Significantly Increasing Porosity of Mesoporous Carbon by NaNH₂ Activation for Enhanced CO₂ Adsorption

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ABSTRACT Sodium amide (NaNH_2), a readily available strong base, was investigated as an efficient reagent for chemical activation of mesoporous carbon (MC) in the temperature range of 400–900°C, aiming to enhance the CO_2 adsorption performance. Total surface area and pore volume of the activated MC increase greatly with the activation temperature up to 700°C and then tend to level off. Small micropores with a diameter $<1\text{nm}$ are developed mainly at low temperatures (400–550°C) and decrease continuously in volume as the activation temperature increases. Nitrogen species are incorporated onto the carbon activated at 400°C but completely disappear at higher activation temperatures due to poor thermal stability. CO_2 adsorption experiments illustrated a substantial improvement in capacities at 0°C for the NaNH_2 -activated carbons (6.31mmol/g at 1bar and 2.06mmol/g at 0.15bar) in comparison to pristine MC (2.01mmol/g at 1bar and 1.00mmol/g at 0.15bar). The low-pressure CO_2 capacities are well correlated with the volume of small micropores rather than the total micropore volume and surface area. The activation ability of NaNH_2 was compared with those of KOH and NaOH, verifying the superiority of NaNH_2 in the MC activation under relatively moderate conditions, *i.e.*, activation reagent/MC weight ratio of two and activation temperature of 550°C.

KEYWORDS Mesoporous carbon; activation; sodium amide; microporosity; CO_2 adsorption

1. INTRODUCTION

The emission of CO₂, which is mostly produced from the combustion of fossil fuels, has attracted extensive attention across academic and industrial communities because of its potentially destructive impact on the environment. Carbon dioxide is a well-known greenhouse gas and its accumulation in the atmosphere is believed to be a major contribution to the continuous global warming over the past century. In the near future, fossil fuels will still be the major source of energy for human activities; therefore, the capture of CO₂ has been proposed as an essential solution to limit or slow climate change. A method commonly used in industry for the reduction of CO₂ emissions is absorption in aqueous amine solutions [1]. However, organic amines are highly volatile and corrosive, and the regeneration of these absorbents is an energy-intensive process. These factors depict the inherently unfavorable nature of aqueous amines, and the exploration of new materials for CO₂ capture has thus been widely demanded.

Porous solid adsorbents such as metal-organic frameworks (MOFs) [2], porous polymer networks (PPNs) [3], covalent organic frameworks (COFs) [4], porous carbons (PCs) [5], and supported amines [6] are potential alternatives that have been widely investigated. Among them, porous carbons feature many inherent advantages, including potentially low cost, high stability, large surface areas, tunable pore structures, high thermal conductivity, and ease of surface functionalization [7]. Carbons have been demonstrated to have potential applications in many fields such as

electrochemistry [8], catalysis [9], and gas separations [10]. Porous carbons with well-developed microporosity, especially small micropores with size below 1 nm, are particularly attractive for application in CO₂ adsorption, as described in several previous works [11-14]. To create abundant micropores, pristine carbons are usually subjected to post-synthesis activation. KOH [15-18] is the most frequently used activation agent, while K₂CO₃ [19], H₃PO₄ [20], ZnCl₂ [21], NH₃ [22, 23], CO₂ [24, 25], and H₂O [26, 27] have been less frequently employed. Jaroniec et al. [28] compared the ability of different agents for the activation of a commercial carbon and found KOH-activated carbon had the most developed microporosity and enhanced adsorption capacity for CO₂.

However, the KOH-activation method usually requires high activation temperatures (>600°C) to obtain porous carbons with optimized CO₂ adsorption performance. For example, Machnikowski et al. [29] synthesized granular activated carbons that could adsorb 6.2 mmol/g of CO₂ at 0°C and 1 bar by activating coal-based cokes with KOH at 800°C. Jaroniec et al. [11] reported the activation of phenolic resin-based mesoporous carbons by KOH at 700°C to result in products showing a CO₂ adsorption capacity of 4.37 mmol/g at 25°C and 1 bar. Park et al. [30] investigated the effect of KOH-activation temperature on CO₂ adsorption of carbon aerogels and found the sample activated at 900°C exhibited the highest CO₂ adsorption capacity of 2.48 mmol/g at 25°C and 1 bar. Suarez-Garcia et al. [31]

activated carbon xerogels with KOH at 800°C to result in products displaying CO₂ adsorption capacity of 4.9 mmol/g at 0°C and 1 bar.

