

Sulfur removal from municipal gas using magnesium oxides and a magnesium oxide/silicon dioxide composite



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ABSTRACT

Magnesium oxides (MgOs) were synthesized by polyol-mediation thermolysis, hydrothermal, and aerogel methods and utilized to remove sulfur compounds from municipal gas. The capacity to remove methyl mercaptan (291 $\mu\text{mol/mol}$) from methane was evaluated by using an adsorption breakthrough method at different temperatures. Then, to improve the sulfur removal capacity, a MgO–SiO₂ composite was developed using the aerogel method and its breakthrough capacity was compared to those of the MgOs. The synthesized MgOs and MgO–SiO₂ composite were characterized by XRD, BET, TGA, and HR-TEM. The MgO prepared by the aerogel method had the highest surface area and sorption capacity among the as-synthesized MgOs. Furthermore, the sulfur sorption capacity of the MgO–SiO₂ composite prepared by the same aerogel method as MgO was three times higher than the aerogel MgO even though the sorption capacity of SiO₂ was negligible.

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1. Introduction

In the past decade, research concerning clean fuels has become an important subject in energy and environmental fields [1]. Because the sulfur compounds in fossil fuels are converted to SO_x during combustion, they not only result in acid rain but also poison catalysts in catalytic converters used to reduce CO and NO_x emissions [2,3]. Therefore, since environmental regulations are ever tightening, many countries have legislated lower sulfur content in liquid fuels and natural gas products. As a result, fossil fuel energy producers in most parts of the world are facing the inevitable reality that they need to produce clean fuels with low sulfur levels in the foreseeable future [4,5].

It has been proposed that hydrogen can be supplied by the steam reforming of natural gas due to its safety and adaptability [6–8]. However, sulfur compounds are present in the hydrogen product resulting from their presence in natural gas and they should be reduced to less than 10 ppmw for solid oxide fuel cells (SOFCs) and less than 1 ppmw for proton exchange membrane fuel cells (PEMFCs) because the sulfur compounds are poisons to reforming and shift catalysts as well as electrode catalysts [3]. Therefore, the removal of sulfur compounds is the very important first step in the fuel stream before the steam reforming process.

The removal of sulfur-containing compounds from natural or municipal gas has traditionally been achieved by the catalytic hydrodesulfurization (HDS) process and an adsorptive process for H₂S removal produced during the HDS [9]. However, to overcome the harsh operating conditions including elevated temperatures and pressures with hydrogen consumption, adsorption technology is a promising alternative because sulfur compounds can be adsorbed at ambient temperature and pressure.

The adsorptive desulfurization of gas fuels under mild conditions has been performed by using activated carbon [10], alumina [11], zinc oxide [12,13], various structures of zeolites [14,15], transition metal exchanged zeolites [16], and mesoporous silica-based adsorbents [17,18] as sulfur adsorbents. It was reported that zeolites with a high thermal stability showed high removal capacities of dimethyl sulfide (DMS) and t-butylmercaptan (TBM) from city gas at ambient temperature and pressure while their strong affinity for water is disadvantageous for application in water-containing conditions [14,16]. It was also reported that a Cu/ZnO/Al₂O₃ sorbent showed high catalytic removal capacities of tetrahydrothiophene, DMS, and TBM from CH₄ at high temperatures [11,13]. The removal of odorous CH₃SH from air or gas streams has been achieved by catalytic oxidation and chemisorption on surface-treated activated carbons [17]. The pore structure and surface properties of activated carbon are closely related to the adsorption of methyl mercaptan [18].

In our previous studies, it was demonstrated that metal ion-modified silica adsorbents showed high adsorptive and regenerative

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performances in the desulfurization and denitrogenation of a raw diesel fuel [5,19,20]. It was also determined from the breakthrough results that the sorption rate is equally important as the sorption capacity. Then, mesoporous silica-based adsorbents, such as magnetite-mesoporous silica composites [21] and lithium-modified mesoporous silica adsorbents [22], could contribute to minimizing the mass transfer resistance in the adsorption and regeneration processes in sulfur removal from natural gas due to their relatively large pore size.

MgO and CaO nanoparticles were reported to be very effective adsorbents for toxic chemicals at ambient temperature [23,24]. In addition, it was proposed that the high reactivity of these oxides is close related to their high surface area and crystal shape [25]. Also, MgFe₂O₄ nano-spheres synthesized by a facile solvothermal method demonstrated good potential for the adsorption of SO₂ [26].

It has been proposed that hydrogen for fuel cells can be supplied by steam reforming of municipal gas [14,22]. However, municipal gas contains certain levels of organic sulfur compounds, which are also present in natural gas, to safely allow leak detection. Therefore, the development of high efficiency adsorbents is needed for adsorptive desulfurization to use municipal gas as a hydrogen source.

