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Nanocomposite sodalite/ceramic membrane for pre-combustion CO_2 capture: synthesis and morphological characterization

Michael O. Daramola[1] · Olawale Oloye[1] · Abu Yaya[2]

Abstract Carbon capture and storage (CCS) is amongst the possible options to reduce CO_2 emission. In the application of CCS, CO_2 capture techniques such as adsorption and membrane system have been proposed due to less energy requirement and environmental benign than the absorption process. However, membrane system has drawbacks such as poor membrane reproducibility, scale-up difficulty and high cost of the membrane supports. In this study synthesis and characterization of nanocomposite sodalite (HS)/ceramic membrane via "pore-plugging" hydrothermal synthesis (PPH) protocol for pre-combustion CO_2 capture is reported. The morphology and crystallinity of the as-prepared membranes were checked with scanning electron microscopy and X-ray diffraction. Surface chemistry of the membrane was examined with Fourier Transform Infrared spectroscopy. In nanocomposite architecture membranes, zeolite crystals are embedded within the pores of the supports instead of forming thin-film layers of the zeolite crystals on the surface of the supports. Compared to the conventional in situ direct hydrothermal synthesis, membranes obtained from PPH possess higher mechanical strength and thermal stability. In addition, defect control with nanocomposite architecture membranes is possible because the zeolite crystals are embedded within the pores of the support, thereby limiting the maximum defect size to the pore size of the support. Furthermore, the nanocomposite architecture nature of the membranes safeguards the membrane from shocks or abrasion that could promote formation of defects. The aforementioned advantages of the nanocomposite architecture membranes could be beneficial in developing high performance and cost-effective membrane materials for pre-combustion CO_2 capture.

Keywords Nanocomposite · Sodalite · Membrane · Carbon capture and storage

1 Introduction

Investigations have shown that greenhouse gases (GHG), such as carbon dioxide (CO_2), is the cause of global climate change and other related environmental disasters. In sub-Saharan Africa, industrial activities such as coal-fired power plant for the generation of electricity, mining activities, production of cement, coal mining and steel production will generate large quantity of CO_2 to the atmosphere. Numerous strategies are being applied today to mitigate continuous emission of GHG, some of which include, energy efficiency in electrical appliances, renewable energy; wind, tidal, solar, water energy, geothermal and biomass, nuclear energy, less carbon intensive sources; natural gas and hydrogen fuels, increase in biological sinks; forestation and carbon sequestration which enables the continuous use of fossil fuels (IPCC 2005). From these available options, carbon sequestration occurs to be a renewable and sustainable form with great potentials. Carbon sequestration mostly known as carbon capture and

✉ Michael O. Daramola
   michael.daramola@wits.ac.za

1 School of Chemical and Metallurgical Engineering, Faculty of Engineering and the Built Environment, University of the Witwatersrand, Wits, Johannesburg 2050, South Africa

2 Department of Materials Science & Engineering, School of Engineering Sciences, University of Ghana, P.O Box LG 77, Legon, Accra, Ghana

storage which can best be described as a technology in which CO$_2$ is separated from other gases either from mobile or stationary point source. The captured CO$_2$ is then compressed, transported and stored either in a geological formation, ocean storage or used industrially as a chemical feedstock (Pires et al. 2011).

Amongst the capture approaches, pre-combustion CO$_2$ capture provides opportunity for economic feasibility of the application of membrane system due to the high pressure of CO$_2$ in the gas mixture. In a pre-combustion setup, the fuel (coal) is partially oxidized with oxygen (O$_2$), air or steam to liberate carbon monoxide (CO) and hydrogen (H$_2$) in a chemical process known as reforming. A further shift reaction of carbon monoxide and hydrogen liberates carbon dioxide (CO$_2$) and hydrogen (H$_2$). This occurs in a water gas shift (WGS) reactor where the CO$_2$/H$_2$ gas mixtures can be separated into the individual components. Hydrogen can serve as fuel in a gas turbine combined cycle plant. This technology is employed in Integrated Gasification Combined Cycle (IGCC) for coal gasification. The CO$_2$ concentration in the IGCC is in the range of 35 %–40 % (vol/vol) with a total pressure of about 20 bar or more in the stream leaving the IGCC, forming a good basis for CO$_2$ pre-combustion capture using a membrane system (Olajire 2010). Furthermore, compared to existing technologies like absorption and adsorption, membranes possess noticeable advantages over absorption and adsorption processes, they have simple modular system, no waste streams and no regeneration energy required. Membrane technology eliminates limitations of conventional gas absorption towers and adsorption processes, thus offering high selectivity and high driving force with a simple modular design (Aoki et al. 2000).