It is of significance to develop a new method for the efficient activation of carbon materials under relatively mild conditions. In our recent work [32], we introduced a low-temperature (230–380°C) route to N-doped mesoporous carbons using a strong base – sodium amide (NaNH₂) as the N-doping agent. It was interesting to find that the incorporation of nitrogen species to the framework of mesoporous carbons was accompanied with the development of microposity. This result demonstrated the potential utility of NaNH₂ for the activation of carbon materials. In this work, we have further explored NaNH₂ as an activation agent for the preparation of porous carbons with ultrahigh specific surface areas as well as large micropore volumes. A phenolic resin-based mesoporous carbon synthesized by a previously established soft-templating method [33–35] was used as the pristine carbon for activation, and prepared activated mesoporous carbons were found to display significantly enhanced CO₂ adsorption.

2. EXPERIMENTAL SECTION

2.1 Chemicals

CO₂ (99.99 mol%) and N₂ (99.99mol%) were supplied by Airgas Co. Ltd.. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (EO₁₀₆PO₇₀EO₁₀₆, Pluronic F127), phloroglucinol (98wt%), formaldehyde (37% in aqueous solution, stabilized with 10–15wt% methanol), sodium amide (99wt%), sodium hydroxide (99wt%) and potassium hydroxide (99wt%) were purchased from

Sigma-Aldrich Chemicals Co. Ltd.. All the chemicals were used as received without further purification. Warning: sodium amide is highly **hygroscopic** and should be operated in a dry box!

2.2 Synthesis of materials

The pristine mesoporous carbon (MC) was synthesized by carbonization of a nanostructured polymeric composite at 600 °C, which was obtained by self-assembly of block copolymer (Pluronic F127) and phenolic resin (phloroglucinol-formaldehyde) under acidic condition via an established soft-templating route [33-35]. The activation of MC by NaNH_2 was performed as following: 1 g of MC and 2 g of NaNH_2 were mixed manually in a nickel crucible, and then heated in a tubular furnace under flowing N_2 (100 mL/min) to a target temperature (400–900°C) at 10°C/min and kept for 1 h. The activation of MC by NaOH or KOH was performed as following: 1 g of MC was mixed with 5 g of 40wt.% aqueous NaOH or KOH (**containing 2 g of activators**) in a nickel crucible and sonicated for 1 h, then heated in a tubular furnace under flowing N_2 (100 mL/min) to 120°C at 10°C/min and kept for 12 h **to ensure the evaporation of water**, and finally heated to a target temperature (550 or 700°C) at 10°C/min and kept for 1 h. After cooling down naturally to room temperature, the resultant powder was washed with deionized water to neutral pH, followed by being dried at 120°C for 12 h. The obtained activated MCs were named as AMC- NaNH_2 - T , AMC-NaOH- T or AMC-KOH- T , where T is the activation temperature.

2.3 Gas adsorption measurements

CO₂ adsorption at 0 and 25°C, and N₂ adsorption at -196°C and 25°C were measured on a Micromeritics Gemini 2390a surface area analyser. Prior to the measurement, each sample was dried at 200 °C under flowing N₂ for 2 h.

2.4 Characterizations

N₂ adsorption isotherms at -196°C and CO₂ adsorption isotherms at 0°C were used to calculate the textural properties of porous carbons. Total surface area was calculated from N₂ adsorption isotherms using the BET equation in the relative pressure range of 0.02–0.15. Total pore volume was determined from the amount of N₂ adsorbed at the relative pressure of 0.97. Micropore surface area and micropore volume were calculated from N₂ adsorption isotherms using the Carbon Black STSA *t*-plot equation within the thickness range of 0.45–0.60 nm. Mesopore volume was calculated by subtracting the micropore volume from the total pore volume. The pore size distribution was derived from the N₂ adsorption isotherms using the BJH model. Moreover, the volume of small micropores (size < 1nm) was calculated from CO₂ adsorption isotherms using NLDFT theory by assuming a slit-like geometry of the micropores.

X-ray photoelectron spectra (XPS) were acquired using a PHI 3056 spectrometer with an Al anode source operated at 15 kV and an applied power of 350 W to determine the surface elementary nature of porous carbons. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a Zeiss Auriga Crossbeam scanning electron microscope at an acceleration voltage of 5 kV to illustrate the morphology of porous carbons.

