The Transitional Transmittance Response of ZIF-8 Gas Adsorption Observed Using Terahertz Waves*

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In this study, we recorded the transitional response in terms of terahertz transmittance of zeolitic imidazole framework-8 [Zn(2-methylimidazolate)$_2$, ZIF-8] at 2.0 THz as a function of exposure time to gaseous propane and n-butane. The transmittance at 2.0 THz increased as gas adsorbed onto the ZIF-8. Conversely, during a nitrogen purge, transmittance decreased as the alkane gas desorbed. We estimated time constants for the adsorption and desorption of the two gases by comparing the plots of their responses. We also demonstrated the potential of using a combination of ZIF materials and terahertz technology as a novel gas analyzer. [DOI: 10.1380/ejssnt.2018.142]

Keywords: Porous solids; Adsorption kinetics; Infrared absorption spectroscopy; Terahertz vibration; Metal-organic frameworks

I. INTRODUCTION

A metal-organic framework (MOF) is a porous material composed of metal ions and organic ligands. MOFs can be used to store, separate, and discriminate among gas molecules. ZIF-8 is a MOF that has several interesting characteristics including the gate-opening or swing effect. Specifically, ZIF-8 gate-opening involves the twisting of all 2-methylimidazolate ligands, which increases pore volume and enlarges pore apertures. ZIF-8 can also adsorb several gas species, including propane and n-butane, at room temperature and atmospheric pressure [1].

A terahertz (THz) wave is defined as an electromagnetic wave that ranges in frequency from 10$^{11}$ Hz to 10$^{13}$ Hz (3–333 cm$^{-1}$). We designed experiments to investigate the gas adsorption properties of MOFs, based on the assumption that inter- and/or intramolecular vibrations related to gas adsorption by MOFs can be measured using terahertz spectroscopy. Then we used these experiments to observe the 2.0-THz vibration of ZIF-8 [2–4], and assigned the vibration to the swing motion of 2-methylimidazole (i.e., gate-opening) [4].

In this study, the transitional transmittance response of ZIF-8 at 2.0 THz was recorded as a function of time during alternate exposures to propane or n-butane and nitrogen. This was to consider the feasibility of using MOFs combined with terahertz technology as gas analyzers.

ZIF-8 was deposited on a thin polytetrafluoroethylene (PTFE) membrane filter (T300A013A; Advantec, Tokyo, Japan) by filtering the suspension. The absorbance of the PTFE membrane filter in the terahertz range is negligible [5]. Solid ZIF-8 (typically 5–5.5 mg as a disk of diameter ca. 8 mm) that remained on the membrane filter was positioned in a tube with windows. The inner volume of the tube was ca. 6 mL. The specimen in the tube was dried under vacuum for 12 h at 373 K to remove residual methanol. The tube was then set in the sampling point of the terahertz spectrometer. Thin polymer films were used as a window material, as they are transparent in the terahertz frequency range. In this study, terahertz absorption spectra in the range of 1–6 THz were measured at room temperature and atmospheric pressure using a terahertz spectrometer (model TSS-I; Terahertz Laboratory, Akita, Japan) [6–11]. The typical diameter of the terahertz beam was 0.85 mm at 2 THz. ZIF-8 in the sample tube was exposed alternately to nitrogen (99.9995%; Japan Fine Products, Kawasaki, Japan) and propane (99.5%; Takachiho Chemical Industrial, Tokyo, Japan), or n-butane (99.0%; Takachiho Chemical Industrial) for 20 min each. We used a gas flow rate of 50 mL/min, which was controlled using a float-type flowmeter (scaled for N$_2$).

II. EXPERIMENTAL

First, powdered ZIF-8 (7.2 mg, Basolite® Z1200; Sigma-Aldrich) was suspended in methanol (1 mL). Then

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III. RESULTS AND DISCUSSION

Figures 1 and 2 show the transmittance of ZIF-8 at 2.0 THz as a function of time with alternating exposure to propane/N$_2$ (Fig. 1) and n-butane/N$_2$ (Fig. 2). The vertical axes of these figures indicate normalized transmittance, which is the transmittance divided by the initial transmittance. Closed triangles indicate the introduction of alkane, and open triangles indicate the introduction of N$_2$. When the atmosphere was switched to N$_2$, alkane desorbed from ZIF-8. It was previously reported that N$_2$ does...
not adsorb onto ZIF-8 under these conditions [12]. The adsorption and desorption of alkanes on and from ZIF-8 are recorded in Figs. 1 and 2. Changes in transmittance were synchronized to changes in the gas; plateau values were constant. This implies that ZIF-8 pores were completely refreshed during the N\textsubscript{2} purge and completely recovered to the initial condition over at least several cycles. We estimated time constants for the adsorption process of the alkane gas ($\tau_0$) from the slope of the time profiles following gas introduction using the following equation:

$$\frac{(T - T_0)}{(T\infty - T_0)} = 1 - \exp(-t/\tau_0).$$  \hfill (1)

In this equation, $T$ is the transmittance, $T_0$ is the initial transmittance at the introduction of test gases [$T_0 = T(t = 0)$], $T\infty$ is the final transmittance after reaching the plateau [$T\infty = T(t = \infty)$], and $t$ is time. Similarly, the time constant for the gas desorption process ($\tau_d$) was estimated using Eq. (2):

$$\frac{(T - T\infty)}{(T_0 - T\infty)} = \exp(-t/\tau_d).$$  \hfill (2)

The values of $\tau_0$ and $\tau_d$ for propane and $n$-butane are summarized in Table I. These values may vary depending on experimental conditions such as temperature and pressure. As displayed in Table I, values of $\tau_0$ were almost the same for propane and $n$-butane. This implies that the height of the potential barrier during adsorption onto ZIF-8 was similar for the two alkanes. Both alkanes are short-chained, straight molecules, and the only obstacle to adsorption is to pass through the pore aperture. This is probably why their $\tau_0$ values are similar. However, $\tau_d$ of $n$-butane was much greater than that of propane. In contrast to the adsorption process, desorption is a multi-step process. An adsorbed molecule has to first get away from the pore wall and then pass through the aperture. The first step is directly affected by the affinity of the adsorbate to the inner wall of the pore. The presented results suggest that $n$-butane has a higher affinity to the inner wall of the pore than does propane. In other words, relative to propane, $n$-butane requires a greater amount of energy to desorb from the inner wall of the pore.

### IV. CONCLUSION

We successfully estimated time constants for gas adsorption and desorption onto and from ZIF-8 by fitting the transitional response in terahertz transmittance to an exponential curve. Values of $\tau_d$ were quite different for propane and $n$-butane; however, values of $\tau_0$ were similar for the two gases. This reflects differences in the affinity of ZIF-8 between propane and $n$-butane. Our results indicate that propane and $n$-butane can be successfully discriminated using a combination of MOFs and terahertz waves. Several authors have suggested that MOFs can be used in gas sensing [13–15]; our study implies that the time constant for the adsorption/desorption process,

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**TABLE I. $\tau$ after the introduction of alkanes and N\textsubscript{2} (27°C)**

| Gas     | $\tau_0$ (s) | $\tau_d$ (s) |
|---------|--------------|--------------|
| Propane | 12–20        | 9–20         |
| $n$-Butane | 10–23     | 170–177     |
which can easily be obtained using terahertz technology, is another key parameter for discriminating among gas molecules within such sensors.

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