Polymer membranes have been extensively studied for CO$_2$ capture, but polymeric membranes are prone to degradation in harsh conditions, making them unsuitable for CO$_2$ capture from flue gas (with contaminants like sulphur (IV) oxide and water vapour) (Kazemimoghadam and Mohammadi 2005); Chung et al. 2007; Olajire 2010). However, zeolite based membrane technology provides CCS with a great numbers of potentials such as chemical inertness, high thermal stability. For example, sodalite-supported membrane systems possess good chemical resistance and high thermal stability than the polymeric membranes. Zeolite membranes are known to be thermally stable up to 450 °C with reasonable mechanical strength, making them materials of choice in catalytic and separation applications (Khajavi et al. 2007; Daramola et al. 2015; Sunita and Sib 2015).

Out of the proposed technologies for CCS, adsorption and membrane systems have been extensively researched because of less energy consumption and environmental friendliness of these systems. However, reproducibility of

highly CO$_2$ selective membranes and high cost of membrane supports (for inorganic membranes) are major setbacks for membrane applications (Daramola et al. 2012). In this study synthesis and characterization of nanocomposite sodalite (HS)/ceramic membrane via "pore-plugging" hydrothermal synthesis (PPH) protocol for pre-combustion CO$_2$ capture is reported for the first time. Compared to the conventional in situ direct hydrothermal synthesis, membranes obtained from PPH possess higher mechanical and thermal stability. In addition, defect control with nanocomposite architecture membrane is possible because the zeolite crystals are embedded within the support pores of the membrane, thereby limiting the maximum defect size to the pore sizes of support. Furthermore, hydroxy sodalite (HS), which is a crystalline zeolite made of cubic array of β-cages as primary building block (Breck 1974), possesses cage aperture in the range of 0.26 and 0.29 nm, making it a good candidate for separation of small gas molecules like water (0.27 nm), helium (0.26 nm) and hydrogen (0.27 nm) under certain process conditions (Khajavi et al. 2007; Daramola et al. 2015). In addition, the nanocomposite architecture nature of the membrane, which could protect the separative layer of the membrane from abrasion during membrane assembly, could be instrumental to developing high performance H$_2$-selective membrane for IGCC system.

2 Experimental procedure

2.1 Material and method

The chemicals used for the synthesis of the membranes, anhydrous sodium metasilicate (Na$_2$SiO$_3$), sodium hydroxide (NaOH) and anhydrous sodium aluminate (NaAlO$_2$) were purchased from Sigma Aldrich (Pty) SA. The de-ionized water was prepared in-house and the chemicals were used as supplied without any further purification. The substrates for the membranes were asymmetrical α-alumina tubes (o.d. 10 mm, i.d. 7 mm, length 5 cm) purchased from Pall-Exekia (Germany). The cross-sectional layers of the support were of dimensions: outer layer, 1200 nm; intermediate layer, 800 nm; inner layer, 200 nm.