3. RESULTS AND DISCUSSION

3.1 Textural properties

We first investigated the activation of MC by NaNH_2 at different temperatures. [Figure 1](#) shows the N_2 adsorption isotherms at -196°C and pore size distributions of the pristine MC and NaNH_2 -activated MCs. The calculated textural properties are summarized in [Table 1](#). MC displays a type IV N_2 adsorption isotherm with a steep capillary condensation step at the relative pressure of around 0.7–0.8, indicating the presence of mesopores. With the activation temperature increasing from 400 to 550°C , the capillary condensation step in the N_2 adsorption isotherms of AMCs gradually vanishes, and the N_2 adsorption isotherms of AMC- NaNH_2 -500 and AMC- NaNH_2 -550 become more like type I isotherms (see [Figure 1A](#)). This phenomenon indicates the mesoporous structure of MC collapses after activation by NaNH_2 , which can be further observed from the pore size distributions illustrated in [Figure 1C](#). As presented in [Table 1](#), the mesopore volumes of AMC- NaNH_2 -500 and AMC- NaNH_2 -550 are 0.24 and $0.34\text{ cm}^3/\text{g}$ respectively, lower than that of the pristine MC ($0.43\text{ cm}^3/\text{g}$). With the activation temperature further increasing from 550 to 900°C , the capillary condensation step in the N_2 adsorption isotherms of AMCs gradually emerges again (see [Figure 1B](#)), indicating additional mesopores can be created during the activation of MC by NaNH_2 at higher temperatures. As presented in [Table 1](#), the mesopore volume of AMCs increases significantly from 0.34 to $1.27\text{ cm}^3/\text{g}$ when the activation temperature increases from 550 to 900°C . However, most of the additionally created mesopores in AMCs prepared at temperatures higher than 550°C are relatively small in size, from 2–6 nm (see [Figure 1D](#)). The reduction in the

mesopore size could be related to the partial collapse and/or shrinkage of the carbon framework during the activation process.

In terms of the development of microporosity in the MC after activation by NaNH_2 , as shown in Table 1, the micropore surface areas and micropore volumes of the AMCs are in the range of 676–2264 m^2/g and 0.30–0.98 cm^3/g , respectively, being about 2.7–9.1 times and 2.5–8.2 times higher than those of the pristine MC, demonstrating the powerful ability of NaNH_2 to activate carbon materials. In general, the activation temperature has a significantly positive effect on the microporosity of AMCs prepared at temperatures below 600°C, while further increasing the activation temperature from 600 to 900°C has no obvious contribution to creating more micropores. As a combined result of the evolution of microporosity and mesoporosity, activation of MC by NaNH_2 results in a 1.9–6.5 fold increase in total surface area (from 519 to 1008–3325 m^2/g). Both mesopores and micropores can also be clearly observed from the TEM images, as shown in Figure 2.

Our previous work has disclosed that NaNH_2 can be used as a nitrogen source for nitrogen-doping of mesoporous carbon at low temperatures (230–380°C) because of its excellent nucleophilicity that facilitates the substitution of residual oxygen species in the carbon material with nitrogen [32]. Figure 3 shows the representative XPS spectra of AMCs. For the carbon activated at 400°C, a strong and broad peak can be observed at around 400.0 eV, indicating that the major nitrogen species could be related to imine/amine/amide and/or pyrrole/pyridone. A weak XPS peak found

between 404 and 405 eV could be attributed to oxidized nitrogen in a small amount. However, the characteristic N1s peaks completely disappeared when the activation temperature is higher than 400°C, possibly due to poor thermal stability of these nitrogen species. Since the XPS spectra can only be used to analysis the surface elemental composition, elemental analysis was further performed to investigate the possible existence of nitrogen in the deeper layers. However, results validate that nitrogen can not be detected on AMCs prepared at 500 °C or higher temperatures, which is in consistence with the XPS analysis.

