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Superior CO₂ uptake on nitrogen doped carbonaceous adsorbents from commercial phenolic resin

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ABSTRACT

In this study, N-doped porous carbons were produced with commercial phenolic resin as the raw material, urea as the nitrogen source and KOH as the activation agent. Different from conventional carbonization-nitriding-activation three-step method, a facile two-step process was explored to produce N-incorporated porous carbons. The as-obtained adsorbents hold superior CO₂ uptake, i.e. 5.01 and 7.47 mmol/g at 25 °C and 0 °C under 1 bar, respectively. The synergistic effects of N species on the surface and narrow micropores of the adsorbents decide their CO₂ uptake under 25 °C and atmospheric pressure. These phenolic resin-derived adsorbents also possess many extremely promising CO₂ adsorption features like good recyclability, quick adsorption kinetics, modest heat of adsorption, great selectivity of CO₂ over N₂ and outstanding dynamic adsorption capacity. Cheap precursor, easy preparation strategy and excellent CO₂ adsorption properties make these phenolic resin-derived N-doped carbonaceous adsorbents highly promising in CO₂ capture.

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Introduction

The progress of the world is inseparable from energy. Driven by the growth of energy consumption, CO₂ releases because of the burning of fossil fuel continue to rise in the last decade. As stated by the Earth System Research Laboratory, the global atmospheric CO₂ concentration has gotten 407.65 ppm by September 2019, which is nearly 128 ppm higher than the preindustrial time. Since CO₂ is widely recognized as the major greenhouse gas, its emission is considered as one of the culprits causing frequent catastrophic climate. Under such circumstance, mitigation of CO₂ emission becomes imminent. CO₂ capture is proposed as a viable strategy to reduce CO₂ releases. Various CO₂ capture methods have been rapidly developed including amine scrubbing (Guo et al., 2019),

membrane separation (Wang et al., 2016), ionic liquid absorption (Chen et al., 2016a; Liu et al., 2018) and adsorption by solid adsorbents (Chen et al., 2018; Lv et al., 2019; Mukherjee et al., 2019; Peng et al., 2019; Rao et al., 2019a; Rao et al., 2019b), etc. Of the technologies mentioned above, adsorption by porous solid adsorbents have attracted a wide range of research interests recently, since it has several outstanding advantages such as easy handling, low expense, small energy penalty and free of corrosion etc (Li et al., 2015). The achievement of adsorbents with superb CO₂ adsorption properties is vital to the successful application of this technology. Up to now, various porous materials like zeolites (Bae et al., 2013), metal-organic frameworks (MOFs) (Millward & Yaghi, 2005), carbons (An et al., 2019; Choi et al., 2019; Geng et al., 2017; Liu et al., 2016), and porous polymers (Huang et al., 2016; Liu et al., 2017; Sun et al., 2015) have been used as CO₂ adsorbents. Of these CO₂ sorbents, porous carbons attract wide attention in the research community, which is owing to their manifold advan-

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tages like easy synthesis, low cost, tunable porosity, chemical inertness and hydrophobicity, to name a few (Du et al., 2018; Du et al., 2019). A prominent advantage of porous carbons is their easy preparation through physical or chemical activation of extensive cheap raw materials like biomass materials (Liu et al., 2020; Yang et al., 2020; Yue et al., 2018), petroleum coke (Jang et al., 2018) and carbon-riched polymers (Geng et al., 2017; Kou & Sun, 2016) etc. Some porous carbonaceous adsorbents have shown very promising CO₂ adsorption ability under 25 °C and atmospheric pressure. For example, the carbon adsorbent made from petroleum pitch had 4.7 mmol/g of CO₂ adsorption capacity (Wahby et al., 2010). Another porous carbon derived from biomass material-pine nut shell possessed 5.0 mmol/g in CO₂ uptake (Deng et al., 2014). It is found that the narrow micropores (< 1 nm) is the crucial factor that determines the CO₂ adsorption abilities for these sorbents under 25 °C and 1 bar (Deng et al., 2014; Wahby et al., 2010). Apart from the narrow microporosity, nitrogen incorporation into the carbon framework is promising to further boost the CO₂ uptake of a carbon sorbent due to acidic-basic interaction of CO₂ and N-containing moieties (Liu et al., 2019b). CO₂ uptake greater than 5.0 mmol/g at ambient conditions has been reported for some N-doped porous carbonaceous adsorbents. For instance, the N-incorporated porous carbons produced by Sayari (Sethia & Sayari, 2015) and Mokaya (Adeniran & Mokaya, 2015) group, respectively, accomplished the maximum of 5.4 and 5.5 mmol/g of CO₂ adsorption capacity. Therefore, to obtain carbonaceous adsorbents with better CO₂ capture performance, it should start from optimizing both the porous structure and surface chemistry of the porous carbons.