2.2 Membrane synthesis and characterization

Prior to membrane synthesis, the supports were cleaned in boiling water for 1–2 h to remove dirt and loose particles from their pores. The synthesis of the membrane was carried out using pore-plugging technique as described in Daramola et al. (2015) and illustrated schematically in Fig. 1. Certain quantities of anhydrous sodium aluminate
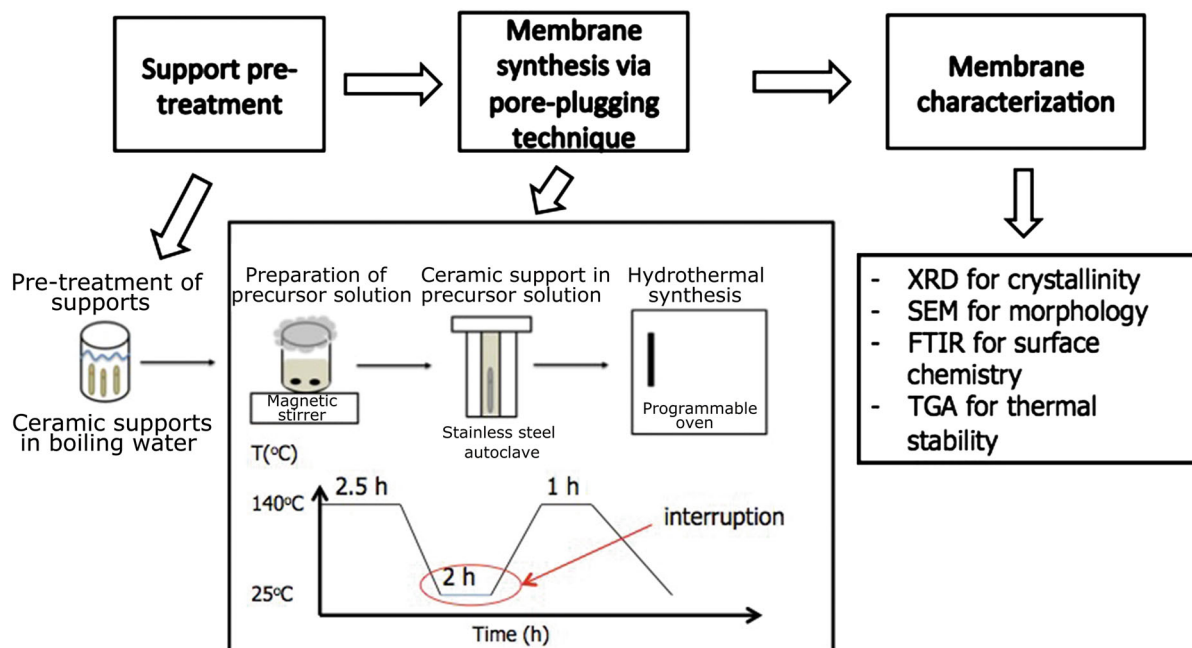
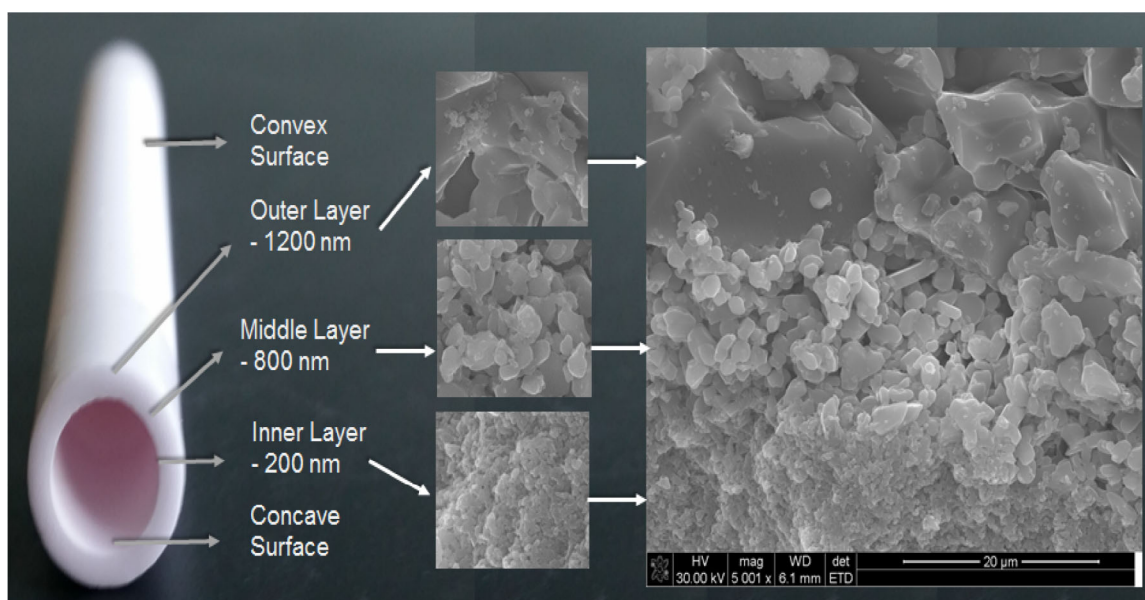**Fig. 1** Experimental procedure for the synthesis of the sodalite/ceramic membranes

