Novel fabrication of an efficient solid base: carbon-doped MgO–ZnO composite and its CO$_2$ capture at 473 K†

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A new strategy for fabricating an optimal porous strong base was reported for the first time. Magnesium and zinc acetates were mixed by microwave irradiation followed by carbonization at 823 K. Zn incorporation enabled the magnesia nanoparticles to have more surface defects, and about 80% of the basic sites were strong ones with the ability to capture CO$_2$ at 473 K, which is the highest proportion to date. These porous binary metal oxides had large surface areas between 130–296 m$^2$ g$^{-1}$.

Introduction

It is a challenge to fabricate optimal composites for social requirements, not only being low in cost and using an environmentally-benign process, but also having high efficiencies themselves. One noteworthy example is the special solid base to control CO$_2$ in flue gas that causes 30–40% of CO$_2$ emission in the world.1,2 The temperature of flue gas is usually over 423 K,3 and it would cost lots of energy-input to cool down the gas to below 373 K and capture the CO$_2$ with conventional adsorbents or absorbents.4 However, directly adsorbing the CO$_2$ in flue gas requires a special basic sorbent to capture CO$_2$ at 423 K or 473 K but desorb CO$_2$ at around 673 K in order to cut down the regeneration energy, which excludes many candidates. Zeolites, hydrotalcite, amine-functionalized materials and metal–organic frameworks (MOFs) fail to trap CO$_2$ at the elevated temperature,5–7 while Li or Ca-based capturers suffer from a high regeneration temperature (1073–1173 K).8 MgO is regarded as a promising candidate because of its abundant source, low cost and appropriate basic strength9 in comparison with new ionic liquid/alumina or mesoporous Al$_2$O$_3$–ZrO$_2$–organosilica adsorbents.10,11

It is crucial for a basic sorbent to have a sufficient capability, that is, the amount of CO$_2$ captured per gram of the sample at an elevated temperature such as 473 K must be adequate.9 MgO itself has a small value because of its small surface area so it has been improved through three main routes: supporting MgO on porous materials, creating pores in MgO, and admixing MgO with other components.12–21 However, the well dispersed MgO often lacks enough strong basicity and the inactive support inevitably lowers the adsorption capacity per gram of the sorbent.12,13 Forming pores in MgO is a complicated process using surfactants and solvents,13,14 and is accompanied by a high cost. Consequently, more attention is paid on admixing MgO with carbon, metal oxide or inorganic salts.15–17,21 This method is frequently used to prepare catalysts and photo-catalysts where MgO is used as the modifier to form MgO–TiO$_2$ and (ZnO)$_x$(MgO)$_{1-x}$15,18,19 or modified with alkali metal oxides,20–22 but few investigations have been performed on MgO-based CO$_2$ sorbents, let alone the CO$_2$ capturers at 473 K. For fabrication of the special basic CO$_2$ sorbents, low cost and high efficiency are crucial. The former demands cheap raw materials rather than expensive ones like magnesium alkoxide,23 and the latter requires the sorbent to have a high proportion of strong basic sites that can adsorb CO$_2$ at 473 K. Common MgO has various surface sites to adsorb CO$_2$ at ambient temperature, even the OH group,24 so its proportion of strong basic sites is low. Gregg and Ramsay subtly prepared a special sample of MgO from magnesium methoxide with a large surface area of 112 m$^2$ g$^{-1}$ and it adsorbed 0.64 mmol g$^{-1}$ of CO$_2$ at 273 K but 0.24 mmol g$^{-1}$ at 473 K so this ratio was 37%. How can this ratio for MgO-based sorbents be increased? This is a real challenge not only for the design of CO$_2$ sorbents in flue gas, but also involving the efficiency of the solid base related to the nature of the active sites and the surface state, which spurs us to seek a new strategy. It is reported that low-coordination sites on the surface of MgO are inefficient adsorptive sites,27 thus we try to create plenty of defects in magnesia through the special substitution between MgO and ZnO.

ZnO is one kind of amphoteric oxide featuring high abundance, low toxicity and photocatalytic ability,28 and it has many potential applications in electronics, catalysis and sensors.19 Nonetheless, ZnO lacks the basic sites with basic strength $H_0 \geq$
6.8 (ref. 29) so it cannot catalyze oxidative dehydrogenation until the addition of K₂O.²⁹ Substitution of Mg²⁺, with a smaller ion radius, for larger Zn²⁺ has been reported,³¹ which may be beneficial to inducing the migration of Mg²⁺ cations and tuning the surface state of magnesia to form more defects. Herein, magnesium acetate was employed to make a binary metal oxide with zinc acetate, and they were carbonized in nitrogen rather than air in order to suppress the CO₂ emission during the decomposition of acetate. The former salt provides newly-formed MgO accompanied with the carbon nano-particles and these MgO particles can be in situ separated by these carbons,³ while the latter acts as the accessory ingredient to adjust the surface state of MgO, enhancing the defect number of MgO and elevating the proportion of its strong basic sites. These two inorganic salts were mixed with different methods including microwave irradiation, solution and grinding, followed by carbonization at 823 K. The influences of the Mg/Zn ratio and the preparative procedures on the structure and properties of resulting composites were carefully investigated in order to select the optimal preparation method. To assess the potential application of these new basic sorbents in controlling CO₂ emission in flue gas, they were evaluated in the extremely harsh instantaneous CO₂ adsorption at 473 K as previously reported,³⁶³⁹⁻¹¹ in which the CO₂ concentration was lowered to 5% and the contact time between CO₂ and the adsorbent was shorter than 2 s.⁹

