Surface modification of porous alumina filters for CO_2 separation using silane coupling agents

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ARTICLE INFO

ABSTRACT

Inorganic membranes are becoming increasingly interesting for CO_2 gas separation processes considering their potential in CO_2 capture and storage for mitigating global warming. Porous alumina filters with the ability of CO_2 gas separation were prepared by modifying four types of silane coupling agents: 3-Aminopropyltriethoxysilane (APTES), 3-Ureidopropyltriethoxysilane (Ureido), Octadecyltrimethoxysilane (ODS), and Heptadecafluorodecyltrimethoxysilane (FAS17). CO_2/N_2 gas selectivity was less than 1.0 for all the filters, meaning that less CO_2 gas could permeate the filter, compared with N_2 gas. The difference of gas selectivity among the prepared filters was ascribed to two main factors. The first was the relative electric charges of the atoms in both the gas molecules and the functional groups of the silane coupling agents. Oppositely charged atoms result in a physical interaction between CO_2 molecule and the silane coupling agent at the surface of porous alumina structure. The second factor was the configuration of the CO_2 molecule. It could be considered that the oxygen atoms at the exterior of the CO_2 molecule have a stronger physical interaction with other charged species than the carbon atoms located at the center of the molecule.

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1. Introduction

At present, global warming, which has been linked to anthropogenic greenhouse gas emissions, especially CO_2, is widely recognized to be one of the most urgent and crucial problems facing humankind. One feasible approach for limiting CO_2 emissions is CO_2 capture and storage (CCS) systems [1]. This technology aims to selectively capture CO_2 from emission sources, compress the gas, and achieve long-term storage by pumping it into deep underground. Considering that increasing number of countries and corporations have been launching projects related to CCS, this technology could be one of the means of curtailing the amount of greenhouse gas emissions in the coming decades. To enhance the feasibility of CCS systems, realizing an effective and economic process for gas separation is essential [2]. Inorganic membranes are being investigated for use as separation membranes as they are common materials with a good balance between cost and separation ability. Some inorganic materials have already been employed for this purpose. Xomeritakis et al. prepared silica membranes with pore sizes of 0.3–0.4 nm on alumina supports [3]. Abidi et al. prepared titania and alumina membranes that were surface modified with average pore sizes of approximately 4 nm

using a trimethoxysilane fluorinated coupling agent [4]. Both reports show that these porous membranes are more permeable to CO_2 gas compared with N_2 gas, which is the similar to the tendency of the general polymer membrane [5]. Isobe et al. prepared porous alumina filters with a CO_2 gas selectivity of less than 1.0 by modifying AlOOH on the surface of porous structures [6,7]. Their results showed that CO_2 gas was prevented from permeating through the filter, contrary to the behavior of previously reported membranes [5]. Another approach to effectively separate CO_2 gas is to modify silane coupling agents on the filter surface [8]. Ostwal et al. indicated that CO_2 molecules interact with amino functions, and they achieved moderate CO_2 gas separation [9]. Based on these findings, we prepared alumina filters with the ability to prevent CO_2 gas flow by modifying silane coupling agents on the porous surface. Various types of silane coupling agents, which were expected to interact with CO_2 gas, were employed in this study.

2. Materials and methods

2.1. Alumina filter fabrication

The fabrication process for the alumina filters was based on a previously employed process [6,7]. α-Al_2O_3 powder (TM-DAR; Taimei Chemicals Co. Ltd., Nagano, Japan) was mixed with 30 vol%

distilled water and 0.62 mass% ammonium poly(acrylic acid) (Celuna D-305; Chukyo Yushi Co. Ltd., Aichi, Japan) using a planetary-type mixer with a stainless steel mesh for 2 min, rotated at 800 rpm and revolved at 2000 rpm. Next, the obtained slurries were slip-cast into 14.6 mm diameter gypsum molds for 5 min, dried overnight at room temperature, and heated at 1000 °C for 2 h. Evaluation of the porosity, mean pore size, and surface morphology of the obtained alumina filter samples were conducted using the Archimedes method, mercury porosimetry (Pascal 240, CE Instruments, Italy) and field emission scanning electron microscopy (FE-SEM, S4500; Hitachi High-technologies Corp., Tokyo, Japan), respectively.

