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## H<sub>2</sub>O-prompted CO<sub>2</sub> capture on metal silicates *in situ* generated from SBA-15†

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A series of metal silicates, NaMSi<sub>10</sub>Ox (M = Cu, Mn and Ni), were prepared by *in situ* doping of metals into mesoporous SBA-15 under a hydrothermal process, displaying a continuous framework of SiO<sub>4</sub> structure with a narrow pore size distribution. These metal silicate materials were tested for CO<sub>2</sub> adsorption behavior in the absence and presence of water. The results exhibited that the effect of H<sub>2</sub>O on the CO<sub>2</sub> capture capability of metal silicates depends on the types of metal inserted into SBA-15. Compared to the dry condition, H<sub>2</sub>O addition enhances CO<sub>2</sub> uptake dramatically for NaCuSi<sub>10</sub>Ox by 25%, and slightly for NaNiSi<sub>10</sub>Ox (~10%), whereas little effect is shown on NaMnSi<sub>10</sub>Ox. The metal silicate materials are stable after adsorption of CO<sub>2</sub> under wet conditions, which is benefited from their synthesis method, hydrothermal conditions. The improvement of CO<sub>2</sub> uptake on metal silicates by H<sub>2</sub>O is attributed to the competitive and synergistic adsorption mechanism on the basis of IR investigations, where initially adsorbed H<sub>2</sub>O acts as a promoter for further CO<sub>2</sub> capture through a hydration reaction, *i.e.*, formation of bicarbonate and carbonates on the surface of the samples. These observations provide new possibilities for the design and synthesis of porous metal silicate materials for CO<sub>2</sub> capture under practical conditions where moisture is present.

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### Introduction

The significantly increased concentration of carbon dioxide in the atmosphere is the major contributor to global warming, and CO<sub>2</sub> is mainly generated from processes such as vehicles, refineries, and thermal power stations and the combustion of natural gas.<sup>1–3</sup> Therefore, developing technologies for reducing the amount of carbon dioxide emission has been attracting wide attention throughout the industrial and academic communities<sup>4,5</sup> owing to the environmental sustainability. There are many techniques available to remove CO<sub>2</sub> with different advantages and limitations. To date, the most effective way is carbon capture and storage (CCS) based on solid adsorbents.<sup>6,7</sup>

Currently, a wide range of materials with fine structural and chemical properties have been investigated as possible CO<sub>2</sub> captors at low (303–353 K) or high ( $T > 473$  K) temperatures, such as various activated carbons,<sup>8–10</sup> zeolites,<sup>11–13</sup> silicates,<sup>14–16</sup> metal oxides,<sup>17–19</sup> metal–organic frameworks (MOFs)<sup>20–25</sup> and

zirconates/aluminates,<sup>26–29</sup> each presenting some advantages and disadvantages. Solid sorbents impregnated or grafted with polyamines and related groups are widely researched materials, which combine the advantages of both the amine group and solid materials to maximize the sorption properties. These functionalized solids not only present higher CO<sub>2</sub> selectivity and adsorption capacity, but also possess lower temperatures and less energy input for regeneration. For example, a capture capacity of 12 mmol g<sup>−1</sup> is reported for cationic polymerization of oxazolines on mesoporous silica under simulated flue gas conditions.<sup>30</sup> However, the thermal stability of the amine group employed should be considered carefully for long term implementation, which is particularly important when the adsorbent is subject to steam stripping and/or high temperature regeneration. In addition, MOFs<sup>20–25</sup> have been extensively investigated in carbon storage/separation due to their enriched morphological texture, chemical tunability, highly available porous surface, aromaticity and densely coordinated unsaturated metal sites. However, most MOF adsorbents exhibit decreased CO<sub>2</sub> uptake capacities under wet conditions. Many efforts have been dedicated to improving the water resistance properties of MOFs. Recently, Ibarra *et al.*<sup>31</sup> reported the progress in CO<sub>2</sub> capture under humid conditions in MOFs in their review paper, which includes an emerging technology of enhancement of CO<sub>2</sub> capture by confining water within the pores of MOFs.

Alkaline ceramics, such as alkali-based silicates, zirconates or aluminates, have attracted much attention for CO<sub>2</sub> capture

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because this type of material exhibits high CO<sub>2</sub> uptake, thermal stability, low cost, repeated regenerability and tolerance against water, and have been used in recent attempts towards tailoring materials for selective CO<sub>2</sub> capture.<sup>32</sup> Typically, CO<sub>2</sub> capture on alkali-based silicates presents a double-step sorption mechanism, with an initial chemical sorption of CO<sub>2</sub> to form carbonates on the surface and further reaction with the alkaline atom, which accordingly depends on different factors such as the chemical composition, the structure, different microstructural factors and the presence of water.<sup>33–36</sup> Therefore, CO<sub>2</sub> capture can be significantly affected by the tunability of their compositions and structure, such as replacement of alkali elements by transition metals.

Notably, CO<sub>2</sub> capture on metal silicates/aluminates has received little attention,<sup>37,38</sup> and it has been only recently shown that microporous copper silicate synthesized from sodium silicate and copper sulfate has a stable CO<sub>2</sub> uptake of 156 cm<sup>3</sup> cm<sup>-3</sup> in the presence of water vapor.<sup>38</sup> It is well known that most flue gas streams under consideration for carbon capture are highly humid, which typically causes the reduction of CO<sub>2</sub> uptake capabilities, or leads to absorbent decomposition in some cases. Therefore, the development of efficient, stable and sustainable absorbents based on more available and low-cost materials, such as transition metal salts, could favor the technologies of the CO<sub>2</sub> capture processes in the presence of H<sub>2</sub>O. Herein, we develop a new synthetic method for metal (Cu, Ni and Mn) silicate sorbents derived by *in situ* doping of metals into mesoporous SBA-15 through a hydrothermal synthesis. The synthesized metal silicates, exhibiting a quartz crystallized structure with narrow pore size distribution, are found to possess comparable or even increased CO<sub>2</sub> sorption capacity in the presence of water vapor. Based on *in situ* FTIR study, a competitive/synergistic adsorption model is proposed for CO<sub>2</sub> adsorption with H<sub>2</sub>O addition on the metal silicate materials.

## Experimental

### Materials

The following raw materials were used as provided: copper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Acros Organics); manganese(II) nitrate tetrahydrate (Mn(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Sigma-Aldrich); nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Sigma-Aldrich); sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>, Fisher Chemicals); tetraethyl orthosilicate (TEOS, Acros Organics); hydrochloric acid (HCl, 37%, Fisher Chemicals).

