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Mesoporous magnesium oxide and its composites: Preparation, characterization, and removal of 2-chloroethyl ethyl sulfide

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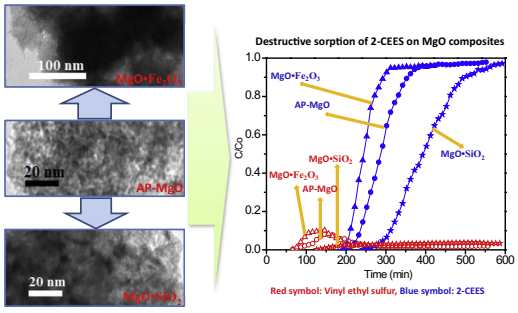
HIGHLIGHTS

- Mesoporous MgO, MgO·SiO_2 and MgO·Fe_2O_3 were synthesized using an aerogel method.
- Their reactivity and sorption of 2-CEES were evaluated by breakthrough experiments.
- Adding Fe_2O_3 to MgO led to improved reactivity, but decreased sorption capacity.
- Adding SiO_2 to MgO contributed to enhanced surface area and sorption capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnesium oxide and its composites with Fe_2O_3 or SiO_2 particles were prepared by an aerogel method for the removal of 2-chloroethyl ethyl sulfide (2-CEES) under ambient condition. Their sorption capacity and reactivity were evaluated by breakthrough experiments using 2-CEES of 0.26 μg/mL in N_2 flow. The surface area and sorption capacity of aerogel MgO (AP-MgO) were about five times greater than those of commercial MgO. All of the prepared materials could decompose 2-CEES at 25 °C with different conversion degrees. The reactivity of MgO·Fe_2O_3 composites was higher than that of AP-MgO and MgO·SiO_2. On the other hand, the increased surface area, imparted by the addition of SiO_2, led to the enhanced sorption capacity (49.3 mg/g). The order of sorption capacity was MgO·SiO_2 > AP-MgO > MgO·Fe_2O_3, but the order of reactivity was MgO·Fe_2O_3 > AP-MgO > MgO·SiO_2.

1. Introduction

Presently, removal of hazardous materials from the environment has become a critical issue from a biological and environmental standpoint. Adsorptive removal of toxic components from fuel, wastewater or air is one of the most attractive cleaning technologies [1]. The most abundant hazardous compounds that exist in our environment is anthropogenic pollution such as toxic gases (NO_x, SO_x, CO_2, NH_3, H_2S, VOC_s) [2], chemical weapon agents (mustard, never, and chocking agents) [3].

Among many solid materials to treat toxic chemicals, metal oxide particles have proven to be effective materials for adsorption and decomposition of a large amount of toxic and persistent chemicals [4,5] due to their advantages such as ultrahigh surface areas, a large number of highly reactive edges, corner defect sites, unusual lattice planes, a high surface-to-volume ratio, and reusability. Particularly, magnesium oxide has received a great attention for decontamination of toxic chemicals in recent years because of its unique physical and chemical properties. Many studies have

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focused on methods to synthesize MgO with high surface area and pore volume, small crystal size, and high activity. It has been reported that MgO with high surface area and pore volume can be obtained via an aerogel method using magnesium alkoxide and hypercritical drying [6]. Compared to polyol-meditation thermolysis and hydrothermal methods, aerogel MgO has shown outstanding textural properties and high sorption capacity of methylmercaptan in municipal gas [7].

Single magnesium oxide shows a promise as a sorbent; however, it can be further modified by adding other metals to improve the sorption capacity and reaction activity. MgO added by Fe_2O_3 has been synthesized successfully by several different routes such as the precipitation method (a specific surface area between 23 and 34.5 m^2/g) [8] and the wet impregnated method (a specific surface area of around 170 m^2/g) [9]. As an alternative route, it was reported that silica impregnated with magnetite nanoparticles [10] and surface modified silica [11–14] are a good candidate to improve the adsorption capacity and reactivity of sulfur and nitrogen compounds. Then, to improve the physical properties and sorption capacity, porous silica was added to MgO particle by using various methods such as spray pyrolysis (a specific surface area of about 148 m^2/g) [5], supercritical drying under different prehydrolysis conditions for TEOS (a specific surface between 207 and 340 m^2/g) [15], a wet mixing method (a specific surface area under 520 m^2/g) [16], and a sol–gel method (a specific surface area between 86 and 317 m^2/g) [17].