2.2. Surface modification by silane coupling agents

In this experiment, 4 different types of silane coupling agents were employed; Heptadecafluorodecyltrimethoxysilane (FAS17; GE Toshiba Silicon, $(CH_3O)_3Si(CH_2)_2(CF_2)_7CF_3$), Octadecyltrimethoxysilane (ODS; Aldrich, $(CH_3O)_3Si(CH_2)_{17}CH_3$), 3-Aminopropyltriethoxysilane (APTES; momentive performance materials, Japan, $(C_2H_5O)_3SiC_3H_6NH_2$), 3-Ureidopropyltriethoxysilane (Ureido; momentive performance materials, Japan, $(C_2H_5O)_3SiC_3H_6NHCONH_2$). Each silane coupling agent possessed a different function: the fluorocarbon function, the alkyl function, the amino function, or the Ureido function, respectively. The FAS17 or ODS modification and APTES or Ureido modification followed different processes. The chemical vapor deposition process was employed to modify FAS17 or ODS on the surface of porous alumina. The alumina filters were exposed to ultraviolet radiation (λ = 172 nm, UER-20; Ushio Inc.) for 30 min to decompose any organics existing on the alumina surface. Subsequently, the filters were placed in a glass container with 20 μl of ODS or FAS17, and they were heated at 155 °C for 3 h (ODS) or 1.5 h (FAS17). For APTES and Ureido modifications, the alumina bodies were immersed in an ethanol solvent containing 1 mass% of APTES or Ureido overnight, and then, were dried at 100 °C again overnight. Electron probe microanalysis (EPMA, JXA-8200, JEOL) was conducted for all samples after the above processes to confirm whether the silane coupling agents were modified on the alumina surface.

2.3. Gas selectivity measurements

The gas permeability measurements were conducted using the previously described system [9]. The calculations of the gas permeability coefficient used Eq. (1);

$$\mu = \frac{Q}{\Delta P} \cdot \frac{L}{A} \tag{1}$$

where ΔP is the pressure drop between the inlet and outlet of the gas flow as measured by a digital pressure gauge (GC61; Nagano Keiko Co. Ltd., Tokyo, Japan), Q is the gas flow rate measured by a mass flow meter (Model8500; Kojima Instruments Inc., Kyoto, Japan), and A and L correspond to the cross-sectional area and the thickness of the prepared filter, respectively. All processes were conducted under about 20 °C. All the samples were placed under a constant gas flow with a pressure of 0.2 MPa for 30 min prior to the gas flow measurements. During gas flow measurements, all samples were left under each of the measured pressures for approximately 15 min to allow the gas flow to stabilize. The N_2 gas flow was measured first, followed by the measurement of the CO_2 gas flow. This procedure was repeated twice for each sample, and consequently, only small fluctuations in the values of gas permeability were observed.

The gas selectivity, α, is defined as a ratio between the permeability of two different gases as follows:

$$\alpha_{CO_2/N_2} = \frac{\mu_{CO_2}}{\mu_{N_2}}. \tag{2}$$

2.4. Electrical charge calculations

The Mulliken electric charge was subsequently studied using a density functional theory technique with the model compounds. A restricted hybrid nonlocal density function, B3LYP [10] with the 6-311++G(d,p) basis set [11–16] was used in the calculations. The calculation was conducted using the Gaussian 09 program [17].

3. Results and discussions

3.1. Characterization of the filters

The prepared alumina filters were disks with the diameter of 14 cm and the thickness of about 3 mm, as shown in Fig. 1(a). Fig. 1(b) shows the porous microstructures observed using SEM. The porosity and the mean pore size of the unmodified alumina filter were 40% and 74 nm, respectively. The results of EPMA measurements showed that Si atoms were homogenously distributed through the sample, although the atomic ratio between Si and Al (Si/Al) steadily declined as the depth increased (Fig. 2). The Si/Al of the modified filters with ODS and FAS17 was approximately seven times larger than that of the alumina filter before modification, and those of the filters modified with APTES and Ureido were around 10 times larger. This indicates that all types of silane coupling agents were successfully modified on the alumina surfaces (Table 1).

The change in physical properties caused by the modification of silane coupling agents on the porous Al_2O_3 samples was investigated. Fig. 3 shows the microstructure of the porous Al_2O_3 and the porous Al_2O_3 modified by FAS17. Both micrographs show
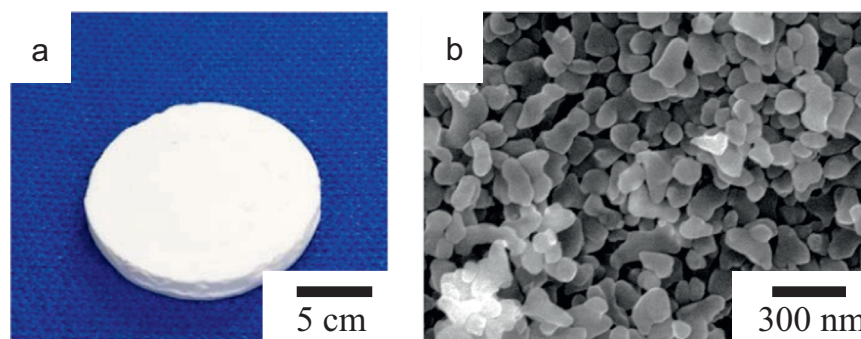

Fig. 1. (a) Photo of a prepared porous alumina filter, (b) SEM image of the porous structure of an alumina filter.