### Sample preparation

Ordered mesoporous SBA-15 was synthesized by a hydrothermal method as reported in the literature<sup>39</sup> with some modifications. In a typical synthesis, 2.8 mmol P123 and 2.9 mol HCl (83 mL) were added into DI water (28 mol) in a Nalgene PP bottle (1000 mL), followed by stirring for 3 hours until P123 was fully dissolved and the solution was clear. Tetraethyl orthosilicate (TEOS, 0.17 mol) was then added to this solution and stirred for another 30 min. The bottle was then capped and kept in an oven at 373 K for 24 hours. The reaction mixture was cooled down

and then filtered. The white powder was dried at 333 K for 24 h, followed by air calcination at 823 K for 4 hours with a heating rate of 1 K min<sup>-1</sup> and air flow rate of ~120 mL min<sup>-1</sup>.

The metal silicates were prepared through a hydrothermal method in an autoclave. The metal salts (0.5 mmol) (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Mn(NO<sub>3</sub>)<sub>2</sub>), Na<sub>2</sub>CO<sub>3</sub> (2.5 mmol), and SBA-15 (2 mmol) were loaded into a PTFE-lined stainless-steel autoclave along with 5 mL of deionized water. The autoclave was sealed and heated to 463 K for 48 hours and then cooled to room temperature. The products were washed with deionized water and ethanol to remove excess starting materials. The obtained metal silicates were dried at 373 K for 12 hours. The actual metal and silicon content in the materials was analyzed by ICP. It was found that the actual ratio of metal to silicon (~1/10) was lower than the ratio of metal to silicon in the starting solution. Therefore, the samples are denoted as NaMSi<sub>10</sub>O<sub>x</sub> (M = Cu, Ni and Mn).

### Characterization

The scanning electron microscope (SEM) imaging was performed on a Zeiss Auriga microscope with an electron beam operation of 5 keV, which is a dual beam FIB (Focused Ion Beam) with a field emission electron column for high resolution electron imaging and a Canion Ga+ column for precision ion beam milling. Elemental distributions of the samples were characterized by energy dispersive X-ray spectroscopy (EDS) performed in a Zeiss EVO MA15 scanning electron microscope (SEM) working at 20 kV. The resolution of this microscope is about 5 nm. The EDS spectra were analyzed by the Bruker QUANTAX software.

Nitrogen adsorption isotherms were measured at 77 K using a Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Prior to the adsorption measurements, the metal silicate samples were degassed under flowing nitrogen for 2 h at 453 K to remove any residual water and surface species. The surface area was calculated using the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05 to 0.25. The total pore volume (*V<sub>t</sub>*) was estimated from the N<sub>2</sub> adsorption isotherm at a relative pressure *P/P<sub>0</sub>* = 0.97. The pore size distributions (PSDs) were calculated using the Barrett–Joyner–Halenda (BJH) algorithm for cylindrical pores according to the improved Kruk–Jaroniec–Sayari (KJS) method.

X-ray diffraction (XRD) patterns were collected on a PANalytical powder diffractometer using CuK $\alpha$  radiation. The working voltage was 40 kV, and the current was 40 mA. The intensity data were collected at room temperature in the  $2\theta$  range of 0°–4° and 15°–70°.

CO<sub>2</sub> sorption measurements were carried out at 303 and 273 K using a Gemini VII 2390 Surface Area Analyzer (Micrometrics Instrument Corp.). Prior to the CO<sub>2</sub> adsorption measurements, all metal silicate samples were treated under flowing nitrogen for 5 h at 453 K.

Adsorption of dry CO<sub>2</sub>, N<sub>2</sub>/H<sub>2</sub>O, and CO<sub>2</sub>/H<sub>2</sub>O was performed using a thermogravimetric analysis (TGA) device (Model Seiko 6300 TG/DTA, RT Instruments, Inc.) at 323 K. The experiments were performed using distilled water and two different carrier

gases: bubbling nitrogen ( $N_2$ ) or carbon dioxide ( $CO_2$ ) through distilled water at room temperature to get saturated water vapor pressure. The relative humidity of pristine flue gas varies from case to case, but is normally at low levels. Therefore, a relative humidity of  $\sim 25\%$  (saturated water vapor pressure at room temperature) was chosen as a representative case for investigation. The gas flow rate used in all of the experiments was  $60 \text{ mL min}^{-1}$ . The net  $CO_2$  adsorption capacity in the presence of  $H_2O$  was calculated by subtracting the  $N_2/H_2O$  adsorption value from the  $CO_2/H_2O$  adsorption value.

*In situ* IR study of dry  $CO_2$  and  $CO_2/H_2O$  adsorption on the metal silicate samples was conducted using a Thermo Nicolet Nexus 670 spectrometer in diffuse reflectance mode (DRIFTS) while the exiting stream was analyzed by an OmniStar GSD-301 (Pfeiffer-Balzer) quadrupole mass spectrometer (QMS). The

samples were pretreated in a DRIFTS cell (HC-900, Pike Technologies, nominal cell volume of  $6 \text{ cm}^3$ ) at  $453 \text{ K}$  in helium flow ( $25 \text{ mL min}^{-1}$ ) for  $1.5 \text{ h}$  before cooling down to  $298 \text{ K}$  for  $CO_2$  adsorption.  $2\% \text{ CO}_2/\text{He}$  ( $25 \text{ mL min}^{-1}$ ) was flowed over the samples at room temperature for  $30 \text{ min}$  before switching to helium purging for another  $30 \text{ min}$ . Time-resolved IR spectra were collected during the adsorption process and the subsequent thermal desorption process.

## Results and discussion

The successful synthesis of the metal silicates with the SBA-15 doped by different types of metals is confirmed by XRD,  $N_2$  isothermal adsorption and SEM characterization. The small angle XRD patterns of the samples (Fig. S1†) indicate that SBA-15 is successfully produced, characterized by three well-resolved diffraction peaks at  $0.86$ ,  $1.49$ , and  $1.70$ . These typical peaks disappeared with the introduction of metal salt under hydrothermal conditions, which results in the appearance of different diffraction peaks at a higher angle range (Fig. 1). Fig. 1 shows the XRD profiles of the synthesized metal silicates and pristine SBA-15 from  $15^\circ$  to  $70^\circ$ . The pristine SBA-15 only exhibits a broad diffraction peak at higher angle diffraction (Fig. 1A-a).