**Experimental section**

**Materials**

Magnesium acetate tetrahydrate and zinc acetate dihydrate were the product of Sinopharm and J&K Chemical (China), and MgO and ZnO were purchased from Shanghai Zhixin and Shanghai Chemical Reagent, respectively. Coconut carbon with an average pore size of 3–5 nm was provided by British American Tobacco.¹² All chemicals were of analytical grade and used as received without further purification.

**Synthesis of carbon-doped binary metal oxides**

(a) Microwave irradiation method. 0.963 g Mg(CH₃COO)₂·4H₂O and 0.110 g Zn(CH₃COO)₂·2H₂O were first ground for 5 min and then wetted with 0.75 ml water. After the mixture was irradiated in a National NN-S570MFS microwave oven with a power of 525 W for 4 min, it was carbonized at 823 K for 2 h in N₂.¹² The obtained solid was denoted as 82MZ where 82 is the weight percent of MgO in the binary metal oxide. Similarly, other nMZ samples like 78MZ or 80MZ with different n values were prepared. To explore the impacts of irradiation time and water content, various 82MZ(t, v) samples were synthesized, where t and v represent the microwave irradiation time (min) and the amount of water added (ml), respectively.

(b) Grinding method. Zn(CH₃COO)₂·2H₂O and Mg(CH₃COO)₂·4H₂O, with different molar ratios were ground at 298 K and a humidity of 45–55% for 20 min, followed by carbonization as mentioned above to give the sample of nMZ-g, where n signifies the calculated weight ratio of MgO in the binary metal oxide, and g means grinding.

(c) Solution-evaporation method. Zn(CH₃COO)₂·2H₂O and Mg(CH₃COO)₂·4H₂O, with the molar ratio of 1 : 9, were dissolved into 5 g H₂O and evaporated at 353 K overnight, followed by carbonization as mentioned above to give 82MZ-s sample where 82 is the weight percent of MgO in the solid, and s indicates the solution method. Other nMZ-s samples such as 54MZ-s and 3MZ-s were prepared using similar procedures.

For comparison, magnesium or zinc acetates were carbonized at 823 K to form MgO–C or ZnO–C, respectively.⁸ 82MZ-air was made using the same procedure as that of 82MZ, but calcined in air. To get the mixture called MZAC, 0.5 g MgO and 0.113 g ZnO as well as 0.008 g coconut carbon were ground for 10 min.

**Characterizations**

Wide-angle X-ray diffraction (XRD) patterns of the samples were recorded on an XRD-6000 diffractometer (power 40 kV, 30 mA) using Cu-Kα radiation in the 2-theta range from 10° to 80°, and low-angle XRD patterns were obtained on an ARL XTRA diffractometer (40 kV, 40 mA, Cu-Kα radiation) in the 2-theta range from 0.5° to 6°. Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 system at 77 K, and the sample was evacuated at 573 K for 4 h prior to the test. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area of the samples using the adsorption branch acquired at a relative pressure (P/P₀) range of 0.05–0.22, and the total pore volume was estimated from the amount adsorbed at a relative pressure (P/P₀) of 0.98. Scanning electron microscopy (SEM) images were obtained on Hitachi S4800 microscopes at 10 kV, 10 μA, and elemental mapping and Energy Dispersive X-ray Spectroscopy (EDX) analysis of samples was taken using the same instrument at 20 kV, 15 μA. Transmission electron microscopy (TEM) images were collected on a JEM-1011 electron microscope operating at 200 kV.¹⁶ High-resolution transmission electron microscopy (HRTEM) images were acquired using JEM-2000CX equipment at an acceleration voltage of 200 kV. For the measurement the sample was ground into powder and dispersed into ethanol solvent, and the obtained suspensions were dripped and dried on a carbon film supported on copper mesh. Photoluminescence (PL) properties were detected using a Varian Cary Eclips luminescence spectrometer with a wavelength of 325 nm as the excitation using a HeCd laser. Elemental analysis was conducted using a vario EL II instrument. UV-visible diffuse reflectance spectra was measured on a Shimadzu UV3600 instrument and converted from reflection to absorbance using the Kubelka–Munk method.