Fig. 2 SEM micrograph of the cross-sectional view of the membrane support

($NaAlO_2$), anhydrous sodium metasilicate (Na_2SiO_3), sodium hydroxide and de-ionised water were measured and vigorously mixed in a polytetrafluoroethylene bottle on a magnetic stirrer. About 45 mL of the homogeneous mixture was then poured into a Teflon-lined stainless steel autoclave and the cleaned support was then inserted into the solution in the autoclave and sealed. In order to obtain nanocomposite architecture membrane via pore plugging

hydrothermal synthesis, the sealed autoclave was subjected to hydrothermal synthesis with interruption at 413 K using the temperature programme described in Daramola et al. (2015). The morphology of the cleaned support, the as-prepared membranes and the sodalite particles was checked with scanning electron microscopy (SEM) (Phillips XL 20). Furthermore, the crystal phases in the as-prepared samples were identified with X-ray diffraction (XRD)
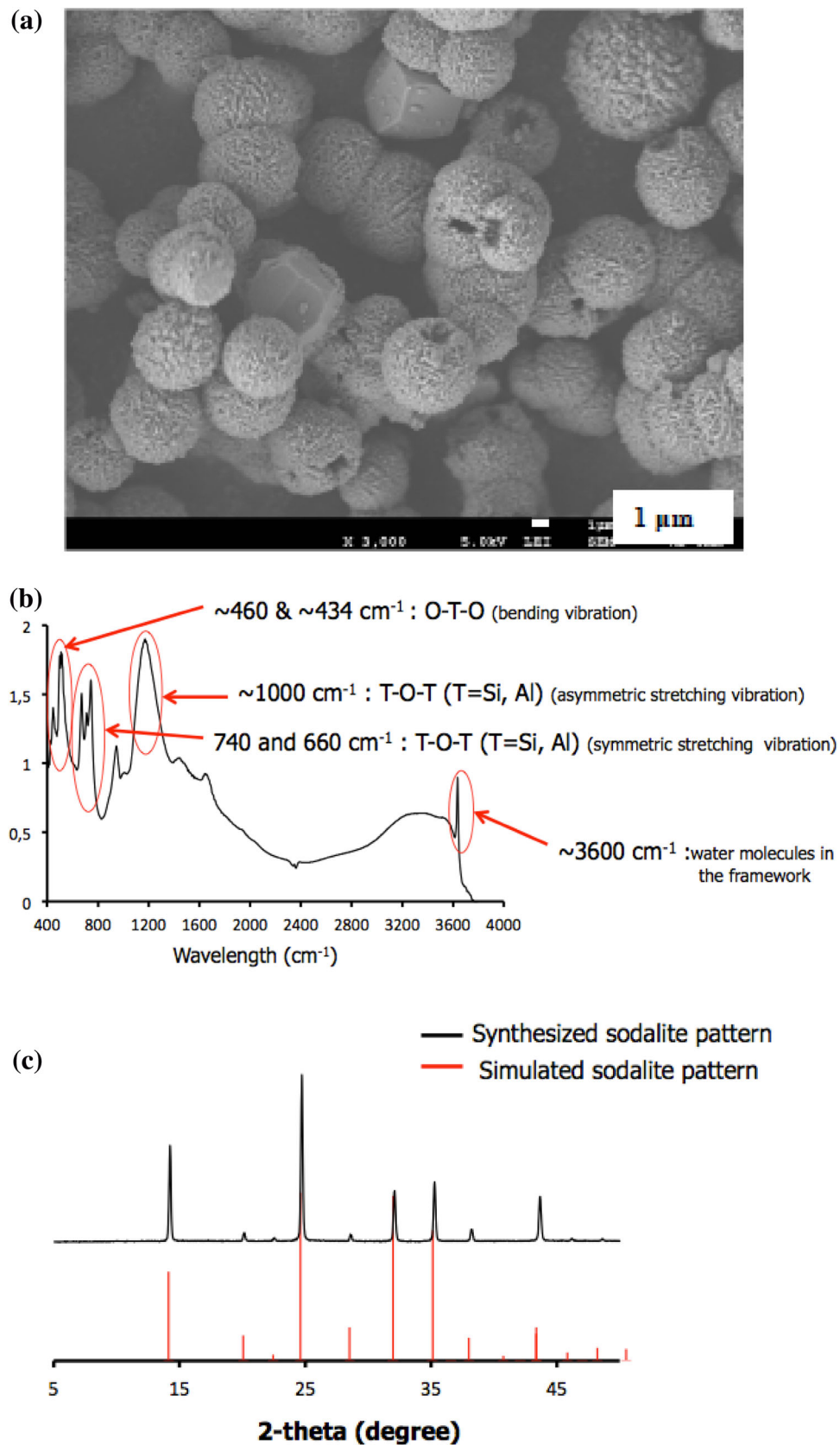
(a)