Lately, phenolic-resin-derived porous carbons as CO₂ adsorbents have appealed many research interests. Long et al prepared nitrogen riched phenolic microspheres with tunable porous structures for CO₂ adsorption. The highest CO₂ uptake is found to be under 2 mmol/g at 25 °C and ambient pressure (Zhou et al., 2013). In another work, Jin and co-workers synthesized carbon composite monoliths using commercial phenolic resin and small amount of carbon nanotube as the raw materials. The resultant sorbents show maximum CO₂ uptake of 3.6 mmol/g at 25 °C and 1 bar (Jin et al., 2013). The low CO₂ adsorption capacities of above-mentioned phenolic-resin-derived carbons are due to their less developed porous structures. More recently, KOH activation was explored to synthesize phenolic-resin-derived porous carbons, which showed an abundant improvement in CO₂ uptake i.e. 4.4 (de Souza et al., 2013) and 8.9 (Wickramaratne & Jaroniec, 2013) mmol/g at atmospheric pressure, 25 °C and 0 °C, respectively. However, tedious synthesis method and costly precursors were used in these studies (de Souza et al., 2013; Wickramaratne & Jaroniec, 2013), which limits the large-scale production and potential application of these carbonaceous sorbents. Cheap and wide available precursor and facile preparation procedure should be employed to prepare porous carbons.

Herein, N-incorporated porous carbons were produced by KOH activation employing a commercial phenolic resin as raw material and urea as nitrogen source. Unlike the frequently used carbonization-nitriding-activation three-step method of obtaining N-incorporated porous carbons (Chen et al., 2016b), here, the mixture of phenolic resin and urea was firstly pyrolyzed to form the nitrogen-enriched precursor, then the N-doped porous carbons were achieved by following KOH treatment at different reaction conditions. This strategy reduces one reaction step and thus saves the cost of adsorbent preparation. In this work, KOH quantity and activation temperature were adjusted to modify the porous structure and surface properties of the resulting sorbents. The detailed characterization and CO₂ adsorption properties of these carbons were carefully investigated. The major features that decide the CO₂ uptake for these sorbents were also prudently discussed. The findings in this work will deliver valuable information in the research field of carbonaceous CO₂ adsorbents.