To assess the performance of porous samples in instantaneous CO₂ adsorption at 473 K,¹⁴ the in situ prepared sample after carbonization in a u-type quartz tube in N₂ was kept at 473 K, and 0.164 ml of CO₂ was injected each time accompanied with carrier gas (H₂, 30 ml min⁻¹). The residual CO₂ was detected using an “online” Varian 3380 gas chromatograph and quantitatively measured using the external standard method.⁵
In the cyclic CO$_2$ adsorption–desorption detection, once the adsorption of CO$_2$ was finished, the sample was allowed to re-adsorb CO$_2$ in the same manner aforementioned as soon as the entire desorption process (sample was directly heated from 473 K to 673 K and held at 673 K for 1 h) was finished. A temperature programmed desorption (TPD) test was performed as follows: 20 mg of sample was put into a u-type quartz tube to be activated in N$_2$ (99.995%) at 823 K for 2 h, and then cooled to 298 K for adsorbing CO$_2$ as stated above, and then was purged with N$_2$ for 10 min. Finally it was heated from 298 K to 823 K at a rate of 8.8 K min$^{-1}$ and maintained at 823 K for 1 h, meanwhile the liberated CO$_2$ was detected and recorded using an “online” Varian 3380 gas chromatograph.

Static adsorption of CO$_2$ at 298 K was performed using a Micromeritics ASAP 2020 static volumetric instrument, in which samples were degassed at 573 K for 12 h before CO$_2$ adsorption. The CO$_2$ adsorption isotherm at 423 K and 473 K was recorded also using a Micromeritics ASAP 2020 instrument.$^{9,13}$ Prior to the adsorption of CO$_2$, the sample was degassed at 673 K for 6 h, and then was cooled down to the given temperature, followed by the introduction of CO$_2$ to contact with the sample. The CO$_2$ adsorption amount was then recorded according to the adsorbed volume under standard temperature and pressure (STP).

To monitor the dynamic adsorption and desorption of CO$_2$ on the 82MZ sample, a Netzsch STA449C TG/DSC analyzer was employed. In the CO$_2$ adsorption experiment, 20 mg of the sample was first heated under a N$_2$ flow (25 ml min$^{-1}$) at 823 K for 2 h and then cooled down to 473 K, followed by CO$_2$ introduction into the system (25 ml min$^{-1}$, 1.5 h). Meanwhile, the weight increase of the sample was recorded. For the desorption of CO$_2$, the 82MZ sample that had adsorbed CO$_2$ at 473 K was purged under N$_2$ at 473 K for 1 h, and then was heated to 673 K at a rate of 10 K min$^{-1}$, followed by holding at 673 K for 1 h. The decrease in the sample weight was also recorded. The regeneration property of the 82MZ composite was measured using a cyclic CO$_2$ adsorption–desorption experiment. The sample was also activated as stated above and adsorbed CO$_2$ for 1 h at 473 K with N$_2$ purging for 5 min, then CO$_2$ desorption was performed as above. Once the first cycle was completed, the sample was allowed to re-adsorb CO$_2$ for another cycle.

**Results**

**Characterization of carbon-doped binary metal oxide**

Fig. 1 displays the wide-angle XRD patterns of nMZ composites along with MgO–C and ZnO–C. The cubic crystalline phase of MgO appeared on the patterns of the nMZ composites, with the 2-theta values of 42.9$^\circ$ and 62.3$^\circ$ corresponding to the (200) and (220) planes respectively,$^{32}$ together with the wurtzite ZnO structure with typical diffraction peaks between 2-theta values of 30$^\circ$ and 40$^\circ$ for the (100), (002) and (101) planes.$^{19}$ This phenomenon demonstrated that a certain amount of MgO and ZnO components had a phase-disengagement with each other on a macrolevel,$^{19}$ which was very different from that of zinc-doped MgO (Zn$_x$Mg$_{1-x}$O) powders where no signature of the ZnO phase could be identified when 10% ($x = 0.1$, molar ratio) of Zn was doped.$^{33}$ As shown in the inset of magnified patterns, one peak of the ZnO (002) plane in the nMZ samples shifted ~0.1$^\circ$ higher in comparison with that of ZnO–C, and such a shift of the (002) peak in 88MZ was more obvious than in 78MZ, which is very similar to that seen with (ZnO)$_x$ (MgO)$_{1-x}$ nanoparticles.$^{19}$

A similar shift was also observed in the XRD patterns of other 82MZ(t, v) composites (Fig. S1b†), but was absent in the 82MZ-g sample. In the 82MZ-air sample which was calcined and carbon-free (Fig. S2†), a similar shift of the ZnO (002) plane was found, indicating the major role played by microwave irradiation instead of the carbon component for the shift phenomenon. These results implied the substitution of Zn$^{2+}$ with a radius of 0.060 nm (ref. 34 and 35) by the Mg$^{2+}$ ion with a smaller radius of 0.057 nm.$^{36}$ Although the 82MZ-s sample contained the same MgO content as 82MZ did, it had faint characteristic peaks of MgO and ZnO (Fig. S1a†) so that the ZnO (002) plane was indiscernible.

