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A titanium carbide-derived novel tetrafluoromethane adsorbent with outstanding adsorption performance

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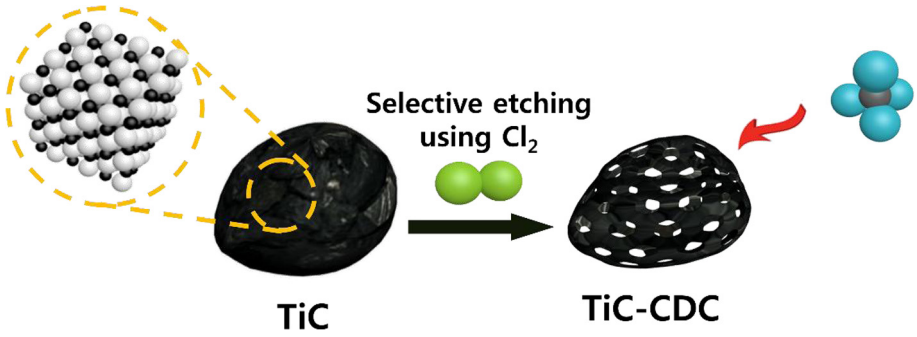
HIGHLIGHTS

- Microporous carbon with uniform pore size was prepared by chlorination of TiC.
- The synthesized microporous carbon showed high CF_4 adsorption capacity.
- Fast adsorption-desorption kinetics and excellent cyclic stability were achieved.
- The effects of textural properties on CF_4 adsorption were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

CF_4, which is widely used in the production of semiconductors and aluminum, has a very high global warming potential and extremely long atmospheric lifetime. Adsorption is an alternative technique to the energy-consuming conventional CF_4 combustion disposal method, and the development of appropriate adsorbents is important for a competent CF_4 adsorption process. Here, microporous carbons are synthesized for new CF_4 adsorbents by the selective etching of titanium carbide using chlorine gas at high temperatures (800, 900, and 1000 °C). Additionally, post-treatment with H_2 eliminates any unreacted chlorine. Interestingly, the CF_4 adsorption capacity has a linear relation with the micropore volume for pores less than 0.9 nm. The titanium carbide-based microporous carbon chlorinated at 800 °C and post-treated with H_2 has the highest CF_4 adsorption capacity of 2.96 mol kg^{-1} at 25 °C and 1 atm, which is the highest reported value to date. Besides the high CF_4 adsorption capacity, the prepared microporous carbon shows a high selectivity for CF_4 over N_2 at low CF_4 partial pressures and an excellent cyclic stability.

1. Introduction

Greenhouse gases have received considerable attention because of their adverse global warming effects that cause climate change issues [1]. CO_2 is considered a major greenhouse gas because it is emitted in large quantities [2]. However, the contribution of other greenhouse gases to global warming is much higher than that of CO_2 based on the mass. For a reasonable comparison, a quantitative value called the global warming potential (GWP) takes into account the amount of heat trapped by a greenhouse gas and its atmospheric lifetime compared to the same amount of CO_2 [3]. This means that gases with high GWP values have a strong

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influence on global warming even when only a small amount is present. Therefore, the disposal of greenhouse gases with high GWPs can effectively mitigate global warming problems. The GWPs on a 100-year time horizon are 25 for methane, 298 for nitrous oxide, 12–14,800 for hydrofluorocarbons, and 7,390–22,800 for perfluorinated compounds [4]. Although much research has been performed for the reduction of CO_2 emissions and for CO_2 sequestration [5–9], there are few studies of greenhouse gases with high GWP values.