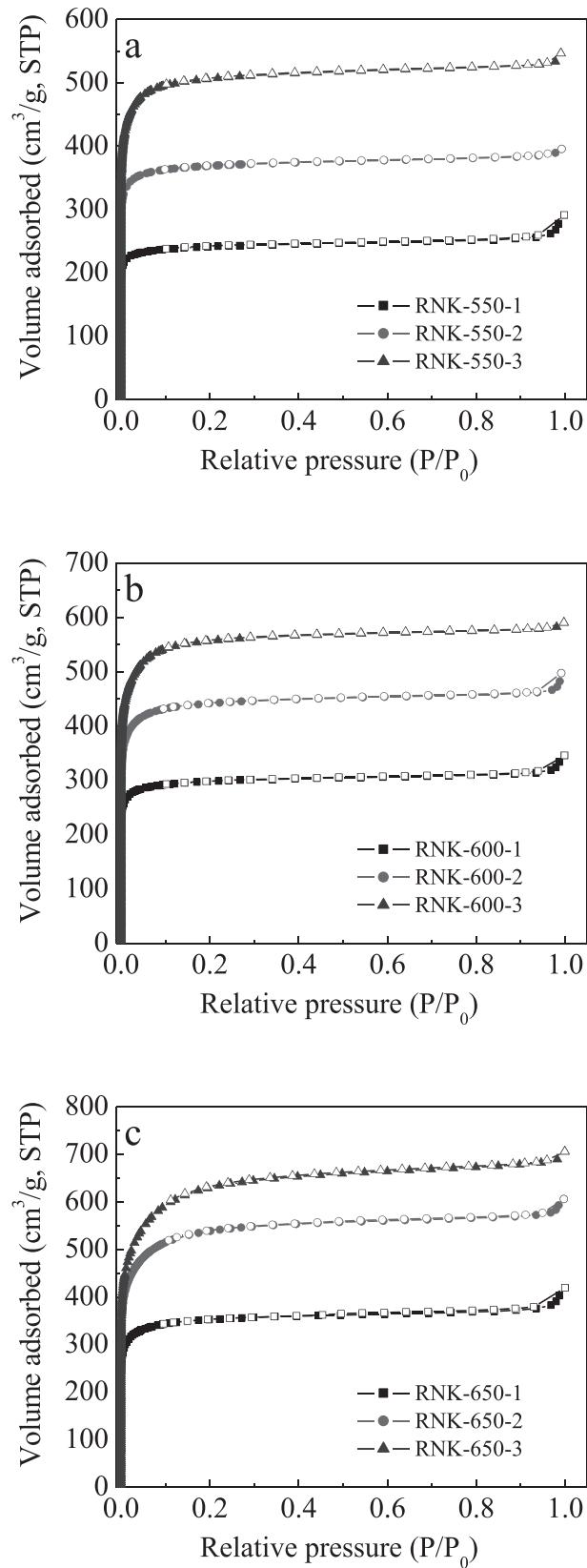


Fig. 1 – N₂ sorption isotherms of the phenolic resin-based carbonaceous adsorbents prepared at different conditions. Filled and empty symbols represent adsorption and desorption branches, respectively.

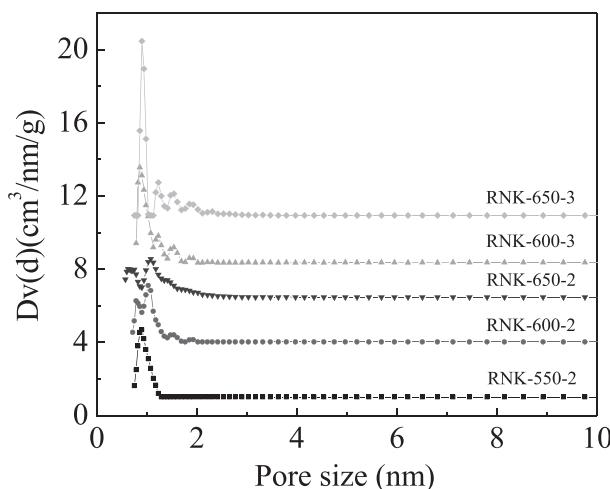


Fig. 2 – Pore size distribution of the samples prepared at different conditions.

1. Materials and methods

1.1. Preparation and characterization of phenolic resin-based N-incorporated porous carbons

The mixture of commercial phenolic resin (2123-type, Xinxiang Bomafengfan Industrial Co., Ltd., China) and urea in mass ratio of 1:2 were heated at 500 °C for 2 hr under the flow of nitrogen. The obtained N-enriched carbon precursor is denoted as RN. The sample attained through direct carbonization of phenolic resin without adding urea is named as R.

Detailed KOH activation process is recorded in the supplementary materials. In KOH activation, temperature of 550, 600, or 650 °C and the KOH/RN mass ratio of 1, 2 or 3 were adopted. The acquired N-incorporated carbons were assigned as RNK-X-Y. X and Y is the activation temperature and the mass ratio of KOH/RN, respectively. The yield ranges from 61.73 to 78.22% for these obtained carbons. For the purpose of comparison, a comparative sample was

achieved by (i) carbonization, (ii) urea treatment and (iii) KOH activation three-step process and this sample was named as RUK-550-2. The detailed procedure of three-step procedure is described in the supplementary materials. Additionally, the details concerning the material characterization and CO₂ adsorption measurement is introduced in the supplementary materials.