In the N$_2$ adsorption–desorption experiment, 82MZ, 82MZ-s and 82MZ-g samples showed the type IV isotherm (Fig. 2a) with a H3 hysteresis loop in the relative pressure range from 0.4 to 0.9, demonstrating the characteristic of disordered mesoporous structure.$^{37,38}$ Actually they had a narrow pore-size distribution centered at 3–4 nm (Fig. 2b). Other 82MZ(t, v) and nMZ-g samples also demonstrated a similar character of mesoporous structure as shown in Fig. S3,† but ZnO–C showed an isotherm of type II with a H3 hysteresis loop in the relative pressure range of 0.8–1.0, signifying the presence of macroporous structure with slit-like pores,$^{39}$ and it had large pores of 20–100 nm (Fig. 2b). Low-angle XRD patterns of 82MZ-s and 82MZ samples were characterized with one broad reflection peak at the 2-theta value of 1$^\circ$ (Fig. 2c), mirroring the existence of mesoporous structure with no long-range order in the pore organization.$^{40}$ 82MZ-s and nMZ composites had surface areas of 130–170 m$^2$ g$^{-1}$, lower than those of the MZ-g samples (Table 1). The surface

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*Fig. 1* Wide-angle XRD patterns of (a) 78MZ, (b) 80MZ, (c) 82MZ, (d) 84MZ, (e) 86MZ, (f) 88MZ, and ZnO–C, MgO–C samples. Inset: the corresponding amplified XRD patterns.
areas and pore volumes of MZ-g increased gradually as the MgO content increased from 78% to 94%, and achieved 295.7 m² g⁻¹ and 0.27 cm³ g⁻¹, close to that of the carbon-inserted MgO sample.  

82MZ and 82MZ-s samples were composed of various small particles (Fig. 3), but those in the former had relatively uniform sizes below 2 µm while those in the latter varied from 0.2 to 8 µm. Such heterogeneous particle aggregation was also found in the 54MZ-s and 88MZ-s samples. According to the TEM images in Fig. S5† the 82MZ sample had a worm-like, irregular pore structure (Fig. S5†), while 82MZ-s was comprised of relatively big and round particles. Both of them contained individual particulates on their surface (Fig. 4a and c), but those on 82MZ-s seemed a little bigger (Fig. 4e). The emergence of multiple electron diffraction rings on 82MZ and 82MZ-s (insets of Fig. 4a and c) demonstrated the formation of polycrystalline structure.  

In comparison with those of the MgO–C sample (Fig. 4e), their new diffraction rings/spots (insets of Fig. 4a and c) could be indexed to ZnO diffraction patterns. The diffraction rings of 82MZ-s were not as distinct and regular as those of 82MZ because of its weak crystallization (Fig. S1a†). Unlike the lattice fringes of MgO–C and ZnO–C (Fig. 4f and h), the incorporation of ZnO in 82MZ and 82MZ-s caused more disordered structures in these composites and some of the fringes twisted or disconnected (labelled with red circle) (Fig. 4b and d), indicating the possible alloying process of MgO with ZnO, which dovetailed well with the XRD results (Fig. 1). The ZnO–C sample had a single crystal structure (inset of Fig. 4g), and the lattice spacing was about 0.26 nm (Fig. 4h) which could be indexed to the (002) plane of wurtzite-structured ZnO. These results showed the growth of ZnO–C along the (002) direction, which was the reason why only the (002) peak shift occurred in the XRD patterns (Fig. 1). Elements C, Mg and Zn were uniformly distributed in the 82MZ and 82MZ-s samples (Fig. 5a and S6†), but accumulation of the Zn species was found in 82MZ-g (marked with a red ellipse, Fig. 5b) due to the non-homogeneous distribution of Zn related to the grinding preparation. EDX spectra confirmed the existence of Mg, Zn and a small quantity of carbon in these composites. 

Surface defects and vacancies directly affect the properties of MgO in adsorption, catalysis, fluorescence etc. and in particular, they provide the necessary strong basic sites for CO₂ adsorption at 473 K. PL spectra which can give the instructive evidence of surface structural defects were employed to analyze the prepared samples (Fig. 6a). A remarkable enhanced PL emission was detected in the 82MZ composite in comparison with that of MgO–C or ZnO (Fig. 6a), and this spectrum was

Table 1 Textural properties of the MgO–ZnO binary oxides and their CO₂ adsorption capacities