Since the adsorption of CO₂ on porous carbons is mainly controlled by small micropores with size below 1 nm [12, 28], it is more interesting to examine the variation of small micropore volume of the MC after activation by NaNH₂. It can be seen from Table 1 that three AMC samples prepared at temperatures below 550°C (AMC-NaNH₂-400, AMC-NaNH₂-500 and AMC-NaNH₂-550) exhibit comparable small micropore volumes of 0.168–0.174 cm³/g, being about two times that of the pristine MC (0.080 cm³/g). However, increasing the activation temperature from 550 to 900°C results in the decrease of small micropore volume of AMCs. The small micropore volumes of AMC-NaNH₂-800 and AMC-NaNH₂-900 (0.079 and 0.070 cm³/g) are even inferior to that of the pristine MC (0.080 cm³/g), although the two AMC samples have very high total micropore volumes (0.95 and 0.98 cm³/g). Therefore, a proper, moderate activation temperature is essential for obtaining AMC with a highly developed, small micropore rich structure.

We compared NaNH_2 with NaOH and KOH for their ability in the activation of MC. Figure 4 shows the N_2 adsorption isotherms at -196°C and the pore size distributions of the pristine MC and NaNH_2 , NaOH and KOH -activated MC. In addition, the calculated textural properties are summarized in Table 1. Obviously, AMC- NaOH -550 has the lowest porosity among the three AMC samples prepared at the same temperature but using the different activation agents. The small micropore volume of AMC- KOH -550 ($0.164\text{ cm}^3/\text{g}$) is slightly smaller than that of AMC- NaNH_2 -550 ($0.174\text{ cm}^3/\text{g}$), but its total micropore volume ($0.38\text{ cm}^3/\text{g}$) is much smaller than that of AMC- NaNH_2 -550 ($0.66\text{ cm}^3/\text{g}$). From this comparison, it can be concluded that the ability of different agents for the activation of MC at a relatively mild condition (activation agent/carbon mass ratio: 2/1, activation temperature: 550°C) follows the sequence of $\text{NaNH}_2 > \text{KOH} \gg \text{NaOH}$. Actually, the activation of carbon materials by KOH is usually performed at a high temperature of $>600^\circ\text{C}$ to achieve highly microporous carbons. However, even when the activation of MC by NaOH or KOH was performed at a relatively high temperature of 700°C , resulted AMC- NaOH -700 or AMC- KOH -700 are still inferior to AMC- NaNH_2 -550 in micropore volume, except that AMC- KOH -700 has a comparable small micropore volume as AMC- NaNH_2 -550 (0.177 vs. $0.174\text{ cm}^3/\text{g}$, see Table 1). Therefore, using NaNH_2 as the activation agent represents an efficient method for the synthesis of highly microporous carbons under relatively mild conditions.

In our recent work [32] on low-temperature N-doping of MCs with NaNH_2 , the creation of micropores in N-doped MCs (NMCs) did not likely occur from the direct etching of carbon considering the low-temperature reaction conditions (230–380 °C) and high yields of synthesized NMCs (>90%). Alternatively, it was attributed to the substitution of oxygen species by NaNH_2 , which might open some originally closed channels and/or create new cavities. The development of microporosity through this substitution mechanism was very limited, and therefore, the micropore surface areas and micropore volumes of the synthesized NMCs were smaller than 697 m^2/g and 0.29 cm^3/g , respectively. However, the activation of MC by NaNH_2 at temperatures higher than 400°C mainly involves the direct etching of carbon, which can be evidenced by the low yields of prepared AMC samples (69.4–41.0%). In contrast, AMC- NaNH_2 -400 still displays a high yield (93.4%) and contains a large amount of nitrogen (4.7 at.%). The mechanism of reaction between carbon and NaNH_2 is rather complicated and remains to be fully elucidated in future work. Besides the direct reaction of carbon with NaNH_2 , in principle, there are several other possible contributions to the considerable addition of porosity to MC through NaNH_2 activation at temperatures higher than 400°C. The first is some oxygen species being substituted by NaNH_2 during the ramping of temperature, as in the case of N-doping of MCs at low temperatures, with the incorporated nitrogen species decomposing again at the target activation temperatures due to their instability at these high temperatures. As shown in [Table 1](#), AMC- NaNH_2 -400 has a nitrogen content of 4.7

at.%, while no nitrogen species can be detected through XPS analysis on the AMC samples prepared at temperatures higher than 400°C. The incorporation/decomposition of nitrogen species results in the formation of cavities, which contribute to the additional porosity and loss of nitrogen. In addition, Na₂O and/or NaOH forming along with the nitrogen doping at the low temperature could act like conventional NaOH or KOH to activate the carbon via a redox mechanism at higher temperatures (600–800 °C) [36]. All these factors enable the strong ability of NaNH₂ for the activation of the carbon materials.