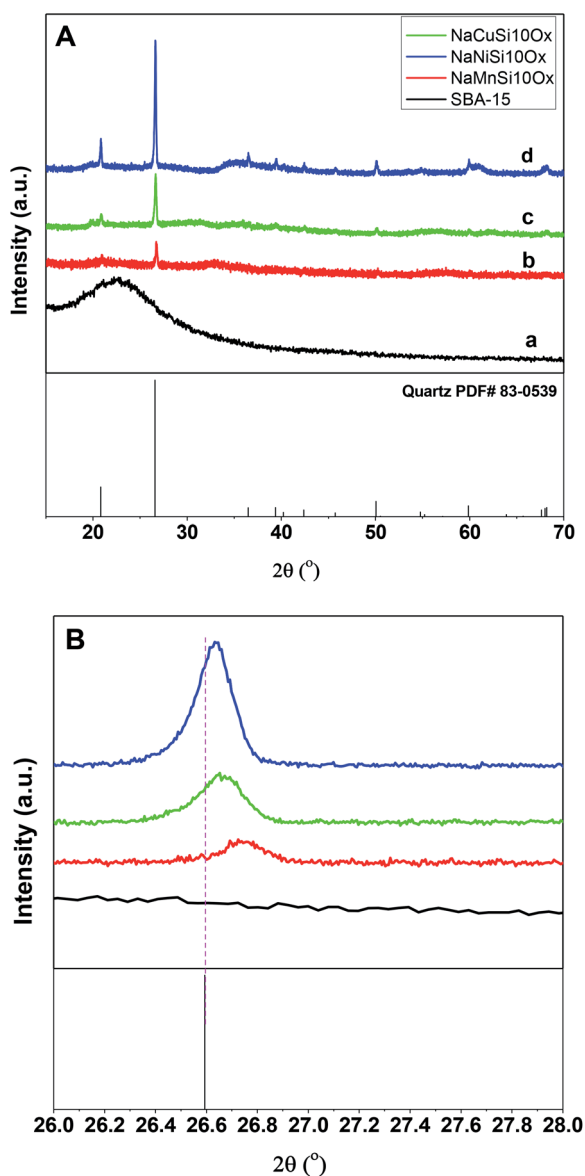


Fig. 1 The XRD patterns (A) and the enlarged XRD patterns (B) of the synthesized metal silicates and pristine SBA-15 materials.

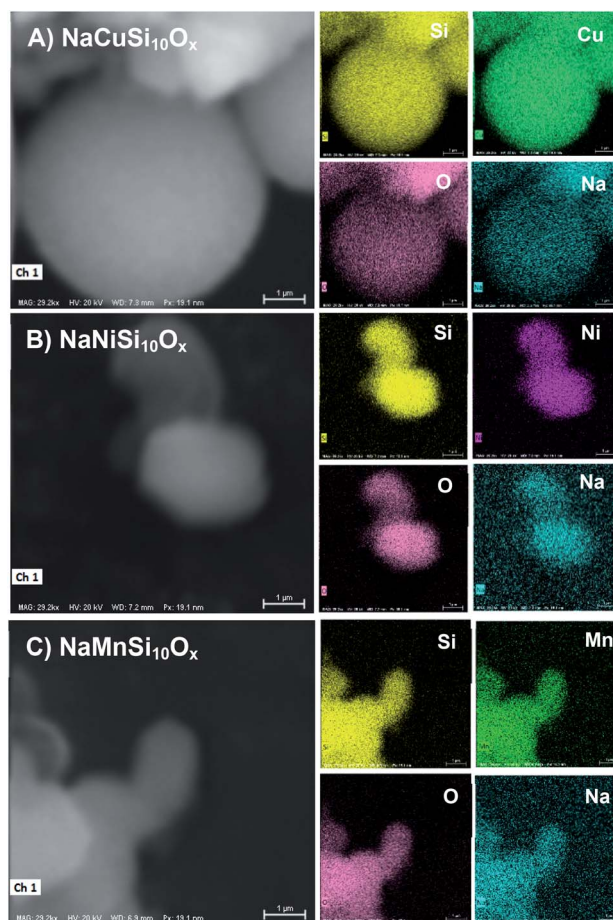


Fig. 2 The SEM-EDS mappings of (A)  $NaCuSi_{10}O_x$ , (B)  $NaNiSi_{10}O_x$  and (C)  $NaMnSi_{10}O_x$ .



All synthesized metal silicate samples present distinct diffraction peaks characteristic of quartz (PDF #: 83-0539) as seen in Fig. 1A–b–d, regardless of the metal type. This suggests that the formed metal (Cu, Ni and Mn) silicate materials have a continuous framework of  $\text{SiO}_4$  (tetrahedrally coordinated) structures. The XRD patterns do not show any evidence of metal oxides forming for CuO, NiO and MnO. From the enlarged portion (the bottom figure, Fig. 1B), it can be seen that the characteristic diffraction peak at around 26.6 degrees of all metal doped samples is slightly shifted to the higher angle side relative to the pure quartz phase (PDF #: 83-0539). The observed key features for metal silicate materials, peak shift and absence of dopant oxide XRD peaks, evidently confirm the successful incorporation of metals (Cu, Ni and Mn) into the synthesized silicates with quartz crystalline phase. To further confirm the location of metals in the synthesized silicates, EDS mapping acquired by SEM (Fig. 2) shows that O, Si, Na and the metal (Cu, Ni and Mn) elements are uniformly distributed at the micrometer scale, and the EDS intensity of Si to Cu (Mn and Ni) is similar, although the ratio of Si/metal is 10 (ICP results). Combined with the XRD results, it's highly possible that part of the introduced metal is incorporated into the structure of the silicate, while the rest of the metal is homogeneously dispersed on the surface of the silicates. Apparently, Na ions are present over the surface of the synthesized silicates. Fig. 3 gives the surface morphology and structure of the prepared metal silicates and pristine SBA-15 examined by SEM. SBA-15 shows a smooth surface and twisted belt morphology with clearly observable porous structure. The synthesized  $\text{NaCuSi}_{10}\text{Ox}$ ,  $\text{NaNiSi}_{10}\text{Ox}$  and  $\text{NaMnSi}_{10}\text{Ox}$  exhibited rod, ball and cotton-like structures, respectively. All three metal silicate samples show rough surface characteristics and irregular porous structures, which indicates the structural changes of the synthesized metal silicates from pristine SBA-15. This is in agreement with the results from XRD and the  $\text{N}_2$  adsorption isotherms as described below.