(b)

~460 & ~434 cm⁻¹ : O-T-O (bending vibration)

~1000 cm⁻¹ : T-O-T (T=Si, Al) (asymmetric stretching vibration)

740 and 660 cm⁻¹ : T-O-T (T=Si, Al) (symmetric stretching vibration)

~3600 cm⁻¹ :water molecules in the framework

Wavelength (cm⁻¹)

(c)

— Synthesized sodalite pattern
— Simulated sodalite pattern

2-theta (degree)

Fig. 3 Morphology, crystallinity and chemical nature of the sodalite particles. SEM micrograph (**a**), FTIR spectrum (**b**), and XRD pattern (**c**)

Table 1 Functional groups from FTIR and interpretation

Functional group	Wavelength position	Attribute
T–O–T (T=Si, Al)	1000 cm^{-1}	Asymmetric stretching vibration of T–O–T
T–O–T (T=Si, Al)	Around 740 and 660 cm^{-1}	Symmetric stretching vibration of T–O–T
Hydroxyl (–OH)	3600 cm^{-1}	Presence of water molecule forming part of the case structure

(model: Bruker D8 advance X-ray diffractometer) using CoKα radiation (λ = 0.179 nm) at a scan rate of 0.25 s/step and a step size of $0.02^{°}$. Fourier transform infrared (FTIR) analysis was conducted with Bruker IFS spectrometer using KBr pellets as background to obtain infrared spectrum that confirmed the purity of the sodalite crystals embedded within the pores.

3 Results and discussion

3.1 Characterization of support and HS crystals

The support was characterized before the synthesis. In addition, the HS crytsals ontained from the bottom of the autoclave after the PPH were characetrized as well. The SEM micrographs showing the cross-sectional view of the support is depicted in Fig. 2. The SEM micrographs, the FTIR spectrum and the XRD pattern of the HS crystals obtained from the bottom of the Teflon-lined autoclave are presented in Fig. 3a–c. The SEM micrograph of the HS crystals depicted in Fig. 3a shows cubic and nanorod-like shape of the crystals. Literature has confirmed other shapes of hydroxy sodalite such as flower-like, urchin, thread-ball and cubic/octahedral shapes (Bayati et al. 2008; Kundu et al. 2010; Naskar et al. 2011), making the results from this study a re-affirmation of these findings. The formation of other morphological shapes, as observed in this study, could be attributed to the interplay between the growth process and the nucleation process that seems to proceed in parallel once high temperature is applied during the synthesis (Chen et al. 2007).

The FTIR spectrum in Fig. 3b shows the chemical nature of the HS crystals. The various functional groups obtained from the FTIR are presented and explained in Table 1. This information from the infrared spectrum of the HS crystals is consistent with literature (Naskar et al. 2011; Buhl et al. 2011). The XRD pattern of the HS crystals (see Fig. 3c) confirm that pure sodalite crystals were obtained during the synthesis.