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Adsorbed CO₂ at 473 K (mg g⁻¹)</th>
<th>Adsorbed CO₂ at 473 K (mg m⁻²)</th>
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<tr>
<td>ZnO–C</td>
<td>0.03</td>
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<td>0.09</td>
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<td>MgO</td>
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<td>0.18</td>
<td>200.9</td>
<td>22.8</td>
<td>0.11</td>
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<tr>
<td>82MZ-g</td>
<td>0.18</td>
<td>203.1</td>
<td>28.2</td>
<td>0.14</td>
</tr>
<tr>
<td>88MZ-g</td>
<td>0.20</td>
<td>228.2</td>
<td>18.4</td>
<td>0.08</td>
</tr>
<tr>
<td>94MZ-g</td>
<td>0.27</td>
<td>295.7</td>
<td>19.4</td>
<td>0.07</td>
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<td>0.18</td>
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<td>138.7</td>
<td>21.8</td>
<td>0.16</td>
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Fig. 2 (a) N₂ adsorption–desorption isotherms, (b) pore-size distributions of the MZ series composites and (c) low-angle XRD patterns of the 82MZ and 82MZ-s samples.

Fig. 3 SEM images of 54MZ-s, 82MZ-s, 88MZ-s and 82MZ samples.
deconvoluted using multi-peak Gaussian fitting (inset of Fig. 6a) to generate three distinguishable peaks at 449, 472 and 537 nm. Among them the 472 nm band corresponded to MgO structural defects,\textsuperscript{18,45} the broad 537 nm emission band related to oxygen vacancies of ZnO\textsuperscript{46} on 82MZ, and the enhanced emission might mirror the recombination between interstitial Mg and zinc vacancies as Mg defects increase.\textsuperscript{47} Apparently, the defect sites of 82MZ were much more abundant than those of MgO–C whose emission was indistinct at 485 nm (Fig. 6a), mirroring the role of ZnO as an important accessory ingredient. The 82MZ sample has the same composition as the MZAC mixture did, but their PL spectra differed dramatically. The defect sites of MgO became prominent and enlarged in the former while the latter was really the mixture of PL bands of MgO, ZnO and carbon, which indicates the interactions between ternary components in the 82MZ composite rather than in the mechanical mixture. In contrast, a broad green emission band centered at 450 nm with a minor shoulder at about 485 nm was observed in the MgO–C and MgO samples, which was associated with the surface OH\textsuperscript{−} in low coordination sites such as corners and edges of MgO,\textsuperscript{18} and the shoulder band of 485 nm was related to MgO defect sites.\textsuperscript{18} One broad emission at roughly 518 nm in ZnO may relate to oxygen vacancies.\textsuperscript{46} In the UV-vis absorbance results shown in Fig. S7,\textsuperscript{†} the ZnO–C and MZAC samples showed a strong absorption in UV region around 365 nm but no obvious absorption in visible-light region while MgO–C exhibited a rather faint absorption. However, the absorption edge of 82MZ shifted to the visible light region with an obviously strengthened intensity, which related to the interaction between the subject (MgO) and the guest (ZnO).\textsuperscript{48,49}

**Adsorption of CO$_2$ at 473 K by MgO-based composites**

Instantaneous CO$_2$ adsorption was used to assess the basicity of the MgO–ZnO composites. 82% of MgO was proven to be

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**Fig. 4** HRTEM images of (a) 82MZ, (c) 82MZ-s, (e) MgO–C and (g) ZnO–C samples, and the insets of (a), (c), (e) and (g) are the corresponding selected area electron diffractions; (b), (d), (f) and (h) are the relevant lattice fringe images.

**Fig. 5** SEM images, X-ray mapping, and EDX spectra of (a) 82MZ and (b) 82MZ-g samples, in which the magnification is 3500x and 4000x respectively.
optimal for the MZ samples no matter if they were prepared through microwave irradiation, grinding or solution procedures (Table 1, Fig. S8†), and 82MZ could capture 33.3 mg g$^{-1}$ of CO$_2$ at 473 K. This value exceeded that of MgO (1.9 mg g$^{-1}$) or carbon-inserted MgO (28 mg g$^{-1}$). The 82MZ sample contained about 1.2% of carbon (Table S1†) and about 82% of MgO, that is, 1 g MgO in this composite can capture 33.3/0.82 = 40.6 mg g$^{-1}$ of CO$_2$ at 473 K, which is the highest efficiency of MgO to date.⁹ Lowering the water content or irradiation time in the preparation of the 82MZ($t,v$) samples only caused a minor effect since these composites kept the adsorption capacities of 24–31 mg g$^{-1}$ (Fig. 7a). Without water added, the 82MZ(4, 0) sample still adsorbed 21.8 mg g$^{-1}$ of CO$_2$ at 473 K (Table 1). For the samples prepared through solution-evaporation, their CO$_2$ adsorption capacities increased as the content of MgO was raised from 5% to 82% (Fig. S8a†), and reached a climax of 24.9 mg g$^{-1}$ in 82MZ-s (Table 1). Further increasing the MgO content could not elevate the adsorption. Similar behavior was seen in the MZ-g samples (Fig. S8b†), and among them 82MZ-g was also the champion to adsorb CO$_2$ of 28.2 mg g$^{-1}$ at 473 K. ZnO–C could hardly adsorb CO$_2$ (Table 1, Fig. S8a†), because of its small surface area and amphoteric character.