3.2 CO₂ adsorption

The effect of activation temperature on the CO₂ adsorption isotherms of NaNH₂-activated MCs at 0°C is shown in [Figure 5A](#), and the CO₂ adsorption capacities at 1 and 0.15 bar are summarized in [Table 2](#). Pristine MC shows poor adsorption capacities for CO₂, with values of 2.01 and 1.00 mmol/g at 1 and 0.15 bar, respectively. However, the CO₂ adsorption capacities of NaNH₂-activated MCs at 1 bar are significantly enhanced in comparison with that of pristine MC. AMCs can adsorb as high as 4.33–6.31 mmol/g of CO₂ at 1 bar, being about 2.2–3.1 times as pristine MC. Since the concentration of CO₂ in flue gas is as low as 10–15v/v%, it is more important to consider the CO₂ adsorption capacities at a low pressure of 0.15 bar. Three AMC samples prepared at temperatures below 550°C (AMC-NaNH₂-400, AMC-NaNH₂-500 and AMC-NaNH₂-550) exhibit comparable adsorption capacities for CO₂ at 0.15 bar, with values of 1.90–2.06 mmol/g, being about 2 times that of the

pristine MC. However, increasing the activation temperature from 550 to 900°C results in a decrease of the CO₂ adsorption capacity at 0.15 bar. The CO₂ adsorption capacity of AMC-NaNH₂-900 at 0.15 bar (0.94 mmol/g) is even slightly inferior to that of the pristine MC (1.00 mmol/g), although AMC-NaNH₂-900 has very high surface area (3325 m²/g). Whether at a pressure of 1 bar or 0.15 bar, the highest adsorption capacity of CO₂ is observed for AMC-NaNH₂-550. Therefore, 550°C is the optimized temperature for the activation of MC by NaNH₂ to obtain AMC with highest CO₂ adsorption performance.

The CO₂ adsorption isotherms at 25°C for the NaNH₂-activated MCs are shown in [Figure 5C](#), and the CO₂ adsorption capacities at 1 and 0.15 bar are also summarized in [Table 2](#). The variation of the CO₂ adsorption capacity at 25°C with activation temperature has a similar trend as that of the CO₂ adsorption capacity at 0°C. The optimized AMC sample, AMC-NaNH₂-550, can adsorb 3.66 and 0.98 mmol/g of CO₂ at 1 and 0.15 bar, respectively, meeting the requirements for solid adsorbents with competitive performance relative to the widely used aqueous amines [37].

Comparing the CO₂ adsorption on NaNH₂-activated MCs with that of NaOH and KOH-activated MCs, as shown in [Figure 5B and 5D](#) and [Table 2](#), the CO₂ adsorption capacities at 1 bar follow the sequence of AMC-NaNH₂-550 > AMC-KOH-550 > AMC-NaOH-550 and AMC-NaNH₂-550 > AMC-KOH-700 > AMC-NaOH-700, while the CO₂ adsorption capacities at 0.15 bar follow the sequence of AMC-NaNH₂-550 ≈ AMC-KOH-550 > AMC-NaOH-550 and AMC-NaNH₂-550 ≈

AMC-KOH-700 > AMC-NaOH-700. This comparison further validates the superiority of NaNH₂ for the activation of MC to obtain highly efficient CO₂ adsorbents.

We determined the N₂ adsorption isotherms at 25°C for all the adsorbents (see Figure 5E and 5F), and calculated the CO₂/N₂ adsorption selectivities from the ratio of the initial slope of the adsorption isotherms and the results are presented in Table 2. The CO₂/N₂ adsorption selectivity of AMC-NaNH₂-400 is enhanced in comparison with that of the pristine MC (28.1 vs. 20.8), which may be related to the nitrogen species present in the two AMC samples. However, the CO₂/N₂ adsorption selectivities of other AMC samples prepared at temperatures higher than 400°C are comparable or even inferior to that of pristine MC (21.4–8.9 vs. 20.8). The activation of MC by NaNH₂ can not only result in an enhancement of CO₂ adsorption, but also result in the enhancement of N₂ adsorption. When the enhancement of N₂ adsorption is more significant than that of CO₂ adsorption (i.e., activation temperature > 400°C), there will be a decrease in CO₂/N₂ adsorption selectivity. Therefore, the activation temperature should be carefully selected to achieve a balance between the CO₂ adsorption capacity and CO₂/N₂ adsorption selectivity. Furthermore, the optimized sample AMC-NaNH₂-550 has comparable selectivity of CO₂/N₂ to AMC-NaOH-550 and AMC-KOH-550, but higher selectivity of CO₂/N₂ than AMC-NaOH-700 and AMC-KOH-700.