In this study, magnesium oxides (MgOs) were synthesized by polyol-mediation thermolysis (PMT), hydrothermal, and aerogel methods to remove sulfur compounds from municipal gas. The capacity to remove methyl mercaptan from methane was evaluated by breakthrough experiments at different temperatures. The concentration of methyl mercaptan was fixed at 291 μmol/mol, which is the typical concentration used as an odorant in Korean municipal gas. The most suitable method among the MgO synthesis methods was applied to synthesize a MgO–SiO₂ composite and its sorption capacity was compared with those of the MgOs and pitch-based activated carbon. All of the as-prepared MgO particles were characterized by XRD, BET, TGA, and TEM.

2. Experimental section

2.1. Materials

Magnesium acetate tetrahydrate (ACS reagent, ≥98%), polyvinyl pyrrolidone (powder, average Mw ~55,000), ethylene glycol (anhydrous, 99.8%), magnesium nitrate hexahydrate (ACS reagent, 99%), sodium hydroxide (reagent grade, 97%, powder), magnesium ribbon (ribbon, ≥99.5% Mg basis), silicon dioxide (nanopowder, 5–15 nm particle size, 99.5% trace metals basis), methanol (CHROMASOLV[®], for HPLC, ≥99.9%), and toluene (CHROMASOLV[®] Plus, for HPLC, ≥99.9%) were purchased from Sigma Aldrich. All chemicals and solvents were used as received. The water utilized in the experiments was Milli-Q deionized water.

2.2. Polyol-mediation thermolysis (PMT) method

The polyol-mediated thermolysis synthesis using ethylene glycol (EG) and polyvinyl pyrrolidone (PVP) has been widely applied for the preparation of metal oxide particles in sizes of 10–100 nm. EG was used to strongly depress the boiling point where alcohol served as a solvent and a reducing agent. In addition, PVP played an important role as a capping agent in the final shape of the nanocrystals [27,28]. The process involves relatively simple and inexpensive operation conditions and the size and shape of the nanoparticles can be controlled by adjusting the reaction time, temperature, pH and concentration of PVP [29]. And MgO particles were successfully prepared by the polyol-mediation thermolysis method [30].

0.1 mol of magnesium acetate tetrahydrate and 0.3 mol of PVP were well mixed with ethylene glycol (EG) under reflux at 470 K for 2 h. By centrifugation, a white flocculate was collected and washed several times by water and ethanol to remove excess PVP and EG. The collected white flocculate was dried in a vacuum oven at 353 K for longer than 24 h. Then, it was calcined at 773 K for 2 h.

2.3. Hydrothermal method

Hydrothermal method is usually carried out at a high temperature-high pressure (>100 °C and >1 atm).[31] However, there is no definite lower limit of temperature and pressure conditions for hydrothermal synthesis. It was reported that MgO synthesized at 353 K has excellent physical properties [32]. The same hydrothermal method in the study was used to prepare MgO particles. Since the characteristics of the products, such as the crystallite size, shape, and structure, can be controlled well by choosing different solvents and reaction conditions, several different magnesium salts can be used as magnesium sources. In this study, magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O) was used.

The autoclave filled with 0.01 mol of magnesium nitrate and 0.1 mol of sodium hydroxide was heated to 353 K for 2 h. After cooling down to room temperature, the collected magnesium hydroxide particles were washed with distilled water and pure ethanol. The magnesium hydroxide powder was dried in a vacuum oven at 333 K for 4 h and calcined at 723 K in air for 5 h.

2.4. Aerogel method

It was reported that an aerogel method resulted in excellent properties of nano-sized MgO but the technique consisted of several steps [33]. The aerogel step used in the study is presented in Fig. 1.

2.4.1. Methoxide step

First, a magnesium ribbon was cut into small pieces (0.5–1.0 inch) and kept in acetone-wet paper (Kimwipe). Then, a magnesium methoxide solution was made from a mixture of 5 g of magnesium and 205 ml of methanol in a round-bottom flask under nitrogen gas at room temperature for 16 h as shown in Fig. 1. The desired reaction is shown below.

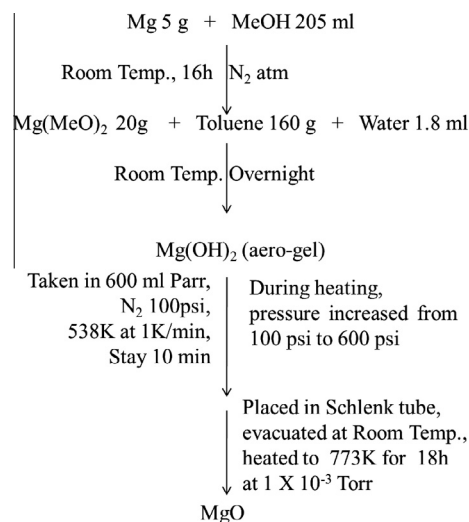
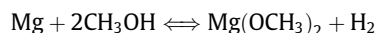


Fig. 1. Schematic of aerogel synthesis procedure for MgO.

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