The porous structures of the metal silicates and pristine SBA-15 were characterized by nitrogen adsorption at 77 K. Fig. 4

gives a comparison of the  $\text{N}_2$  adsorption–desorption isotherms and the corresponding pore size distribution for these materials. SBA-15 displays a typical type IV isotherm, which indicates the presence of a mesoporous structure. The  $\text{N}_2$  adsorption–desorption isotherms for the metal silicate samples can also be classified as type IV isotherms according to the IUPAC classification (Fig. 4A). However, the volume of adsorbed  $\text{N}_2$  and the areas of the hysteresis loops for the metal silicates are much smaller compared with those for the pristine SBA-15. This can be ascribed to the crystallization process of the metal silicates, where the degradation and reconstruction of the framework of pristine SBA-15 occur with the incorporation of metals.<sup>40</sup> The pore size (Fig. 4B) of the synthesized metal silicates is decreased to 1.5–5 nm, compared with the pristine SBA-15 silica which has a mesopore size distribution range of 6–10 nm. In particular, the pore size for copper silicate narrows down to 1.5–2.5 nm, characteristic of super-microporous materials,<sup>41</sup> though the BJH model might not be accurate for analyzing microporosity. The pore size distribution for nickel and manganese silicates covers two ranges, 1.5–2.5 and 3–4.5 nm for manganese silicate, and 1.5–2.5 and 3–5 nm for nickel silicate. The calculated textural properties of SBA-15 silica and the synthesized metal silicates are summarized in Table 1. Compared with pristine SBA-15, the surface area and pore volume decrease for all of the synthesized metal silicate samples. Again, this may be due to the framework

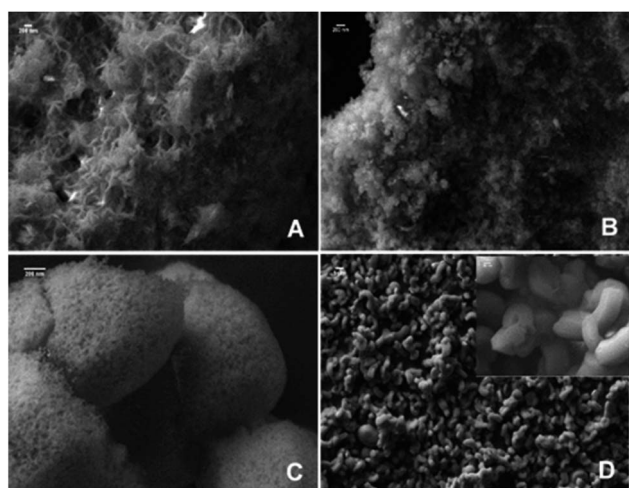


Fig. 3 The SEM images of (A)  $\text{NaCuSi}_{10}\text{Ox}$ , (B)  $\text{NaNiSi}_{10}\text{Ox}$ , (C)  $\text{NaMnSi}_{10}\text{Ox}$  and (D) SBA-15.

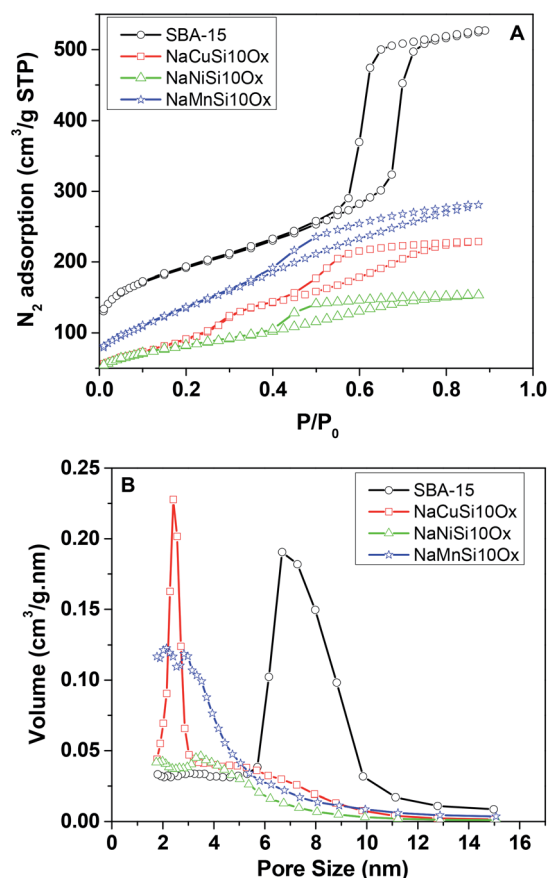


Fig. 4  $\text{N}_2$  adsorption isotherms (A) and corresponding pore size distributions (B) for the metal silicates and SBA-15.

Table 1 The actual ratio of metal to silicon (measured from ICP), BET surface area, pore volume and CO<sub>2</sub> adsorption capacities of all samples

Samples	Actual ratio of metal to silicon	Surface area (m <sup>2</sup> g <sup>-1</sup> )	V <sub>t</sub> (cm <sup>3</sup> g <sup>-1</sup> )	CO <sub>2</sub> adsorption at 273 K (mmol g <sup>-1</sup> )	CO <sub>2</sub> adsorption at 303 K (mmol g <sup>-1</sup> )
NaCuSi <sub>10</sub> Ox	10.7	445	0.46	1.57	1.18
NaNiSi <sub>10</sub> Ox	11.9	314	0.28	1.00	0.80
NaMnSi <sub>10</sub> Ox	11.6	551	0.53	1.75	1.28
SBA-15	0	652	0.83	0.85	0.62

reconstruction and crystallization caused by the incorporation of metals into the pristine SBA-15, in accordance with the XRD results. In brief, the metal silicates with micro-mesoporous composites and quartz structures are successfully made by reconstruction of the pristine SBA-15 framework with *in situ* introduction of metals during the hydrothermal synthesis process.