To have a better understanding of the interaction between CO₂ and the porous carbons prepared in this work, the CO₂ adsorption heats for the MC, AMC-NaNH₂-400 and AMC-NaNH₂-550 materials were calculated from the Clausius-Clapeyron equation through fitting the CO₂ adsorption isotherms at 0°C and 25°C using a dual-site Langmiur-Freundlich model [38, 39]. The three samples were chosen as representatives materials since MC is the pristine carbon, AMC-NaNH₂-400 is an activated carbon with nitrogen species present, and AMC-NaNH₂-550 is an activated carbon without nitrogen species present but with the highest CO₂ adsorption capacity. As presented in [Figure 6](#), the initial CO₂ adsorption heat of AMC-NaNH₂-400 is -44.2 kJ/mol at a low coverage of 0.1 mmol/g, larger than that of MC (-31.1 kJ/mol) and AMC-NaNH₂-550 (-31.3 kJ/mol). This can be attributed to the enhanced interaction between acidic CO₂ molecule and basic nitrogen species in AMC-NaNH₂-400. The CO₂ adsorption heat of AMC-NaNH₂-550 (from -31 to -26 kJ/mol) is a little bit lower than that of MC (from -31 to -28 kJ/mol), although AMC-NaNH₂-550 can accommodate much more CO₂ than MC (see [Table 2](#)). Therefore, the interaction between CO₂ and AMC-NaNH₂-550 is still in the range of physical interactions.

To clearly demonstrate the role of small micropores in CO₂ adsorption, we plotted the CO₂ adsorption capacities of MC and AMCs prepared in this work vs. their volumes of small micropores, as shown in [Figure 7](#). The CO₂ adsorption capacities at 0.15 bar show an excellent linear correlation with the small micropore

volumes ($R^2>0.98$); however, the CO₂ adsorption capacities at 1 bar show a poor linear correlation with the small micropore volumes ($R^2<0.5$). Therefore, small micropores with size below 1 nm mainly control the CO₂ adsorption at a low pressure of 0.15 bar. This result is a little different from other works [28], where the conclusion that small micropores with size below 1 nm governed the CO₂ adsorption on porous carbons under ambient conditions was drawn. This difference can be attributed to the different kinds of carbon materials investigated. Furthermore, if the CO₂ adsorption capacities are normalized to the small micropore volumes (not shown), the AMC sample with nitrogen species present (AMC-NaNH₂-400) did not display any superiority to other samples without nitrogen species present. Therefore, the incorporation of nitrogen species to these porous carbons actually has no contribution to the improvement of the CO₂ adsorption capacity, but is beneficial for the enhancement of the CO₂ adsorption heat as well as the CO₂/N₂ adsorption selectivity. This finding was also demonstrated in some other recent work [13, 14].

4. CONCLUSIONS

In summary, the efficient activation of mesoporous carbons was realized by using NaNH₂ as the activation agent, and a considerable development of microporosity was observed for the NaNH₂-activated carbons. The activation temperature significantly affected the porosity of the resultant activated carbons. For the purpose of obtaining highly efficient adsorbents for CO₂ capture, a relatively moderate activation temperature is required to maintain a high volume of small

micropores (size < 1 nm), which is the major factor controlling the CO₂ adsorption at a low pressure of 0.15 bar. When compared with KOH and NaOH, NaNH₂ has a more powerful ability in the activation of mesoporous carbons under mild conditions (activation agent/carbon mass ratio is 2/1 and activation temperature is 550°C) for enhanced CO₂ adsorption.