Since only the top layer of MgO can contact CO$_2$, it is important to calculate the efficiency of the sorbent by the amount of CO$_2$ trapped on each unit of surface area.⁹ According to the data in Table 1, 82MZ had the highest value of 0.25 mg m$^{-2}$, 4 times larger than that of MgO (0.05 mg m$^{-2}$). Next, the three 82MZ($t,v$) series samples, including 82MZ(6, 0.25), (3, 0.25) and (4, 0) along with 82MZ-s, showed large values of 0.16–0.19 mg m$^{-2}$, more than twice that of MgO (Table 1). Additionally, the 82MZ composite showed good performance in the 7th adsorption–desorption cycle (Fig. 7b), keeping about 70% of the original adsorption capacity within experimental error. Its structure remained stable without phase variation after CO$_2$ adsorption at 473 K and desorption at 673 K (inset of Fig. 7b).

TGA analysis was performed on the 82MZ sample to get the real kinetics of CO$_2$ capture. Its adsorption can divide into two stages (Fig. 8a): the first is a quick adsorption and 33% of the total adsorption is achieved within 9 min. After 19 min of exposure to CO$_2$, the sample weight increased by 1%, achieving half of the total adsorption. The residual half needed another 70 min with a relatively low adsorption rate (Fig. 8a). During TGA analysis, the sample was put into a crucible with an inner diameter of 0.65 cm and length of 1.3 cm (inset of Fig. 8a), CO$_2$ was purged from the bottom up and contacted the sorbent in the crucible through diffusion, which caused a lower adsorption rate within the first 19 min at 473 K than the adsorbents of KCC-
The adsorption rate showed a first quick then slow trend overall, since CO$_2$ was firstly adsorbed on the surface affinity sites of 82MZ, and the remaining adsorption sites in the bottom were not easily accessible, therefore the adsorption rate decreased a lot in the subsequent 70 min. The different adsorption temperature (473 K and 298 K, this is the crucial difference) is the intrinsic reason for the lower adsorption rate for diffusion-controlled MgO-based adsorbent than for KCC-1-N700.

The CO$_2$ desorption finished within 23 min (Fig. 8a), and almost all of the adsorbed species were desorbed from the 82MZ composite at 673 K. Compared with some CaO-based adsorbents, the low regeneration temperature of 82MZ is very advantageous for saving energy and time. Yet, the adsorption capacity of the 82MZ sample at 473 K during this TGA analysis was 20 mg g$^{-1}$, 61% of that in instantaneous CO$_2$ adsorption. One reason for the different results is the flow manner of the carry gas. The gas flow passes throughout the u-type quartz tube containing the sample in the instantaneous CO$_2$ adsorption and thus all particles of the sample can contact the CO$_2$ in the gas stream while in the TGA test, the gas flow passes through the crucible so that only the particles located on the surface of the sample can contact the adsorbate. Obviously, the sample lacks the adequate contact with CO$_2$ in the TGA experiment compared to that in the instantaneous CO$_2$ adsorption.

Continual adsorption–desorption cycles of the 82MZ sample in TGA were also studied (Fig. 8b). After one cycle, the adsorption amount of the sorbent decreased to 73% of the initial value, but basically kept the same value in the following adsorption–desorption processes. After the 5th cycle, the 82MZ composite could keep 70% of the original ability (Fig. 8b). Actually, the reuse capability of 82MZ at 473 K was inferior to that of KCC-1-N700 etc. at 298 K. The CO$_2$-TPD experiment can give instructive evidence on the amount and strength of basic sites of the sorbent, thus it was utilized for the MgO, MgO–C and 82MZ composites as displayed in Fig. 9.

Three corresponding TPD curves were deconvoluted using a multi-peak Gauss fitting method, generating several distinguishable peaks at different temperatures. Two desorption peaks appeared at 368 and 491 K in MgO (Fig. 9a), representing the weak and medium-strong basic sites, respectively. Also, the MgO–C sample has similar basic species, but its basic strength is much stronger in comparison with MgO (Fig. 9b). Once ZnO was incorporated into 82MZ, the climax of the desorption peaks shifted towards the high temperatures of 615 and 669 K (Fig. 9c), and these basic sites can be ascribed to medium-strong ones, which was very significant for the ability of 82MZ to capture CO$_2$ at 473 K while desorbing CO$_2$ at 673 K. Moreover, the kinds of basic sites in 82MZ increased a lot compared to the MgO and MgO–C samples, which dovetailed nicely with the PL results (Fig. 6a). The percentage of basic sites in the 82MZ sample could be calculated through peak area integrals. The medium-strong basic sites with desorption peaks centered at 477 K to 669 K account for 84% of the total basic sites in the 82MZ composite, which is very helpful for the sorbent to capture CO$_2$ at 473 K.