3.2 Characterization of the as-prepared nanocomposite HS/ceramic membrane

The morphology of the cross-sectional view and the surface view of the synthesized membrane are depicted in Fig. 4(top, middle, and bottom). Sodalite crystals could be seen vividly in all the SEM micrographs depicted in Fig. 4(top, middle, and bottom). It is clearly shown that the 200 nm layer of the support seems totally pore-plugged with sodalite crystals (see Fig. 4(middle)). Furthermore, the 800 nm layer of the support contains a lot of the sodalite crystals but not totally plugged when compared to the 200 nm layer. Also the 1200 nm layer of the support has a few crystals embedded within it. The total pore-plugging of the 200 nm layer indicates that the membrane might be defect free, but evaluation of te quality of the membrane using methods such as quick permeation test and/or gas mixture permeation will be required to confirm this speculation. The formation of the nanocomposite architecture could be attributed to the insitu heterogeneous nucleation during the synthesis. As described elsewhere (Li et al. 2008; Daramola et al. 2009, 2015), the HS nanocrystals (could be called seeds as well) formed in situ during the first stage of the PPH (before interruption) of the synthesis promote heterogenous nucleation and growth during the second stage (after interruption) of the synthesis. Eventually, the heterogenous nucleation during the post-interruption stage enhanced the growth into bigger crystals. Change in autogenous pressure in the vessel during the interruption stage, as a result of the change in temperature, might have enhanced the flow of more precursor solution into the porous structure of the support, thereby resulting in the growth of HS crystals within the pores that pore-plugged the pores of the support. The difference between this method and the secondary seeded growth (SSG) technique is in the in situ formation of the seeds insteading of ex situ formation of seeds as the case is in SSG. The ex situ formation of seeds in SSG makes the technique time demanding than the PPH used in this study and SSG technique always produces "thin-film" membranes.
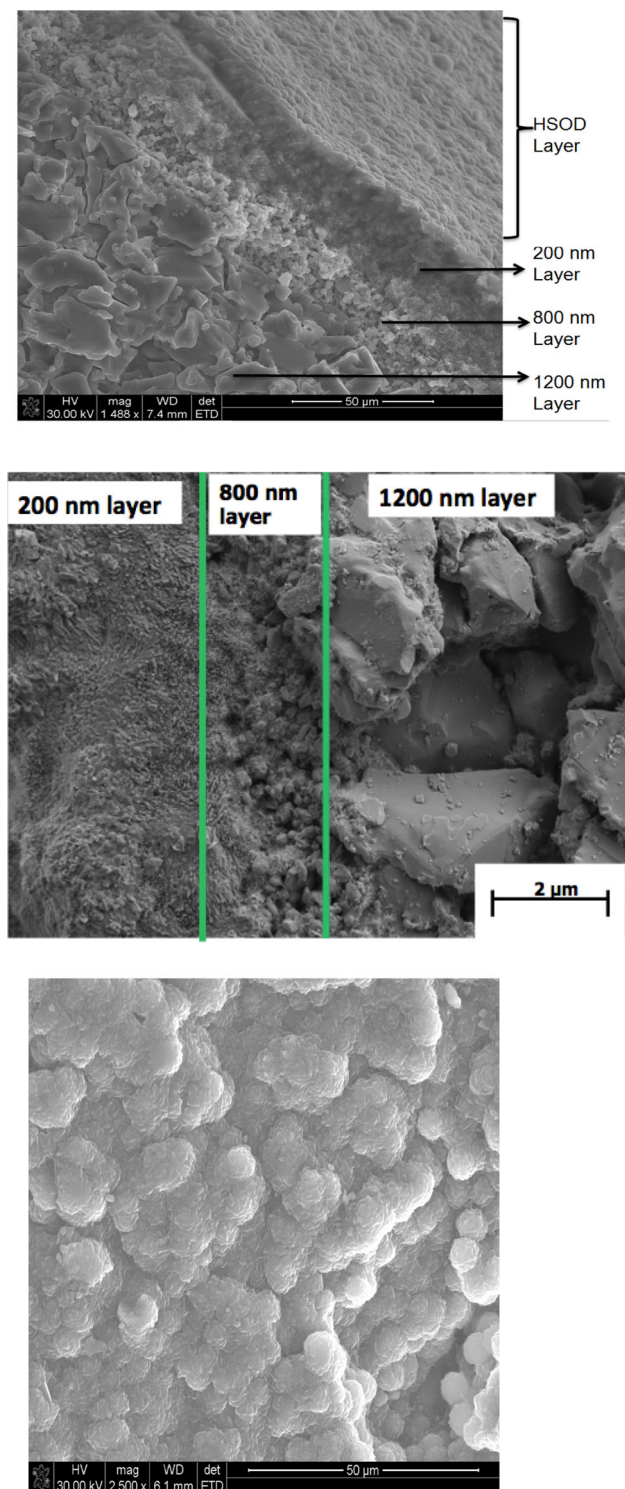
Fig. 4 SEM micrographs of the as-prepared nanocomposite membrane. Showing the crosssectional view with the presence of sodalite crystals (*top*), 1200 nm layer of the support with sodalite crystals within it (*middle*), and the surface view of the membrane (*bottom*)