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Table 1. Textural properties of pristine MC and activated MCs

Sample Name	Yield (%) ^a	S_{BET} (m ² /g) ^b	S_{mi} (m ² /g) ^c	V_{t} (cm ³ /g) ^d	V_{mi} (cm ³ /g) ^e	V_{me} (cm ³ /g) ^f	V_{smi} (cm ³ /g) ^g	N (at.%) ^h
MC	-	519	249	0.65	0.12	0.43	0.080	0
AMC-NaNH ₂ -400	93.4	1008	676	0.70	0.30	0.40	0.170	4.7
AMC-NaNH ₂ -500	69.4	1463	1136	0.75	0.51	0.24	0.168	0
AMC-NaNH ₂ -550	67.2	1917	1482	1.00	0.66	0.34	0.174	0
AMC-NaNH ₂ -600	53.7	2782	2047	1.58	0.88	0.70	0.113	0
AMC-NaNH ₂ -700	44.3	3180	2264	1.86	0.98	0.88	0.084	0
AMC-NaNH ₂ -800	41.4	3158	2110	1.92	0.95	0.97	0.079	0
AMC-NaNH ₂ -900	41.0	3325	1889	2.25	0.98	1.27	0.070	0
AMC-NaOH-550	76.7	867	562	0.69	0.25	0.44	0.130	0
AMC-KOH-550	85.9	1017	849	0.55	0.38	0.17	0.164	0
AMC-NaOH-700	53.4	1217	799	0.99	0.35	0.64	0.109	0
AMC-KOH-700	61.3	1020	976	0.48	0.44	0.04	0.177	0

^aYield based on pristine MC; ^bBET surface area; ^cmicropore surface area; ^dtotal pore volume; ^emicropore volume; ^fmesopore volume; ^gsmall micropore (size < 1 nm) volume; ^hnitrogen content measured by XPS.

Table 2. CO₂ adsorption performance of pristine MC and activated MCs

Sample Name	CO ₂ adsorption at 0°C (mmol/g)		CO ₂ adsorption at 25°C (mmol/g)		<i>S</i> _{CO₂/N₂} at 25°C ^a
	<i>P</i> _{CO₂} =0.15 bar	<i>P</i> _{CO₂} =1 bar	<i>P</i> _{CO₂} =0.15 bar	<i>P</i> _{CO₂} =1 bar	
MC	1.00	2.01	0.54	1.36	20.8
AMC-NaNH ₂ -400	2.06	4.59	1.05	2.86	28.1
AMC-NaNH ₂ -500	1.90	5.17	1.01	3.40	21.4
AMC-NaNH ₂ -550	1.95	6.31	0.98	3.66	16.2
AMC-NaNH ₂ -600	1.38	5.55	0.71	3.16	12.7
AMC-NaNH ₂ -700	1.08	4.80	0.56	2.65	11.9
AMC-NaNH ₂ -800	1.04	4.71	0.54	2.58	9.1
AMC-NaNH ₂ -900	0.94	4.33	0.52	2.40	8.9
AMC-NaOH-550	1.69	3.63	0.91	2.23	24.6
AMC-KOH-550	1.95	4.61	1.02	2.91	20.8
AMC-NaOH-700	1.28	3.88	0.70	2.32	13.0
AMC-KOH-700	1.90	5.03	0.96	3.00	11.3

^aCalculated from the ratio of initial slope of adsorption isotherms.

Figure Captions

Figure 1. N₂ adsorption isotherms at -196°C (A, B) and BJH pore size distributions (C, D) of pristine MC and NaNH₂-activated MCs.

Figure 2. Representative TEM images of AMC-NaNH₂-500 (A, B) and AMC-NaNH₂-900 (C, D).

Figure 3. XPS spectra of AMC-NaNH₂-400 (A), AMC-NaNH₂-500 (B) and AMC-NaNH₂-800 (C) and N1s spectra of AMC-NaNH₂-400 (D).

Figure 4. N₂ adsorption isotherms at -196°C (A) and BJH pore size distributions (B) of pristine MC and AMCs prepared from different activation agents.

Figure 5. CO₂ adsorption isotherms at 0°C (A) and 25°C (C), and N₂ adsorption isotherms at 25°C (E) of pristine MC and NaNH₂-activated MCs; CO₂ adsorption isotherms at 0°C (B) and 25°C (D), and N₂ adsorption isotherms at 25°C (F) of pristine MC and AMCs prepared from different activation agents.

Figure 6. CO₂ adsorption heats of MC, AMC-NaNH₂-400 and AMC-NaNH₂-550.

Figure 7. Dependence of CO₂ adsorption at 0.15 bar (A) and 1 bar (B) vs. small micropore volume.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Graphical Abstract