In this study, 2-CEES ($CH_3CH_2SCH_2CH_2Cl$) was selected as a toxic chemical which should be removed from air. In addition, 2-CEES was often considered as a surrogate compound for the removal study of sulfur mustard (SM), which is a class of related cytotoxic and vesicant agent [18]. Therefore, the development of effective materials for 2-CEES removal can contribute to environmental protection from sulfur compounds as well as the decontamination of chemical warfare agents. Various materials, such as activated carbon-based materials [19], metal organic frameworks [20], and metal oxides [4,21–26], have been presented as effective materials for destructive sorption of 2-CEES in the liquid phase of a batch reactor. However, it has been pointed out that the vapor capture is a critical problem in many practical cases due to its fast vaporization into the atmosphere [3]. Therefore, it is desirable to develop and evaluate a suitable material for the removal of sulfur compounds in the gas phase under ambient conditions.

In this study, for destructive and enhanced sorption of 2-CEES, MgO, $MgO{\cdot}Fe_2O_3$, and $MgO{\cdot}SiO_2$ composites were synthesized using an aerogel route. Their reactivity and sorption capacity for 2-CEES removal were evaluated by breakthrough experiments in the gas phase under ambient conditions (0.26 μg/mL 2-CEES in N_2 flow). The removal performances of MgO and its composites were compared to those of commercial MgO and SiO_2. The characteristics of the as-synthesized materials were investigated by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and N_2 adsorption/desorption isotherms.

2. Experimental

2.1. Materials

The following materials were used in this study: toluene (Aldrich, USA, 99.9%), a magnesium methoxide solution in methanol (Aldrich, 7.82%), 2-CEES (Aldrich, 98%), tetraethyl orthosilicate (Aldrich, 98%), α-Fe_2O_3 powder (Junsei, Japan, 99%), SiO_2 powder (CM-SiO_2) (Aldrich, 99.5%), MgO powder (CM-MgO) (Aldrich, 99%), N_2 (Dae-Deok Gas, Korea, 99.999%), and air (Dae-Deok Gas, 99.999%).

2.2. Preparation of MgO

The magnesium hydroxide (hydrated MgO) was prepared by the following typical aerogel procedure. At room temperature, a mixture of toluene (100 mL) and magnesium methoxide solution in methanol (20 mL) were put into a glass reactor with a stirrer. An excessive stoichiometric amount of distilled water (1.8 mL) was slowly added to the prepared mixture using a syringe. A cloudy white precipitate formed after the addition of each water drop, but a clear solution was observed after a few minutes. The

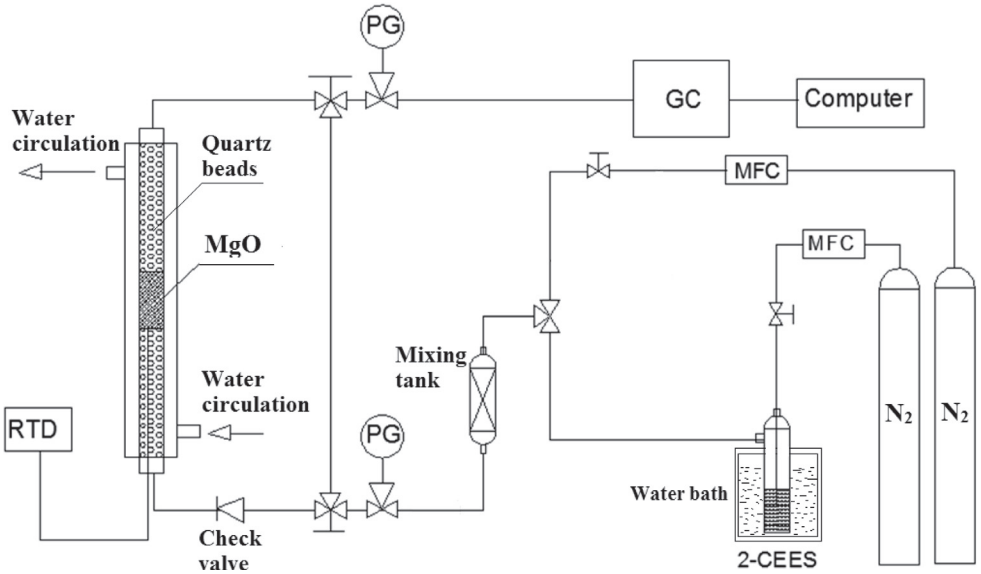

Fig. 1. Schematic diagram of breakthrough experimental apparatus for 2-CEES sorption.