International Journal of Greenhouse Gas Control 55 (2016) 36–41

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

IR emitting Dy^{3+} doped chalcogenide fibers for *in situ* CO_2 monitoring in high pressure microsystems

Florent Starecki[a], Sandy Morais[b], Radwan Chahal[a], Catherine Boussard-Plédel[a], Bruno Bureau[a], Fabien Palencia[b], Carole Lecoutre[b], Yves Garrabos[b], Samuel Marre[b,*], Virginie Nazabal[a,*]

[a] Institut Sciences Chimiques de Rennes, Equipe Verres & Céramiques – UMR-CNRS 6226 Université de Rennes 1-CNRS, F-35042 Rennes, France
[b] CNRS, Univ. Bordeaux, ICMCB, F-33600 Pessac, France

ARTICLE INFO

Article history:
Received 29 April 2016
Received in revised form 1 September 2016
Accepted 28 October 2016

Keywords:
Carbon dioxide
Microreactors
Geological lab-on-chip
Optical absorption spectroscopy
Chalcogenide glass and fiber
Rare earth infrared luminescence

ABSTRACT

This paper reports the carbon dioxide detection in silicon-Pyrex high pressure microfluidic devices mimicking geological conditions encountered in deep saline aquifers using an *in situ* infrared optical sensor. The middle infrared source inserted inside the microchannel is based on infrared emission from Dy^{3+} sulfide glass fibers. The broad emission of the Dy^{3+} doping in infrared fibers is used to directly probe the CO_2 thanks to the perfect overlap between the rare earth emission centered at 4.4 μm and the CO_2 absorption band located at 4.3 μm. CO_2 and water were clearly distinguished when using segmented flow on chip at pressures ranging from 4.5 to 6 MPa. These results demonstrate the feasibility of the infrared optical detection of other gases displaying absorption bands in the middle infrared domain for further developments of gas sensors, which can find applications in geological media monitoring and microfluidics.

1. Introduction

Carbon dioxide capture and storage (CCS) is planned to be performed at a large scale, and remains an appropriate long-term option for the reduction of this greenhouse gas concentration in the atmosphere (Lucier and Zoback, 2008). CO_2 can be typically stored in deep geological formations (carbon Geological Storage – CGS) including depleted coal, oil or gas fields or saline aquifers at depths below one kilometer, where the typical temperature and pressure conditions are in the range 30–80 °C and 5–20 MPa (Carr et al., 2005). Mostly demonstrated on shore, CO_2 injection demonstrations were also performed offshore at lower depths, (Mori et al., 2015) to investigate the environmental impact of CO_2 seeping from the seafloor. Indeed, one of the major issue related to these CGS strategies remains the safety of the storage location. It is therefore critical to be able to monitor for a long-term period the entire reservoir, from the wells to the deep underground geological formation in order to detect leaks occurring during the CO_2 injection or appearing during the storage. Such monitoring requires adapted tools working in such conditions (Chadwick et al., 2006). Optical probes have been demonstrated to be candidates of choice for these types of applications. Some example includes the development of a marine sedimentary optical pH profiler (Quieros et al., 2015) to quantify – for instance – the CCS impact on the ocean's acidification. Similarly, an optical fiber system operating at 1.55 μm was recently developed to monitor the CO_2 solubility in aqueous phase above the seafloor (Hingerl et al., 2014). This sensor is based on the CO_2 reaction with the silica fiber cladding, shifting the evanescent wave attenuation. Although the operating pressure was limited to 2.4 MPa in these experiments, it demonstrates the wide interest for these applications. Still, storage areas monitoring at reasonable costs remain a challenge. The requirements and current challenges associated with for such sensors are: the monitoring of wide covered areas (combining multiple measuring heads), a high reliability, a reasonable sensitivity and response time and a compatibility with the pressure and the temperature operating conditions.

The investigation of the processes related to CO_2 storage are mostly performed at reservoir scale, leading to poor understanding of the mechanisms occurring at small pore scale. Meanwhile, microfluidic tools have been extensively used over the past 15 years for chemical synthesis processes (Hartman and Jensen, 2009; Jensen et al., 2014), biology (Duncombe et al., 2015; El-Ali et al., 2006) and materials science (Marre and Jensen, 2010) due to their fast equilibrium times, allowing a better control of the process and less risky manipulations due to smaller volumes. Recently, the

* Corresponding authors.
E-mail addresses: samuel.marre@icmcb.cnrs.fr (S. Marre), virginie.nazabal@univ-rennes1.fr (V. Nazabal).

http://dx.doi.org/10.1016/j.ijggc.2016.10.015
1750-5836/

development of high pressure microfluidics (Marre et al., 2010) has opened ways for researchers to use microfluidics approaches mimicking geological conditions. These geological labs on chip approaches have proved to be powerful methods to study multiphase flows in porous media at lab scale using model microsystems (micromodels) (Morais et al., 2016; Gunda et al., 2011). Such approaches are directly complementary to conventional core scale approaches used by geoscientists (Perrin et al., 2009). Additionally, the advantage of having an optically transparent device provides means to access data, which cannot be obtained through conventional tools (*e.g.* fluid repartition in the porous structure, diffusion properties, solubility measurements, *etc.*), and which can later be used in modelling studies at larger scale. Therefore, experimental works aiming and developing new characterization tools at their implementation into these devices are currently performed (Beuvier et al., 2015). Optical spectroscopy techniques have already been widely used in microfluidics devices including Raman (Liu et al., 2012; Dochow et al., 2013) or UV–visible (Yue et al., 2013). For instance, the quantification of the CO_2 dissolved in water in microfluidic systems was demonstrated using confocal Raman spectroscopy, by comparing the CO_2 Fermi dyad band intensity to the water stretching band intensity (Liu et al., 2012). Another optical system was used to distinguish either water or CO_2 flows in the microchannel, using refractive index variation as detection technique (Burton et al., 2014). The refractive index shift induced by media changes from water to CO_2 is detected on the sensor tip using the light intensity variation due to the Fresnel reflection property. This optical technique - sensitive to medium changes - cannot easily quantify the amount of CO_2 flowing in the microsystem. However, only few studies have reported the development of tools for microscale investigations operating in the near and middle infrared (mid-IR) region, where CCS gases such as CO_2, CO, NO_x or SO_x exhibit absorption bands. Interestingly, this spectral range matches with some rare earth luminescence, which enables developing detection strategies.