The CO<sub>2</sub> adsorption capacities of all samples were measured at two temperatures (273 and 303 K) and the results are shown in Fig. 5 and Table 1. For the pristine SBA-15, the CO<sub>2</sub> adsorption capacities at 273 K and 303 K are 0.85 and 0.62 mmol g<sup>-1</sup> at 1 bar, respectively. The CO<sub>2</sub> total capacities on the metal silicates at both temperatures are higher than that on SBA-15,

though their surface area and pore volume are lower than those of pristine SBA-15. This can be attributed to the formation of a crystallized metal silicate structure and the incorporation of metals, *i.e.*, CO<sub>2</sub> adsorption on the metal silicates is impacted by both the textural parameters (surface area and pore volume) and the chemical properties (the type of metal). As can be seen in Fig. 5, the CO<sub>2</sub> capacities differ slightly for the metal silicate samples at both temperatures: ~1.75 mmol g<sup>-1</sup> @ 273 K (~1.18 mmol g<sup>-1</sup> @ 303 K) for NaMnSi<sub>10</sub>Ox, ~1.57 mmol g<sup>-1</sup> @ 273 K (~1.02 mmol g<sup>-1</sup> @ 303 K) for NaCuSi<sub>10</sub>Ox and ~1.00 mmol g<sup>-1</sup> @ 273 K (~0.81 mmol g<sup>-1</sup> @ 303 K) for NaNiSi<sub>10</sub>Ox, following the trend of decreasing surface area and pore volume of these samples. To clearly show the effect of metals in the framework/over the silicate surface on CO<sub>2</sub> adsorption behavior, the CO<sub>2</sub> capacities were normalized to the total surface area, as presented in Fig. 6. NaCuSi<sub>10</sub>Ox has higher CO<sub>2</sub> capacity than NaMnSi<sub>10</sub>Ox and NaNiSi<sub>10</sub>Ox at 273 K with the latter two giving similar capacities of CO<sub>2</sub> uptake. This suggests that the type of metal in the silicate plays a role in the CO<sub>2</sub> adsorption behavior, but not significantly. The significant increase in CO<sub>2</sub> adsorption capacity of the metal silicates compared to the pristine SBA-15 demonstrates a stronger effect from the texture parameters. Sorbent materials for CO<sub>2</sub> capture from humid flue gases are urgently required due to the increased cost for prior dehydration of the gas stream. So TGA experiments were carried out to further analyze and evaluate the potential of the synthesized metal silicates for CO<sub>2</sub> capture

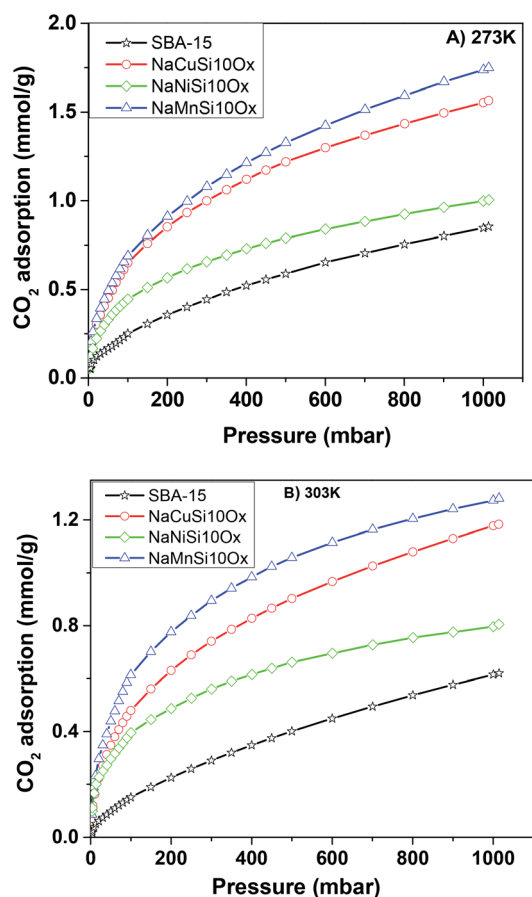


Fig. 5 The CO<sub>2</sub> adsorption isotherms for the metal silicate and pristine SBA-15 samples up to a maximum pressure of 1 bar at (A) 273 K and (B) 303 K.

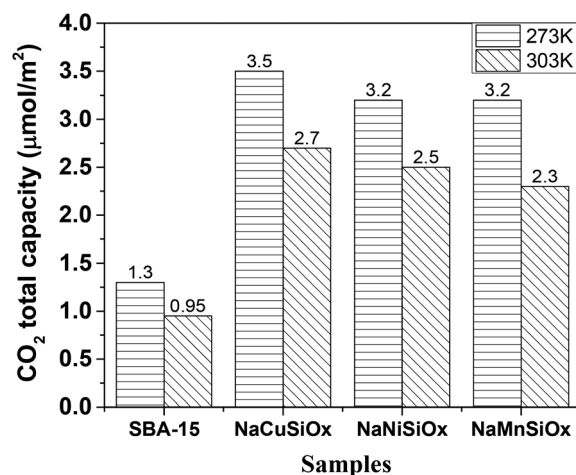


Fig. 6 CO<sub>2</sub> total capacity of metal silicates and SBA-15 samples normalized to the surface area.

under humidified conditions. To test the influence of water vapor, the pretreated metal silicate samples were exposed to dry  $\text{CO}_2$ , humidified  $\text{CO}_2$  and humidified  $\text{N}_2$  for 10 hours at 323 K. The net  $\text{CO}_2$  adsorption capacity in the presence of  $\text{H}_2\text{O}$  is calculated by subtracting the  $\text{N}_2/\text{H}_2\text{O}$  adsorption value from the  $\text{CO}_2/\text{H}_2\text{O}$  adsorption value, and breakthrough curves with time are sketched in Fig. 7. It is found that the presence of water induces a longer breakthrough time for  $\text{CO}_2$  capture compared with dry gases, which implies the existence of competitive adsorption between  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules, *i.e.*, the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  possibly adsorb on the same surface sites of the metal silicate samples. Competitive adsorption is a general phenomenon for multicomponent involved systems. Interestingly, compared with the dry  $\text{CO}_2$  case,  $\text{H}_2\text{O}$  addition clearly enhances the  $\text{CO}_2$  uptake amount for the  $\text{NaCuSi}_{10}\text{Ox}$  and  $\text{NaNiSi}_{10}\text{Ox}$  samples at a longer adsorption time, and has almost no effect on the  $\text{NaMnSi}_{10}\text{Ox}$  sample as shown in Fig. 7A–C. This indicates that adsorbed  $\text{H}_2\text{O}$  could act as a helper for further  $\text{CO}_2$  capture, possibly through hydrogen bonding or a hydration reaction (see below). In the presence of  $\text{H}_2\text{O}$ , the quantity of  $\text{CO}_2$  adsorbed by the  $\text{NaCuSi}_{10}\text{Ox}$  and  $\text{NaNiSi}_{10}\text{Ox}$  samples is 0.76 and 0.46  $\text{mmol g}^{-1}$  at 450 min, respectively, which represents 27% and 10% improvement relative to the dry gas stream conditions. The  $\text{NaMnSi}_{10}\text{Ox}$  sample gives 0.61  $\text{mmol g}^{-1}$   $\text{CO}_2$  capacity, which is similar to that (0.62  $\text{mmol g}^{-1}$ ) under dry gas conditions. Obviously,  $\text{NaCuSi}_{10}\text{Ox}$  is the best adsorbent among