3.3 Thermal stability of the as-prepared nanocomposite HS/ceramic membranes

A "thin-film" HS membrane was prepared as described elswehere (Khajavi et al. 2007) using similar membrane support for comparison. The thermal stability of the as-prepared thin-film membranes was compared to that of the nanocomposite membranes. The thermal stability was investigated by observing the thermal decomposition of a small portion cut-off from the membrane in a TGA. The thermal stability of the nanocomposite sodalite membrane compared to the "thin-film" sodalite membrane and the HS crystals is depicted in Fig. 5. It is vivid from Fig. 5 that the two membranes are more thermal stable when compared to the thermal stability of the HS crsystals. However, the nanocomposite membrane displayed a higher thermal stability than that of the "thin-film" counterpart. The enhanced thermal stability of the nanocomposite sodalite membrane can be attributed to the nanocomposite architecture nature of the membrane (the HS crystals are embedded within the pores of the supports instead of having them on the surface of the support).

4 Conclusions and recommendations

In this article, preparation and morphological characterization of nanocomposite sodalite/ceramic membranes obtained via the pore-plugging hydrothermal synthesis technique have been documented. The SEM micrographs of the as-prepared membranes reveal that nanocomposite sodalite/α-alumina membranes contain sodalite crystals embedded within the pore structure of the support. In addition, the nanocomposite membrane displayed higher thermal stability than that of the "thin-film" membrane synthesized via the conventional direct hydrothermal method. The membrane could be employed to separate CO_2 from H_2/CO_2 mixture in order to capture the CO_2 gas from IGCC. As far as could be ascertained, this article presents the first open report on the preparation and morphological characterization of nanocomposite sodalite/ceramic membranes for pre-combustion CO_2 capture. However dynamic tests, such as single pas permeation test and CO_2/H_2 separation test should be carried out on the membranes to evaluate the separation performance of the membranes during pre-combustion CO_2 capture and at pre-combustion CO_2 capture conditions. Research effort is ongoing in our laboratory on the aforementioned tests and the results obtained thereof will be communicated in the near future.
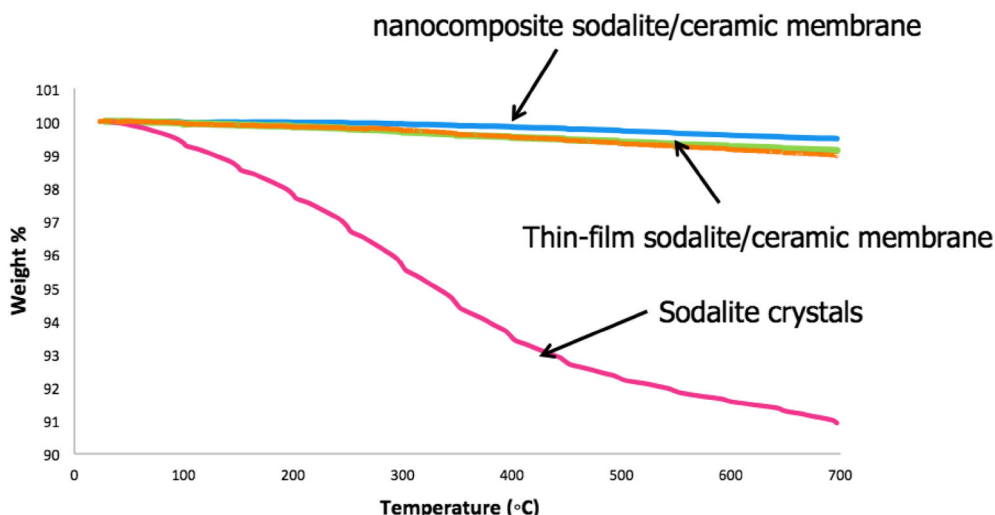
Fig. 5 Thermal stability of the nanocomposite membrane compared to the thin-film HS membrane and HS crystals

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