties of the nanoparticle, a reduction of the distance required for solid state diffusion of reactants to reach the core of the particles, and the morphology of the particles which provides a high proportion of highly reactive edge, corner, and defect sites on the crystal.[6]

Recently we attempted to enhance the reactivity of these nanoparticles by developing a second generation of destructive adsorbents which involved introducing a monolayer of a transition metal oxide onto the surface of the alkaline earth oxide.[7] With Fe_2O_3, the loading is about 1 mol % of Fe_2O_3/mol of CaO or 10 mol %/mol of surface CaO. The motivation behind adding the transition metal oxide is based largely on thermodynamic considerations. For example, thermodynamically, adsorbed carbon tetrachloride readily reacts with Fe_2O_3 to form $FeCl_3$ and CO_2. Calculated heats of formation suggest that $FeCl_3$ can in turn react with calcium oxide to regenerate the Fe_2O_3 species and form calcium chloride salt. In a similar way, the transfer of SO_4^{2-} for O^{2-} is thermodynamically favorable, i.e.

$$Fe_2(SO_4)_3 + 3CaO \rightarrow 3CaSO_4 + Fe_2O_3 \qquad \Delta H_{rxn} = -534.1\ kJ$$

Two types of nanocrystalline calcium oxide have been employed. They are designated CP- and AP-CaO for "conventionally prepared" and "aerogel prepared". Crystallite sizes are 14.6 and 7.3 nm for CP- and AP-CaO, respectively, as determined by powder XRD. The synthesis and characterization, as well as reactions with CCl_4 and DMMP, have been described elsewhere.[1,2,5,6,7] The iron oxide derivatives are indicated by a [Fe_2O_3] prefix. In a typical experiment, 1-mL injections of pure, gaseous SO_2 were pulsed at 6-min intervals over a 50-mg bed of calcium oxide heated to 500 °C and the excess gaseous reactant was detected via gas chromatography (He carrier gas). The experiments were performed so that the amount of SO_2 was in slight stoichiometric excess relative to the CaO. The solid products of the reaction were identified by powder X-ray diffraction. The extent of reaction is indicated by the breakthrough number and the number of moles of SO_2 that are adsorbed per mole of CaO. The breakthrough number is defined here as the number of 1-mL injections that are made until the first trace of excess SO_2 is eluted from the bed of the adsorbent.

Table 1. Breakthrough Numbers and Reaction Efficiencies for SO_2 with CP-CaO, [Fe_2O_3]CP-CaO, AP-CaO, and [Fe_2O_3]AP-CaO at 500 °C

	breakthrough no.	reaction efficiencies[a] (mol of SO_2/mol of CaO)
CP-CaO	11	0.36
[Fe_2O_3]CP-CaO	23	0.55
AP-CaO	19	0.51
[Fe_2O_3]AP-CaO	44	0.94

[a] Theoretical maximum would be 1.0.

We have observed high reactivities of nanocrystalline calcium oxide with SO_2 at relatively low temperatures to generate a mixture of calcium sulfite, calcium sulfate, and calcium sulfide. Residual calcium oxide is observed in some experiments. It has been proposed by Allen and Hayhurst that the mixture of solid sulfur products occurs through two different mechanisms at 500 °C.[8]

$$CaO + SO_2 \rightleftharpoons CaSO_3 \qquad (1)$$

$$CaO + SO_2 \rightleftharpoons {}^{3}/_{4}CaSO_4 + {}^{1}/_{4}CaS \qquad (2)$$

In a 1994 publication, Linares-Solano *et al.* reported a conversion near 0.30 mol of SO_2 per mol of CaO for calcium oxide generated from calcined calcium carbonate when the reaction temperature was 500 °C.[9] Hartman and Trnka observed a conversion of 0.45 at this same temperature.[10] Allen and Hayhurst report a CaO conversion of about 80% at 700 °C and above.[8] O'Neill *et al.* found that extended calcination times for limestone gave a conversion of nearly 90%.[11] While high reaction ratios for SO_2/CaO have been observed before, the temperature of reaction typically exceeds 800 °C.

In our experiments at 500 °C, CP-CaO was found to destructively adsorb 0.36 mol of SO_2 per mole of calcium oxide. For AP-CaO the mol of SO_2/mol of calcium oxide ratio was 0.51 (Table 1 and Figure 1).

When [Fe_2O_3]CP-CaO was utilized as the adsorbent the reaction ratio increased from 0.36 to 0.55. For the [Fe_2O_3]AP-CaO the ratio jumped from 0.51 to 0.94. The complete conversion of CaO to a sulfated species would give a reaction ratio of 1.00. Thus, a *nearly complete conversion of the calcium oxide nanoparticles* was observed at only 500 °C.