2. Results and discussion

2.1. Textural properties

The textural properties of phenolic resin-based N-doped porous carbon sorbents were evaluated by N₂ adsorption/desorption at -196 °C with a Beishide 3H-2000PS2 gas analyzer. From Fig. 1, type I isotherms were found for all the samples. These isotherms show rapid and substantial adsorption at very low relative pressure ($P/P_0 < 0.01$), which is because of the capillary filling of micropores. At moderate relative pressure ($0.3 < P/P_0 < 0.9$), a nearly flat adsorption feature was observed for each sample, indicating the negligible external surface area. Moreover, in the medium relative pressure, no hysteresis loops present in the isotherms for these sorbents suggesting the absence of mesopores, which is affirmed by the pore size distribution (PSD) results illustrated in Fig. 2. A sudden increase in N₂ uptake was found for some samples when P/P_0 is close to 1, indicating the existence of macropores possibly due to the packing of carbon particles. It needs also be noted that the adsorbents synthesized at higher activation temperature or/and KOH dosage possess a wider knee in the isotherms, suggesting a larger micropore size. This inference was also certified by the PSD curves illustrated in Fig. 2. The porous characteristics i.e. BET surface area (S_{BET}), total pore volume (V_0) and micropore volume (V_t) of these phenolic resin-based adsorbents were summarized in Table 1. For these samples, each porous property increases with the increasing of activation temperature or KOH dosage. The maximum S_{BET} , V_0 , and V_t for these carbons are 2374 m²/g, 1.09 and 0.93 cm³/g, respectively.

The volume of narrow micropores (V_n) for as-synthesized adsorbents was gained by the Dubinin–Radushkevich (D–R) equation according to the CO₂ adsorption data at 0 °C. As presented in Table 1, the range of V_n for these sorbents is between 0.57–

Table 1 – Porous properties, elemental compositions, and CO₂ uptakes of sorbents derived from phenolic resin under different conditions.

Sample	S_{BET}^a (m ² /g)	V_0^b (cm ³ /g)	V_t^c (cm ³ /g)	V_n^d (cm ³ /g)	N (wt.%)	C (wt.%)	H (wt.%)	CO ₂ uptake (mmol/g)	
								25 °C	0 °C
R	536	0.20	0.20	0.32	1.05	91.25	1.64	2.82	3.71
RN	2	0.03	0	0.26	3.96	87.46	3.12	2.17	2.79
RNK-550-1	1097	0.47	0.40	0.57	1.77	83.77	3.69	4.55	6.70
RNK-550-2	1482	0.61	0.56	0.70	1.41	86.68	5.13	5.01	6.73
RNK-550-3	2023	0.84	0.75	0.93	1.32	84.54	4.32	4.82	7.39
RNK-600-1	1310	0.70	0.49	0.65	1.54	85.54	4.11	4.77	6.80
RNK-600-2	1802	0.85	0.70	0.88	1.36	84.35	4.37	4.54	7.22
RNK-600-3	2200	0.91	0.83	1.02	1.29	86.54	3.99	4.40	7.47
RNK-650-1	1450	0.68	0.55	0.71	1.37	85.99	4.59	4.30	6.68
RNK-650-2	1875	0.94	0.81	0.92	1.29	87.65	4.25	4.11	6.80
RNK-650-3	2374	1.09	0.93	1.05	1.20	89.90	3.29	3.92	6.92
RUK-550-2	1099	0.46	0.44	0.52	2.74	84.35	2.36	3.81	5.71

^a Surface area was calculated using the BET method at $P/P_0 = 0.01$ –0.1.

^b Total pore volume at $P/P_0 = 0.99$.

^c Evaluated by the t-plot method.

^d Pore volume of narrow micropores (< 1 nm) obtained from the CO₂ adsorption data at 0 °C.