Static adsorption of CO$_2$ was conducted on 82MZ to have an overall assessment on the basic composite. The quantity of CO$_2$ adsorbed at 423 and 473 K positively correlated with the pressure, reaching 36.2 and 32.5 mg g$^{-1}$ respectively, at standard pressure (Fig. 10a). Due to the exothermic process of CO$_2$ adsorption, the adsorption capability of 82MZ at 473 K was inferior to that at 423 K, but its capacity at 473 K in this static condition (32.5 mg g$^{-1}$, Fig. 10a) inosculated well with the value of instantaneous adsorption (33.3 mg g$^{-1}$, Table 1). When CO$_2$ of 4.7 cm$^3$ g$^{-1}$ (STP) was adsorbed on 82MZ, the isosteric heat of adsorption reached the value of 27.8 kJ mol$^{-1}$ (Fig. 10a). However, as the amount of CO$_2$ reached 15 cm$^3$ g$^{-1}$ (STP), a lower adsorption heat of 4.9 kJ mol$^{-1}$ was obtained due to the existence of different basic sites. CO$_2$ adsorption was also performed on the MgO, MgO–C and 82MZ samples at 298 K, and the adsorption capacities increased as the CO$_2$ pressure rose (Fig. 10b). It is worth noting that MgO is the champion in CO$_2$.
adsorption at 298 K, but performs poorly at 473 K (1.9 mg g⁻¹, Table 1).

Discussion

It is meaningful to compare the discrepancy between the CO₂ adsorption capacities of MgO, MgO–C and 82MZ at 298 K and 473 K, in order to obtain the instructive evidence of the roles played by the newly-formed carbon and more importantly, the ZnO modifier. The adsorption capacity at 298 K originates from the contribution of all basic sites while that at 473 K only comes from strong basic sites therefore the proportion of strong basic sites in the sorbent can be estimated through this difference. The MgO, MgO–C and 82MZ samples adsorbed 61.2, 53.1 and 42.1 mg g⁻¹ CO₂ at 298 K (Fig. 6b) but 1.9, 27.7 and 33.3 mg g⁻¹ at 473 K hence their ratios of strong basic sites are 3%, 52% and 79%, respectively. The MgO–C sample contains some carbon nano-particles that in situ separate the MgO particles so that it has a higher ratio of strong basic sites (52%) than that of the MgO made from expensive magnesium methoxide (37% (ref. 25)). The 82MZ sample consists of fewer carbon nano-particles (1.2%) and MgO (about 82%) than MgO–C (2.5%, 87.5%) but it exhibited a higher ratio of strong basic sites owing to the crucial interaction with the ZnO modifier.

Substitution of Zn²⁺ by Mg²⁺ in the 82MZ sample changed its surface state. The position of the (002) crystalline plane of ZnO slightly shifted to a higher 2-theta angle in the 82MZ sample (Fig. 1), due to the substitution of Mg²⁺ with smaller ion radius for larger Zn²⁺. The ZnO composite can be prepared with a preferred c-axis (002) orientation using a special synthesis or particular substrate, resulting in the enhanced properties since the preferred (002) orientation along the c-axis of ZnO is a denotation of the minimization of internal strain, surface free energy and closed-packed arrangements of atoms. Herein, MgO acted as a “substrate”, and ZnO interacted with the

Fig. 9 CO₂-TPD profiles of (a) MgO, (b) MgO–C and (c) 82MZ samples measured from 298 to 823 K at a rate of 8.8 K min⁻¹ and held at 823 K for 1 h.

Fig. 10 (a) The isotherms of CO₂ adsorption at 423 and 473 K for the 82MZ sample, inset is the isosteric heat of adsorption on this sample, (b) isotherms of CO₂ adsorption at 298 K for the MgO, MgO–C and 82MZ samples.
“substrate” through the (002) plane along the c-axis (Scheme 1), in which the small Mg$^{2+}$ substituted Zn$^{2+}$ and led to the shift of the (002) peaks in Fig. 1. Additionally, the displacement of Zn$^{2+}$ by Mg$^{2+}$ caused vacancies or defects in the MgO lattice (Scheme 1), increasing the number of low-coordinated O$^{2-}$ defect sites (Fig. 6a) and enhancing the proportion of strong basic sites to 79% in the 82MZ composite, far beyond that in MgO. Chemisorption plays a dominant role in capturing CO$_2$ at 473 K, and even though the MgO surface had different defect sites, CO$_2$ was chemisorbed and formed carbonate species on these low-coordinated O$^{2-}$ defect sites, therefore the increased low-coordinated O$^{2-}$ defect sites was beneficial for 82MZ in CO$_2$ capture at 473 K.