Yang *et al.* found that the presence of about 4% Fe_2O_3 physically mixed with CaO effectively doubles the sorption rate and reactivity of the CaO with SO_2 at 850 °C while conversion of CaO to $CaSO_4$ for the mixture was about 35%.[12] The observation of the increased reactivity is confirmed by our

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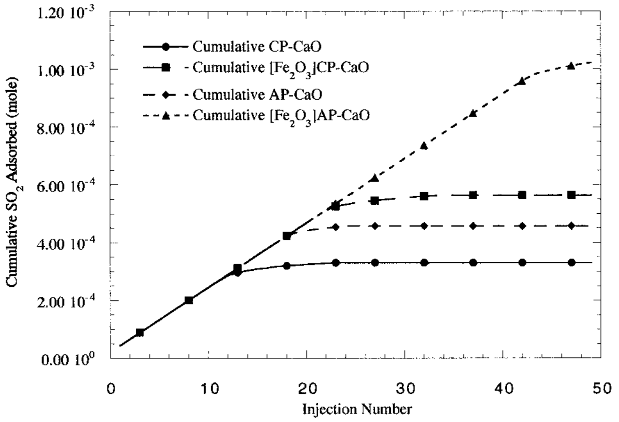

Figure 1. Cumulative Adsorption of SO_2 with CP-CaO, [Fe_2O_3]CP-CaO, AP-CaO, and [Fe_2O_3]AP-CaO. Note: The diagonal portions of the curves show that all of the SO_2 pulse is adsorbed by the nanocrystalline CaO. Deviation from the diagonal represents the breakthrough number while the horizontal portion of the curve indicates that the CaO bed has been exhausted and will not adsorb any additional SO_2.

experiments. However, the reactivity of the nanocrystalline particles is much greater than that of the Fe_2O_3/CaO physical mixture.

This enhancing effect of a small layer of iron oxide has been noted in other systems that we have investigated. An example is the reaction with CCl_4 at 425 °C. A mole of CCl_4/mole of CaO ratio of 0.23 has been observed for CP-CaO while 0.31 was seen for AP-CaO. (Note that for the reaction with CCl_4 a ratio of 0.50 indicates that the entire amount of CaO has reacted.) When [Fe_2O_3]CP-CaO and [Fe_2O_3]AP-CaO were examined the ratios increased to 0.44 and 0.51, respectively (Table 2).[6]

To summarize, the presence of a small amount of iron oxide at the surface of nanocrystalline calcium oxide has a significant effect on the ability of the CaO to act as a destructive adsorbent for sulfur dioxide (and other environmental toxins). This enhancement in reactivity is a kinetic phenomenon. In the case of CCl_4, it has been postulated that the Cl^-/O^{2-} exchange is involved in the mechanism and is rate determining.[7] A similar solid state ion/ion exchange might be occurring for SO_3^{2-}, SO_4^{2-}, S^{2-}, and O^{2-} in the CaO/SO_2 system. One reason why the nanocrystals exhibit such a large reaction rate (efficiency) is that the small size of the particles permits a shorter ion migration distance to the core of the particle than for that of conventional calcium oxide. With the shorter ion migration distances it is easier to react with the entire CaO particle by effectively "eating out" the core.

Table 2. Reaction Efficiencies for the Destructive Adsorption of CCl_4 with CaO

	reaction efficiency[a] (mol of CCl_4/mol of CaO)
CP-CaO	0.23
[Fe_2O_3]CP-CaO	0.31
AP-CaO	0.44
[Fe_2O_3]AP-CaO	0.51

[a] Theoretical maximum would be 0.5.

Taking the size and morphology of the CaO nanocrystals into account explains why the AP-CaO reacts to a greater extent than the CP-CaO. Accounting for the effects of the Fe_2O_3 is more difficult. Shifts in the *d*-spacing from the powder XRD patterns suggest that structural changes occur in the CaO due to the presence of Fe_2O_3. The structural changes should facilitate easier ion/ion exchange between the product layer and unreacted CaO. This, along with the possibility that the iron sulfate species may be mobile and migrate to the more reactive edge/corner sites of the crystal (which would possess even greater structural disorder), could explain the "enhancing" effect of the Fe_2O_3 on the extent of reaction. While the precise mechanism by which the iron oxide enhances the reactivity of the calcium oxide is not yet clear, it is apparent that even a very small amount of surface Fe_2O_3 is extremely beneficial to the process.

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