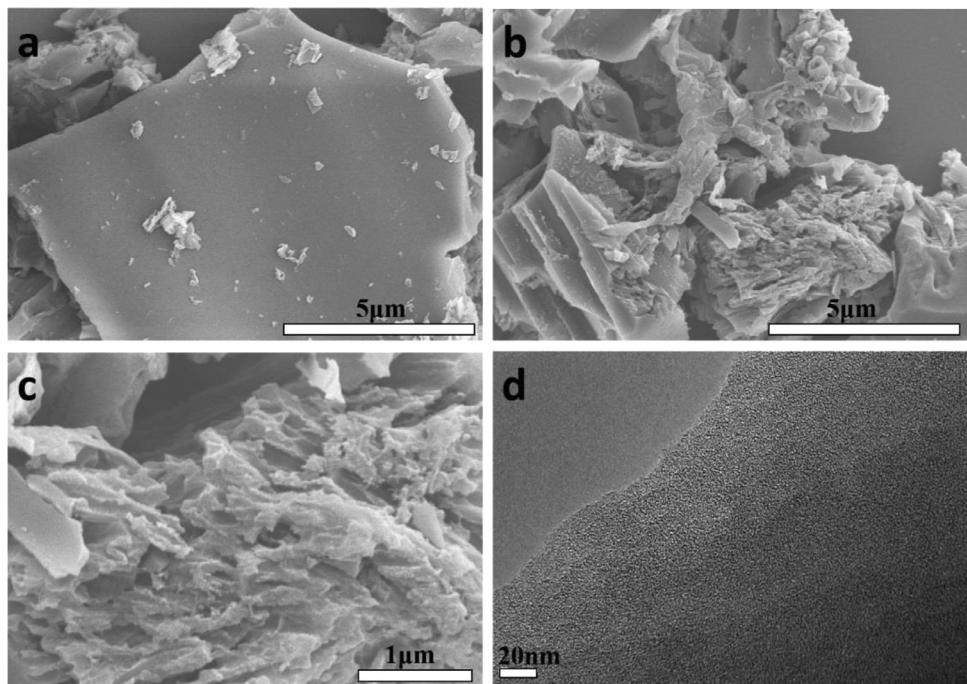


Fig. 3 – SEM images of (a) RN, (b) and (c) RNK-550-2, and (d) TEM image of RNK-550-2.

