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Perspectives on NMR studies of CO_2 adsorption

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ABSTRACT

There is a consensus about a long-term goal of a carbon-neutral energy cycle, but the CO_2 emissions to the atmosphere are currently very large. Carbon Capture and Storage (CCS) technologies could allow a transformation of the global energy system into a carbon-neutral one and simultaneously keeping the temperature rises within agreed bounds. The CO_2 separation step of CCS is, however, very expensive, and adsorption-driven technologies have been put forward as alternatives. Hence, a recent focus has been on studying solid adsorbents for CO_2, which include activated carbons, zeolites, metal-organic frameworks, and amine-modified silica. In this context, we summarize the literature concerning CO_2 sorption studied with Nuclear Magnetic Resonance (NMR), outline selected NMR methods, and present an outlook for further studies.

1. Introduction

Anthropogenic emissions of CO_2 contribute to global warming, and it is generally agreed on the need for significant reductions [1]. This situation has motivated research into Carbon Capture and Storage (CCS) [2]. In most projections, CCS is judged to be needed even if renewable energy alternatives are adopted at scale [1]. However, CCS has been difficult to put into place because of legislative reasons, public perception when it comes to long-term storage of CO_2, and the significant costs to capture CO_2. With suitable adsorbents [3], adsorption-driven capture of CO_2 has thermal advantages over today's amine scrubbers and, hence could reduce the cost of capture. Adsorption-driven CO_2 capture is judged to be at an intermediate level of readiness, in contrast to the well-developed scrubbers and blue-sky membrane systems [4].

The thermal advantages of adsorption-driven capture over CO_2 scrubbing relate to the relative low heat capacities for solids sorbents, and only small needs to evaporate water during recycling. The use of solid sorbents would also reduce the risks for potentially harmful emissions of amines, and amine decomposition products; however, challenges exist for adsorption-driven capture of CO_2 from flue gas. For a 500 MW coal-fired power plant, the mass flow of CO_2 is ~500 tonnes/h at a CO_2 concentration of ~15%. The swing cycles for the regeneration of sorbents need hence to be ultrarapid, maybe at the scale of ~1–2 min to avoid very large installations. Temperature- and vacuum-swing adsorption processes are more suitable than pressure-swing adsorption processes, which operate at elevated pressures.

The separation of CO_2 from biogas, natural gas, and directly from the air, is also actively researched. Such separation can be performed in several ways, which include membrane separation processes, cryogenic distillation, and adsorption- or absorption-driven processes. Membrane processes and cryogenic distillation are competitive for biogas upgrading but appear to be insufficient for post-combustion capture of CO_2 due to the very significant mass flows.

For adsorption-driven separation of CO_2 from gas mixtures, the properties of the adsorbents are important and numerous different compounds are researched. These include activated carbons, zeolites, metal organic frameworks (MOFs), porous polymers, and amine-modified sorbents [5–9]. Fig. 1 presents MOF-74 (Mg) and zeolite 13X, which are both often studied for applications involving CO_2 separation.

Irrespectively of the gas mixture, it must be remembered that CO_2 adsorbents operate with their large capacity to adsorb CO_2 from gas mixtures either with (chemisorption) or without (physisorption) the formation of chemical bonds. Chemisorption of acidic CO_2 molecules relies on Lewis or Brønsted acid-base chemistry. In addition, CO_2 has a large electric quadrupole moment, which interacts with the electric field gradients (EFGs) in the sorbents. In physisorption of CO_2, the interaction of the EFGs with the electric quadrupole is often the dominating form of molecular interaction. Sites with large EFGs have large isosteric heat of sorption of CO_2 ($Q_{st} = -\Delta H$); adsorption is an exothermic process. There are several studies investigating the optimal values of Q_{st} for CO_2 capture, and they appear to fall in the region of about 40–60 kJ/mol,

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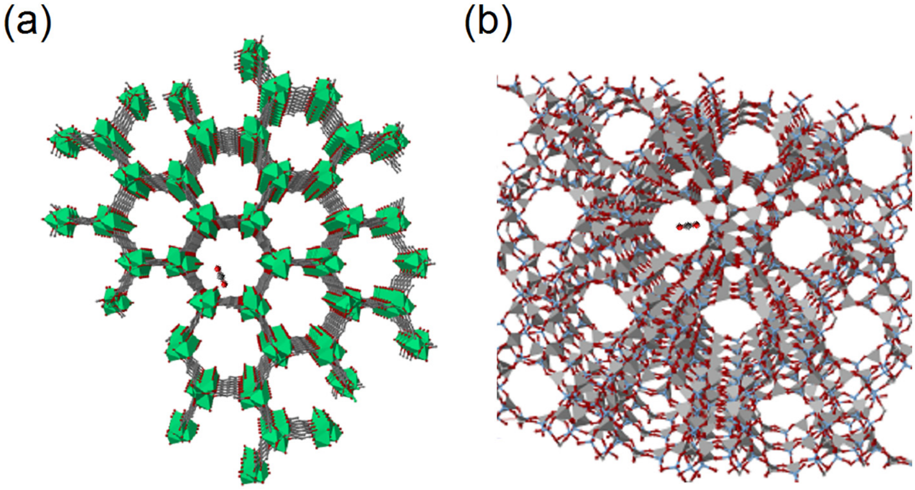

Fig. 1. Promising CO_2 sorbents for physisorption. (a) MOF-74 (Mg) and (b) zeolite 13X (oxygen – red, magnesium containing clusters – green, carbon – dark grey, silicon – grey, aluminum – blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

see for example the study of Lin et al. [3] This region of Q_{st} covers both strong physisorbents and weak chemisorbents. Furthermore, a high value of Q_{st} is preferred when the concentration of CO_2 is low, as it is in the flue gas of natural gas-fired power plants. Even higher values of Q_{st}s are relevant for adsorption-driven capture of CO_2 capture from the air [10]. For physisorbents, the total capacity of CO_2 sorption relates to the micropore (pores smaller <2 nm) or ultramicropore volume (pores smaller <1 nm) [11], as well as to the Q_{st} [3]. Note that for ultramicroporous solids, the concepts of adsorption and absorption start to merge as CO_2 interacts with multiple sites in very small pores [12]. For chemisorbents, the number of basic sites defines the capacity. Mesopores (2–50 nm) are not filled with CO_2 at the relevant process conditions for adsorption-driven separation of CO_2, but are of potential importance to facilitate an effective mass transport.