CF_4 is a perfluorinated compound and is widely used in semiconductor etching and aluminum production because of its extremely stable structure, non-corrosiveness, and non-flammability [10–12]. With the development of semiconductor industries, it is anticipated that CF_4 usage will continuously increase [13,14]. However, the GWP on a 100-year time horizon for CF_4 is 7,390, and CF_4 has an extremely long atmospheric lifetime of 50,000 years [4]. Therefore, we can expect that the appropriate disposal of CF_4 would be helpful to diminish global warming. Generally, used CF_4 is disposed by a combustion-based thermal treatment and converted into other gases with little to no global warming effects, such as CO_2, COF_2, or HF [15]. However, the combustion method has a very low cost-efficiency because of the severe conditions for CF_4 decomposition, and the additional post-treatment of harmful products is required. In contrast, CF_4 can be treated by alternative methods, such as adsorption, absorption, and membrane separation. Among these approaches, adsorption has many advantages of convenient operation, no harmful byproducts, easy scalability, and low cost [16]. Porous materials, such as zeolites, metal-organic framework (MOF), and activated carbon with a high surface area, are promising for CF_4 adsorption because CF_4 has no dipole or quadrupole moments that could induce interactions with specially designed functional groups [17,18]. Recently, the adsorption of fluorinated gases, including CF_4, has been studied using porous materials. Motkuri et al. studied fluorocarbon adsorption using two different types of MOFs and found the relationship between the adsorption capacity and the properties of the MOFs [19]. MDOBDC (M = Ni or Co; DOBDC = 2,5 dioxido-1,4-benzenedi carboxylate) with open metal sites showed a high adsorption capacity (4.58 mol kg^{-1}) for dichlorodifluorocarbon at low relative vapor pressure of 0.01, because the open metal sites played a crucial role in the adsorbate–adsorbent interaction. MIL-101 (M = Cr; MIL: Materials of Institut Lavoisier) with a hierarchical pore structure preferentially adsorbed fluorocarbon in small pockets rather than in mesopores. Both MOFs showed a higher adsorption capacity for fluorocarbons with a higher boiling point, and the adsorption capacity for CF_4 was low due to its low boiling point. Among various fluorocarbons, partially chlorofluorinated methane has higher boiling point than fully substituted one because of its polarity. When fluorocarbons having similar polarity are compared, fluorocarbon having high molecular weight also has high boiling point. Chen et al. synthesized mesoporous fluorinated MOFs and evaluated their adsorption capacity for various fluorinated gases [20]. A fluorinated MOF called MOFF-5 was prepared using a fluorinated aromatic tritopic ligand; the mesoporous MOF with a fluorine-induced highly polarized cavity had a lower adsorption capacity for CF_4 and SF_6 than that for larger gases, such as C_6F_{14}. Recently, our group developed microporous carbons from the carbonization of poly(vinylidene fluoride) and found that microporous carbons with a large specific surface area were good candidate materials for CF_4 adsorption [21]. However, once the specific surface area is sufficiently high, the pore size may also be important to increase the gas adsorption capacity [22]. After industrial usage (as CF_4 is usually emitted in an acidic condition), the chemical stability of the adsorbent is important for the practical application to CF_4 capture [23]. Activated carbons are more chemically durable than zeolites and MOFs; therefore, porous carbons are expected to be relevant for the industrial application of CF_4 adsorption. However, increasing the surface area with simultaneous control of the pore size is challenging for a carbon-based adsorbent [24]. Recently, the pore size of carbide-derived carbons was shown to be easily tuned by selective etching using halogen gas or a further post-synthesis treatment in the preparation procedure [25,26].

Here, we developed microporous carbons with a large surface area and controlled pore size based on the chlorination of titanium carbide (TiC) and tested the materials for CF_4 adsorption. Chlorination at different temperatures and post-treatment with H_2 were applied in the preparation procedure, and their effects on the physical properties and CF_4 adsorption performance were investigated. TiC-derived carbon (TiC-CDC) is known to have more uniform pore size with high specific surface area than other carbide-derived carbons (CDCs) and its pore size distribution can change with controlling chlorination temperature [27,28]. This is the first time that TiC-CDC was applied to CF_4 adsorption and the relation of pore size with CF_4 adsorption was investigated. The characterization of TiC-CDC was performed using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray (EDX) spectroscopy, and Raman spectroscopy. N_2 adsorption analysis was conducted to obtain the textural properties of TiC-CDC. The CF_4 adsorption behaviors, such as the adsorption isotherms, kinetics, and cyclic adsorption–desorption stability, were scrutinized by volumetric and gravimetric adsorption analysis.

2. Experimental section

2.1. Synthesis of titanium carbide-derived carbon

To prepare TiC-CDC, TiC powder (Kojundo Chemical Laboratory, Japan, 99%, 2–5 μm particle size) was scattered in an alumina boat, and the alumina boat was placed in a horizontal tubular furnace. The furnace was heated at a rate of 6 °C min^{-1} with 180 mL min^{-1} Ar flow until a targeted chlorination temperature was reached. The selective etching process based on the reaction with chlorine gas was performed at three different chlorination temperatures of 800, 900, and 1000 °C for 4 h under a mixture flow of 10 mL min^{-1} Cl_2 and 180 mL min^{-1} Ar. To remove the remaining chlorine, the TiC-CDCs were cooled to 800 °C at a rate of 6 °C min^{-1}, and then an additional post-treatment reaction with H_2 was performed under the mixture flow of 10 mL min^{-1} H_2 and 180 mL min^{-1} Ar for 30 min at 800 °C. After the treatment, samples were cooled by exposure to room temperature [29]. The only chlorinated TiC-CDC is denoted as TiC-CDC*x*, and the TiC-CDC further treated with H_2 after chlorination is denoted as TiC-CDC*x*H, where *x* indicates the chlorination temperature.

2.2. Characterization of samples

Scanning electron microscopy (SEM, S-4300, Hitachi) and high-resolution transmission electron microscopy (HR-TEM, G2 F30ST, Tecnai) were used to investigate the morphologies of TiC, TiC-CDCs, and TiC-CDCHs. The change of the crystal structure of samples was analyzed by X-ray diffraction (XRD, X'Pert MPD, Philips) with Cu Kα radiation in the 2θ range of 3–80°. To detect the change of the elemental composition in samples after the chlorination and H_2 treatment, energy dispersive X-ray spectroscopy (EDX, EX-200, Horiba) was used. Defect formation and transition of the sp^2 and sp^3 hybridization in samples were confirmed using micro-Raman spectroscopy with the 532 nm line of a DPSS laser (Omicron) at room temperature, where the beam size at the sample was approximately 3 μm. The textural properties of the