In recent years, IR spectroscopy has proved to be a simple, reliable, relatively fast and cost-effective technique for analyzing complex media, creating unique molecular fingerprint. It is used in several research and industrial areas, from quality control to forensic analysis with non-compact IR spectroscopic systems. However, although the use of mid-IR spectroscopy coupled to microfluidics systems has been demonstrated (Perro et al., 2016; Wagner et al., 2011; Kise et al., 2014; Chan et al., 2010; Pan et al., 2004), it is still challenging because the materials parts used during the fabrication of the microreactors have to be transparent in the IR region and have to exhibit good chemical compatibilities with the flowing medium to analyze.

Nevertheless, some *in situ* technological solutions exist and mid-IR spectroscopy based on the use of fibers probes or waveguides (Bureau et al., 2015; Lu et al., 2015) have addressed part of these issues as they can be miniaturized (Kim et al., 2007) and integrated directly within a microreactor. These probes are made of either chalcogenide glasses (Sanghera et al., 2009; Chahal et al., 2016; Singh et al., 2014; Charrier et al., 2012; Ma et al., 2015; Ganjoo et al., 2008; Anne et al., 2009; Starecki et al., 2015; Bureau et al., 2014), germanium (Chang et al., 2012), gallium arsenide or silver halides (Eyal et al., 1996; Charlton et al., 2005). However, to date, most of the microscale devices (microreactors, micromodels) integrated with mid-IR characterization techniques – considering either transparent microreactors options or *in situ* integrated fibers or waveguide ones – are limited to the normal range of pressure and temperature, thus drastically reducing the number of covered applications.

High pressure compatible mid-IR probes could therefore be used for liquid probing or gas sensing including applications in Carbon Capture and Storage since most of the "CCS gases" (CO_2, CO, NOx, SOx, H_2S, *etc.*) exhibit absorption bands in the mid-IR domain.

IR optical detections are commonly performed by means of black body sources, temperature dependent, with low brightness and strongly influenced by the surrounding. In case of geological probes and microfluidic systems, excitation sources could be favorably replaced by trivalent rare earths ions 4f-shell transitions generating light from UV to mid-IR, depending on their host and intrinsic energy scheme. Glasses with low phonon energy are required to ensure the infrared optical transmission and the rare earth emission efficiency. Among some other candidates, the germanium based sulfide glasses fulfil these requirements. These rare earth (RE) doped glasses are providing low costs mid-IR sources, at discrete wavelengths with emission bandwidth of at least 100 nm due to distortions of the electrical field in a glass matrix. Such characteristics outperform blackbody sources in terms of fluency and compactness, and make these sources much cheaper than infrared supercontinuum lasers, showing promising results in developing new mid-IR laser sources (Kubat et al., 2014). These RE fiber sources are well suited for IR absorption spectroscopy, while meeting the concerns of miniaturization for their further integration into microfluidic systems.

We demonstrate in this study an *in situ* mid-IR optical probe to detect carbon dioxide in high pressure microreactors. The presence of CO_2 is directly detected by means of Dy^{3+} sulfide glass fiber luminescence. We had previously demonstrated that the Dy^{3+} doped GaGeSbS fiber luminescence can be successfully used for the CO_2 gas detection at low pressure. For this specific application, the CO_2 detection threshold was fixed in the range of 400–1000 ppm. This optical sensor exhibits a good temporal response and time stability, a very high robustness suitable for efficient commercial sensor. Additionally, some field operations have been presented and consisted in measurements performed in 100 m deep wells, making this macroscopic optical sensor suitable for on-the-field operations in order to monitor geological reservoirs (Starecki et al., 2015). One of the main challenge was to develop a Dy^{3+} mid-IR sensor allowing *in situ* measurement under high pressure in microreactors. After discussing the design and the microfabrication procedure of the microreactor along with the detector principle, the integration of the mid-IR optical probe into the microfluidic device will be presented. The detection of either water or carbon dioxide is then demonstrated in dynamic conditions and the potentialities of this detector are discussed.

2. Materials and methods

2.1. High pressure microreactors and set-up

Among the existing on chip microfluidic devices capable of handling high pressure, the silicon/Pyrex microreactors were used in here (Marre et al., 2010). The flexible microfabrication of silicon through photolithography, wet etching and further anodic bonding to Pyrex allows designing proper geometries to implement fluid analysis monitoring tools, such as optical fibers. The general microreactor design is shown in Fig. 1.

It consists of a U-shape microchannel (width, w = 300 μm, depth, d = 200 μm) implemented with a detection area aiming at positioning the optical fibers thanks to two perpendicular guiding channels (w = 350 μm, d = 200 μm). The microreactor was integrated into a general set-up consisting of two high pressure piston pumps (ISCO 100DM), a coflow generating system (a small capillary inserted in a larger one through a T-junction), which was used to generate CO_2/water segmented flows upstream the microreactor. A back pressure regulator (BPR) was placed downstream to control the pressure in the range 4.5–6 MPa. An additional on/off valve was mounted between the inlet and outlet of the microreactor