This review summarizes how nuclear magnetic resonance (NMR) spectroscopy provides detailed molecular-level information on dynamics and diffusion of CO_2, and information on the local structure, interactions, and sorbent-CO_2 chemistry with a focus on recent studies. We also highlight a few areas where further studies could be performed to clarify the chemistry, physics, and engineering important to the development of CO_2 sorbents.

2. NMR methods

There is a wide array of NMR methods that are suitable to study molecular and mesoscopic aspects of physi- or chemisorbed CO_2. Some are briefly described below.

2.1. Pulsed field gradient (PFG) NMR to study diffusion

Pulsed field gradients (PFGs) are integrated into NMR and magnetic resonance imaging (MRI) techniques to measure spatial distributions of molecules, molecular displacements, and select coherence pathways. Pulsed gradient spin echo NMR (PGSE NMR) [13••,14] allows measurement of diffusion and flow processes on the time scale of milliseconds to seconds. These methods (which are also referred to as PFG NMR) are widely used to study flow and diffusion in rocks and other macroporous materials [15], food stuffs [16,17], other colloidal systems [18] and in micro- and mesoporous materials [19–21].

The key elements in a PGSE pulse sequence, which encodes for diffusion, are two gradient pulses with a duration δ and amplitude G, and the diffusion time $\varDelta$. The latter is defined as the time between the leading edges of the gradient pulses. The diffusion-weighting factor b is defined as $\gamma^2 G^2 \delta^2 (\varDelta\text{-}\delta/3)$, where γ is the gyromagnetic ratio of the NMR-active nucleus being probed. It is generally expressed at a constant Δ for increasing G. The self-diffusion coefficient D is extracted by minimizing the sum of the squares of the deviation of the b-dependent recorded signal S_{exp} and $S = S_0 \exp(-bD)$, where S_0 is the signal intensity in the absence of a gradient ($b = 0$). In a Stejskal-Tanner representation [13••] with a semi-logarithmic plot of the attenuation of S_{exp}, shown in Fig. 2b, isotropic self-diffusion results in a straight line with a slope of $-D$. Furthermore, a PGSE experiment might be composed of a spin echo [22] or a stimulated echo [14]. Importantly, S_{exp} is not only attenuated by diffusion but also by the longitudinal and transverse relaxation times T_1 and T_2. The spin echo is sensitive to T_2, while the stimulated echo is sensitive to both T_1 and T_2. The T_1 and T_2 of spin $I = 1/2$ nuclei in gas molecules adsorbed on solids might be on the order of milliseconds, leading to a strong attenuation and low signal-to-noise ratio of S_{exp} due to relaxation. For very small T_1 and T_2 values, only a small δ and/or a small $\varDelta$ can be used which necessitate that the gradient amplitudes are strong for the S_{exp} to be attenuated by one or two orders of magnitudes with respect to S_0. Larger gradient amplitudes are furthermore required for ^{13}C than for ^1H, as $(\gamma(^{13}C)/\gamma(^1H))^2 = 0.063$. Due to hardware limitations, large G values may produce potential artifacts in relation to mismatched gradients [23]. In addition, other sample- and B_0 field-dependent artifacts arise from the inherent static gradients that occur due to magnetic susceptibility differences between solid sorbents and gas, which can be minimized by using specific pulse sequences [24]. Importantly, the heat conductivities of porous solids are low and special means should be taken to calibrate the actual temperatures of the solid-gas systems. Small samples are needed for temperature-dependent studies to guarantee a constant temperature throughout the measurement region.

Molecular diffusion of adsorbates in solid sorbents can occur as being depicted in Fig. 2a. It includes diffusion within and between the sorbent particles/crystals, which is denoted as intercrystalline and intracrystalline diffusion. Depending on the size of the crystal, adsorbed molecules might diffuse within the crystal or diffuse as gas molecules between the crystals during the diffusion time $\varDelta$. When the exchange rate of adsorbed and gas molecules is slow, with respect to the diffusion time $\varDelta$, the data (S_{exp}) might be analyzed with a two-site model $S = S_0(f_{intra}\exp(-bD_{intra}) + f_{inter}\exp(-bD_{inter}))$ where the f_{intra} and f_{inter} are the fraction of the molecules diffusing within and between the crystals. Depending on the values of f_{intra}, $f_{inter,}$ and D_{intra}/D_{inter}, a distinct biexponential attenuation of $S_{exp}(b)$ decay may occur as is shown in Fig. 2b. Note that f_{intra} and f_{inter} typically need to be corrected for effects of T_1 and/or T_2 to have a meaning. The intracrystalline diffusion in a so-called 8-ring channel is illustrated as a function of the $\varDelta$ in Fig. 2d (bottom panel), and it is typically many orders of magnitudes slower than the intercrystalline or free molecular gas diffusion.