the three metal silicates under wet conditions, followed by the  $\text{NaNiSi}_{10}\text{Ox}$  and  $\text{NaMnSi}_{10}\text{Ox}$ , despite the differences in surface area and pore volume for all materials (Table 1). Different from the dry conditions, where the  $\text{CO}_2$  uptake mainly relies on the texture parameters of the metal silicate materials, the effect of  $\text{H}_2\text{O}$  addition on the  $\text{CO}_2$  uptake is more dependent on the type of metal in the metal silicate than on the texture parameters. It is worth mentioning that all samples are highly stable after  $\text{CO}_2$  capture in wet conditions, which is evident from the characteristic XRD pattern (Fig. S2†). To better understand how the presence of water vapor affects the  $\text{CO}_2$  capture on the metal silicates, FT-IR was employed to investigate the adsorption of dry and humidified  $\text{CO}_2$  on all samples. Fig. 8 compares the IR spectra taken as a function of time after the  $\text{NaCuSi}_{10}\text{Ox}$  sample was exposed to  $\text{CO}_2$  in the absence and presence of water. As shown in Fig. 8A and B, upon initial  $\text{CO}_2$  adsorption (less than 2 min), the most intense bands appear at 2354, 2342, 1675, 1631 and 1360  $\text{cm}^{-1}$ . The band at 2354  $\text{cm}^{-1}$  with a shoulder at 2342  $\text{cm}^{-1}$  is attributed to physisorbed  $\text{CO}_2$ , while the IR features in the range of 1700 to 1200  $\text{cm}^{-1}$  are characteristic of carbonates and bicarbonates.<sup>42–45</sup> Generally, there are two types of basic sites on inorganic oxide materials, basic hydroxyl groups and basic surface oxygen (normally designated as a Lewis base) that can interact with the acidic  $\text{CO}_2$ . Therefore,  $\text{CO}_2$  adsorption on these two types of basic sites can result in bicarbonate (with OH groups) and various carbonate species

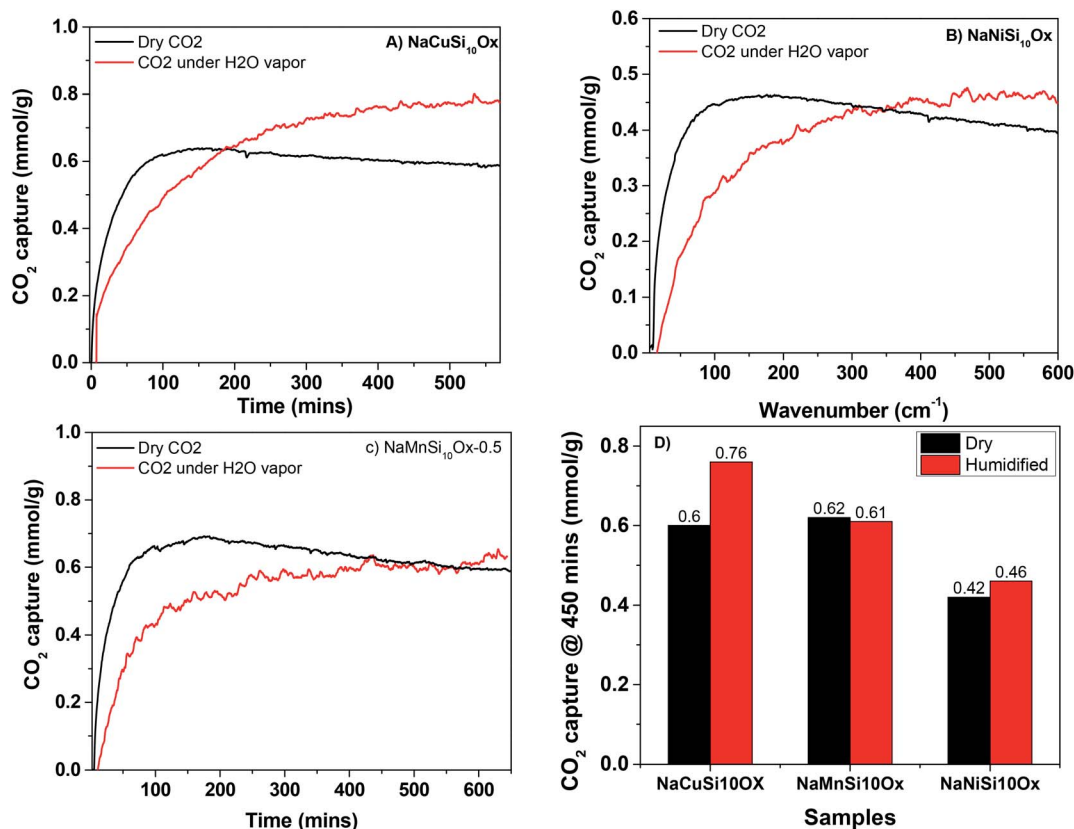


Fig. 7  $\text{CO}_2$  adsorption on metal silicates in the absence and presence of water vapor as a function of time, (A)  $\text{NaCuSi}_{10}\text{Ox}$ , (B)  $\text{NaNiSi}_{10}\text{Ox}$  and (C)  $\text{NaMnSi}_{10}\text{Ox}$ , and (D) the  $\text{CO}_2$  uptakes on the metal silicates at 450 min in the absence and presence of water vapor.

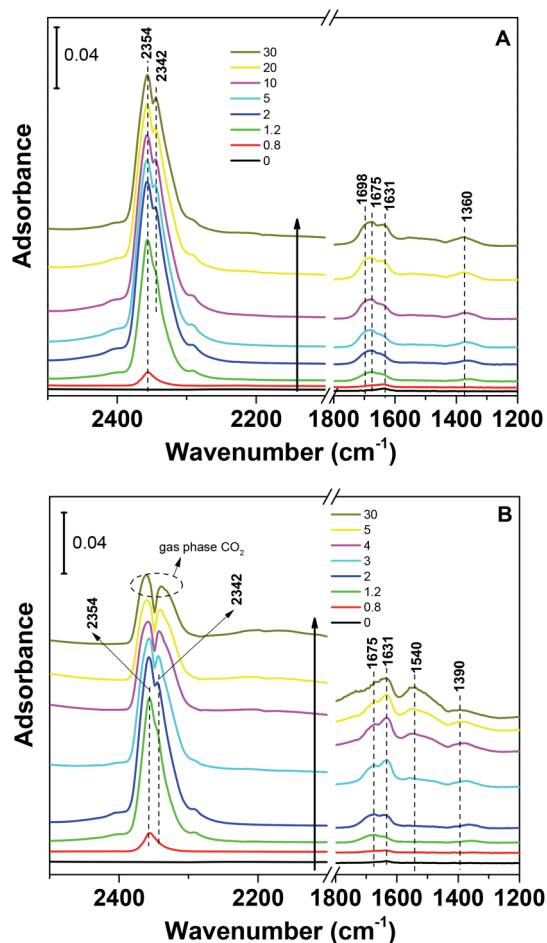


Fig. 8 IR spectra from CO<sub>2</sub> adsorption at room temperature on NaCuSi<sub>10</sub>Ox for 30 min: (A) in the absence of water vapor, and (B) in the presence of water vapor.