It was very important for MgO to keep the original crystals and exposure of defects for adsorbing CO$_2$ at elevated temperature, which was really realized in 82MZ: firstly, the in situ formed carbon nano-particles separated MgO and ZnO in integrated crystals as shown in Fig. 1 where all of the characteristics of MgO and ZnO were well presented, unlike the single-phase with only the preferred orientation along the c-axis of the Co$_{0.2}$Mg$_{0.8}$Zn$_{0.8-x}$O films. Secondly, but most importantly, the added ZnO component increased the defects of the MgO adsorbent (Scheme 1), thus elevating the proportion of strong basic sites for adsorbing CO$_2$ at 473 K. It is the specific separation and modulation of the incorporated ZnO and the in situ formed carbon that endows 82MZ with an effective CO$_2$ adsorption capability.

Two factors impact the optimization of the carbon-doped MgO–ZnO composites as basic sorbents: one is the optimized incorporation of Zn, and the other is the preparation process. Zn incorporation in MgO is definitely important since it can increase the abundance of defect sites (Fig. 6a), but its amount should be optimized: ZnO–C had a small surface area and pore volume (Table 1) so that its introduction was unfavorable for enlarging the surface area of the sorbent. 18% ZnO incorporation enabled nMZ-s, nMZ-g and nMZ to efficiently adsorb CO$_2$ at 473 K (Fig. S8, inset of Table 1), but this amount of ZnO (18 wt%, that is 10 mol%) was lower than the solubility limit of ZnO in the binary MgO–ZnO composites at high temperature (28 mol% (ref. 33 and 54)). By this token, the ZnO crystalline peak should be absent in the wide-angle XRD patterns of 82MZ. However, all the 82MZ-x composites presented the characteristic peaks of ZnO (Fig. 1 and S1α†), probably due to the “carbon insertion” in the composite." These newly-formed carbon extra-fine particles, with a weight ratio of 1–2% (Table S1†), admixed with MgO and ZnO to separate them. Consequently, the ZnO component had phase-separated (Fig. 1 and S1α†) with MgO even though its molar percentage was below the solubility limit (about 28 mol% (ref. 54)).

Preparation of MgO–ZnO composites is very important to determine their structure and properties. Microwave irradiation enabled magnesium and zinc acetates to be properly mixed and interact with the assistance of suitable water, and they could form eutectic salts with similar decomposition temperatures, therefore the newly-formed carbon could isolate the simultaneously produced MgO and ZnO particles well, producing 82MZ with an unexpected proportion of strong basic sites (Fig. 6b). The drawback of the grinding method is its poor repeatability (Fig. S9) and the uneven distribution of Zn species (Fig. 5b); no substitution of Zn$^{2+}$ by Mg$^{2+}$ was found in crystal lattice (Fig. S1b†). ZnO acted as merely an adulterant so that the MZ-g samples showed a low CO$_2$ adsorption efficiency of 0.07–0.14 mg m$^{-2}$ (Table 1).

During the evaporation of the solution, acetate anions can hydrolyze into CH$_3$COOH and OH$^-$ within a chemical equilibrium, and some Mg and Zn cations turn into Mg(OH)$_2$ and Zn(OH)$_2$ (ref. 56). Zn(OH)$_2$ decomposes to form ZnO around 413 K but the thermal-decomposition of Mg(OH)$_2$ takes place at about 573 K. Thus, the production of MgO and ZnO in the sample was asynchronous so that the newly-formed carbon could not separate MgO and ZnO simultaneously, and the pre-produced ZnO might aggregate together as the temperature increased up to 823 K (Fig. 3). Thus, the 82MZ-s sample had a weak crystalline structure (Fig. S1a† inset of Fig. 4c) along with a lower CO$_2$ adsorption ability (24.9 mg g$^{-1}$, Table 1) than 82MZ and 82MZ-g.

Apart from the efficient CO$_2$ adsorption of the 82MZ sample at 473 K, the suppression of CO$_2$ emission in its preparation cannot be ignored. 340 mg of the precursor of 82MZ (equalling 94 mg of the sorbent) released 232 mg CO$_2$ in the calcination in air but 104 mg in the carbonization in nitrogen, that means, carbonization of the acetates suppressed 44% of CO$_2$ emission so that the production of every gram of the sorbent is accompanied with the CO$_2$ emission reduction of (232 – 104)/94 = 1.4 g. Moreover, the 82MZ sample contains 12 mg g$^{-1}$ of carbon that can form 44 mg of CO$_2$. These efforts are beneficial for suppressing the CO$_2$ emission at source.

**Conclusion**

New porous strong bases, carbon-doped MgO–ZnO, have been successfully fabricated from magnesium acetate and zinc acetate. Two cheap acetates were well mixed through microwave irradiation, followed by carbonization at 823 K to form the
optimal mesoporous basic composites like 82MZ with a large surface area of 130–296 m² g⁻¹.

Owing to the addition of ZnO and its interaction with MgO, new composites such as 82MZ have abundant basic sites. Among them, 79% are strong basic sites that can capture CO₂ at 473 K and this proportion is the highest value to date.

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Notes and references