(with surface O). The bands at 1675 and 1360 cm<sup>-1</sup> are assigned to carbonates, and the band at 1631 cm<sup>-1</sup> reflects the presence of bicarbonates.<sup>43–45</sup> It is noted that the initial adsorption bands are similar in frequency for CO<sub>2</sub> adsorption under dry and humid conditions, indicating that similar surface species are formed with/without H<sub>2</sub>O addition. However, these IR features evolve differently as a function of adsorption time in the absence and presence of water. Under dry conditions (Fig. 8A), the overall types of surface adsorbed CO<sub>2</sub>, carbonate and bicarbonate species do not vary as a function of adsorption time, but the relative intensity (amount) continuously increases for the same type of surface species. Under wet conditions (Fig. 8B), in addition to the initial bands at 1675, 1630 and 1360 cm<sup>-1</sup>, there are two new bands appearing at 1550 and 1390 cm<sup>-1</sup> and the band at 1631 cm<sup>-1</sup> is relatively intensified with increased adsorption time (3 to 30 min). The relative enhancement of the 1631 cm<sup>-1</sup> band and the appearance of the band at 1390 cm<sup>-1</sup> are caused by newly developed bicarbonate (acid carbonate) species produced from further reaction of adsorbed CO<sub>2</sub> and H<sub>2</sub>O.<sup>43,45,46</sup> Adsorbed water can also contribute through its bending mode to the 1631 cm<sup>-1</sup> band.

The band at 1550 cm<sup>-1</sup> is possibly due to unidentate carbonate, which is generated by the H<sub>2</sub>O interacting with bidentate carbonate as evidenced from the disappearance of the band at 1698 cm<sup>-1</sup>.<sup>46</sup> These observations confirmed that H<sub>2</sub>O addition is able to react with adsorbed CO<sub>2</sub> species to form bicarbonate and unidentate carbonate, and thus leads to the improvement of the CO<sub>2</sub> uptake on the sample. It was also demonstrated in a number of studies that CO<sub>2</sub> capture on silicates can be enhanced at low temperature by water vapor addition,<sup>47–49</sup> producing acid carbonate (MHCO<sub>3</sub>) species instead of carbonate (Na<sub>2</sub>CO<sub>3</sub>) species. Those reports are in agreement with our IR observations on the NaCuSi<sub>10</sub>Ox sample in the presence of water.

It is worthwhile to mention that the initial bands at 2354 and 2342 cm<sup>-1</sup> (shoulder) due to physisorbed CO<sub>2</sub> are replaced with those from gas phase CO<sub>2</sub> as a function of adsorption time in the presence of H<sub>2</sub>O, which occurs simultaneously with the evolution of the carbonate species. This seems to suggest that H<sub>2</sub>O also competes with physisorbed CO<sub>2</sub> for similar adsorption sites on the NaCuSi<sub>10</sub>Ox sample, where H<sub>2</sub>O eventually dominates the shared sites. These IR results are in agreement with the TGA observations.

To investigate the stability of the various carbonate species formed on the NaCuSi<sub>10</sub>Ox sample, IR spectroscopy was used to follow desorption of the surface species formed from CO<sub>2</sub> adsorption in flowing He gas. The IR spectra during desorption at room temperature are shown in Fig. 9, for both dry and wet conditions. Prolonged purging (30 min in flowing He) at room temperature does not noticeably change the IR features of the carbonates and bicarbonates under both dry and wet conditions. The IR bands corresponding to physisorbed CO<sub>2</sub> species decline in intensity with increased purging time but are still observable even after purging in He for 30 min for the case of CO<sub>2</sub> adsorption in the absence of H<sub>2</sub>O (Fig. 9A). In contrast, the IR bands due to gas phase CO<sub>2</sub> readily vanish upon He purging to 2 min for the case of CO<sub>2</sub> adsorption in the presence of H<sub>2</sub>O (Fig. 9B). This indicates that the water addition is beneficial to the removal of physisorbed CO<sub>2</sub> species. Further heating as shown in Fig. S3A and B† gradually diminishes the IR features of carbonates and bicarbonates, and eventually the IR bands in the region of 1700–1200 cm<sup>-1</sup> disappear when the temperature increases up to 453 K. There is no apparent difference in the IR feature evolution of the various carbonate and bicarbonate species as a function of temperature in the absence and presence of water.

IR experiments for CO<sub>2</sub> adsorption and desorption on NaNiSi<sub>10</sub>Ox and NaMnSi<sub>10</sub>Ox in the absence and presence of water were also conducted and the results are shown in Fig. S3 and S4.† One similar observation is that in the presence of water, IR bands corresponding to the physisorbed CO<sub>2</sub> species are replaced by CO<sub>2</sub> gas phase features with increased adsorption time for all three samples, implying the competitive adsorption between CO<sub>2</sub> and H<sub>2</sub>O on the metal silicates. However, the contrast in IR features due to carbonates between the dry and wet CO<sub>2</sub> gases is much less evident on the NaNiSi<sub>10</sub>Ox and NaMnSi<sub>10</sub>Ox samples than on the NaCuSi<sub>10</sub>Ox sample, especially on NaMnSi<sub>10</sub>Ox. Meanwhile, for the



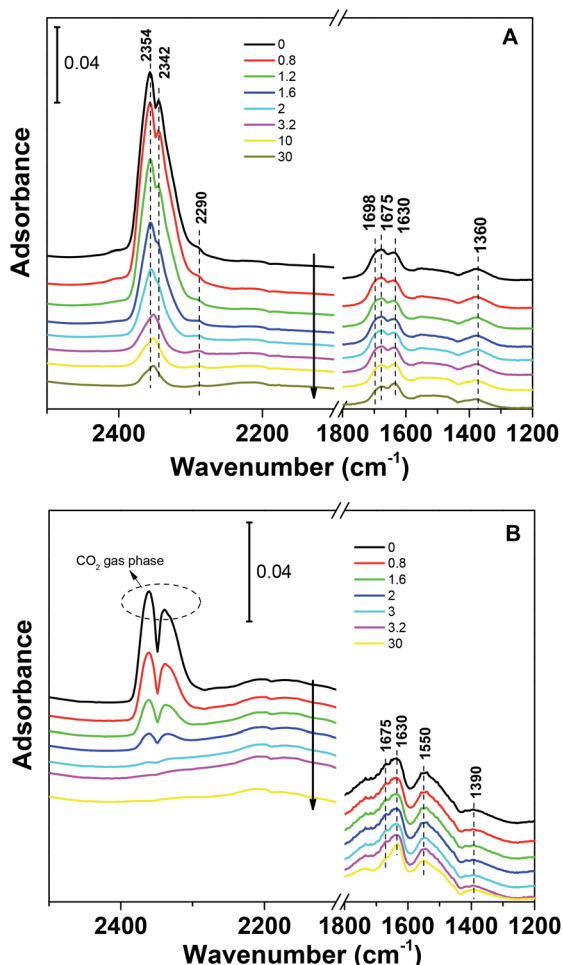


Fig. 9 IR spectra during CO<sub>2</sub> desorption on NaCuSi<sub>10</sub>Ox as a function of He purging time (30 min) for (A) dry and (B) wet conditions, respectively.

NaNiSi<sub>10</sub>Ox sample, the bicarbonate feature at 1633 cm<sup>-1</sup> slightly increases in intensity with adsorption time in the presence of H<sub>2</sub>O, and the weak bands ascribed to bicarbonates at 1493 and 1390 cm<sup>-1</sup> are only observed upon prolonged adsorption time (20–30 min). For NaMnSi<sub>10</sub>Ox, the change in IR features in the carbonates region is barely noticeable with wet CO<sub>2</sub> gas adsorption compared with the dry CO<sub>2</sub> case. Upon desorption at room temperature, the IR features due to the physisorbed CO<sub>2</sub> species under dry conditions decrease dramatically in intensity, and thus disappear with prolonged He purging in 5 min (Fig. S3B and S4B†) for both NaCuSi<sub>10</sub>Ox and NaMnSi<sub>10</sub>Ox. This suggests that interaction of CO<sub>2</sub> with the two silicates (Ni, Mn) is much weaker than that with NaCuSi<sub>10</sub>Ox, where physisorbed CO<sub>2</sub> species still persist after He purging for 30 min at room temperature.

The bonding strength of the chemisorbed CO<sub>2</sub>, *i.e.*, carbonate species, on these metal silicates is comparable according to the MS profiles of CO<sub>2</sub> evolved during the IR-TPD process (Fig. S5†) under both dry and wet conditions. However, it shows that in general the carbonate species formed in the presence of H<sub>2</sub>O require higher temperature to desorb

(up to 573 K) than those formed in the absence of H<sub>2</sub>O (up to 400 K). The higher the desorption temperature, the stronger the interaction is for CO<sub>2</sub> with the materials. So the MS results during CO<sub>2</sub>-TPD signify that H<sub>2</sub>O addition does reinforce the stabilization of the carbonate (bicarbonate) species on the metal silicates, consistent with the IR observation of these new species with the addition of water.

On the basis of the IR results, it is reasonable to postulate that CO<sub>2</sub> and H<sub>2</sub>O exhibit a competitive and cooperative adsorption model on the metal silicate samples, especially for NaCuSi<sub>10</sub>Ox and NaNiSi<sub>10</sub>Ox, a similar behavior to that reported for CO<sub>2</sub> and H<sub>2</sub>O coadsorbed on activated alumina.<sup>50</sup> It can be concluded that the H<sub>2</sub>O and CO<sub>2</sub> molecules competitively coadsorbed on the same sites of the metal silicate surface initially. Depending on the adsorption strength of CO<sub>2</sub> vs. H<sub>2</sub>O, a stronger adsorption strength of CO<sub>2</sub>, for example on NaCuSi<sub>10</sub>Ox, may permit its co-adsorption and synergistic interaction with H<sub>2</sub>O to produce new adsorbed bicarbonate and carbonate species and thus results in enhanced CO<sub>2</sub> capture capacity. In contrast, the presence of H<sub>2</sub>O has little effect on NaMnSi<sub>10</sub>Ox which has a weaker interaction with CO<sub>2</sub>. The results indicate that the three synthesized metal silicate materials could potentially be applied as CO<sub>2</sub> capture sorbents in humidified conditions with better/comparable CO<sub>2</sub> uptakes compared with dry conditions.

## Conclusions

CO<sub>2</sub> capture under dry and wet conditions has been evaluated on metal silicate materials (NaCuSi<sub>10</sub>Ox, NaNiSi<sub>10</sub>Ox and NaMnSi<sub>10</sub>Ox) at low temperatures (273–323 K). These metal silicate samples were directly derived by incorporation of metals into SBA-15 through a hydrothermal method. All of the metal silicates exhibit greatly higher CO<sub>2</sub> capture capability than the pristine SBA-15. CO<sub>2</sub> capture capability strongly depends on the textural parameters, such as surface area, of the metal silicates in the absence of H<sub>2</sub>O. H<sub>2</sub>O addition is able to facilitate the CO<sub>2</sub> uptake on the metal silicates, even though competitive adsorption is present between CO<sub>2</sub> and H<sub>2</sub>O on the samples. The enhancement in CO<sub>2</sub> capture depends on the type of metal introduced in/on the silicates. Metal silicates such as NaCuSi<sub>10</sub>Ox with strongest adsorption strength of CO<sub>2</sub> show the greatest increase in CO<sub>2</sub> capture capacity, due to the competitive and synergistic interaction between CO<sub>2</sub> and H<sub>2</sub>O on the same surface sites in forming new surface bicarbonate and carbonate species. On the basis of the TGA and IR results, the presence of water not only improves the CO<sub>2</sub> capture performance but also facilitates the removal of physisorbed CO<sub>2</sub> during the desorption process. These findings provide insights for designing new sustainable adsorbents based on metal silicate sorbents derived from SBA-15, of which the structure and the CO<sub>2</sub> sorption performance can be modified by controllable incorporation of different types of metals.

## Conflicts of interest

There are no conflicts to declare.



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