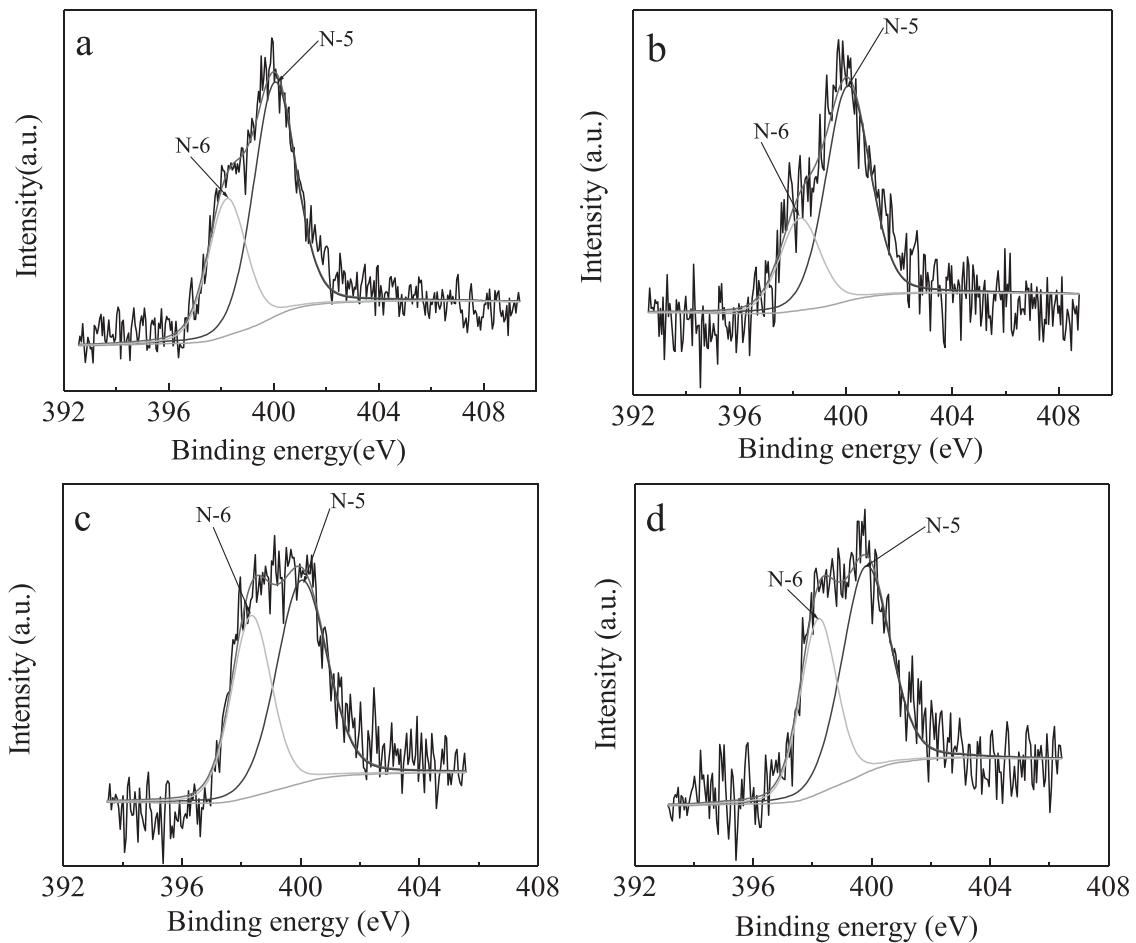


Fig. 4 – N 1 s XPS spectra of the samples (a) RNK-550-1, (b) RNK-550-2, (c) RNK-600-1 and (d) RNK-650-3.

1.05 cm³/g. The trend of V_n with regard to the activation temperature and KOH dosage is same as other porosity characteristics. It should be specially pointed out that for all the sorbents, V_n is higher than V_t , inferring the preferential formation of narrow micropores under the relatively low activation temperature explored in this research.

2.2. Morphology and phase structure

The morphological structures of carbon precursor (RN) and one characteristic activated carbon (RNK-550-2) were studied by scanning electron microscopy (SEM). RN exhibits a blocky morphology with even surface, no pores/defects were observed on its surface (Fig. 3a). After KOH treatment, a rugged and porous morphology was found for RNK-550-2 (Fig. 3b). From a magnified SEM image (Fig. 3c), some randomly distributed craters and pores clearly appear on the surface of RNK-550-2, which is resulted from the KOH etching. The detailed morphology of RNK-550-2 was explored by transmission electron microscopy (TEM). As revealed in Fig. 3d, abundant worm-like micropores present in RNK-550-2. The phase structure of RNK-550-2 was studied by the X-ray diffraction (XRD) analysis. Fig. S1 (supplementary materials) demonstrates XRD pattern of RNK-550-2. One weak and broad peak at 2θ of ca. 43° was obtained, corresponding to (100) diffraction of amorphous carbon (Yang et al., 2015). This discovery is in line with the TEM observation and confirms the amorphous nature of these phenolic resin-derived carbons.

2.3. Surface chemical properties

Based on the elemental analysis results, the N-enriched carbon precursor (RN) contains 3.96 wt.% N and 87.46 wt.% C, suggesting that carbonization and nitrogen incorporation were successfully accomplished by one-step pyrolysis of phenolic resin and urea mixture. Following the subsequent KOH activation, the resulting sorbents exhibit a reduction in nitrogen content at a range from 1.77–1.20 wt.%. The nitrogen content of the activated carbons decreases with the increase of KOH dosage and activation temperature, which agrees well with the earlier studies (Rao et al., 2019b; Yang et al., 2015). The higher temperature will decompose more unstable nitrogen species, while higher KOH dosage means more reaction opportunities between activator and N containing groups, thus consuming more nitrogen species. The identity of nitrogen species was further investigated by XPS spectra. Fig. 4 illustrates the XPS N1s spectra of some characteristic samples, i.e. RNK-550-1, RNK-550-2, RNK-600-1 and RNK-650-3. Two peaks with the binding energies centered at 398.3 and 400.0 eV were found for all the above adsorbents, which can be allotted to pyridinic N (N-6) and pyrrolic N (N-5) species, respectively. Quantitative scrutiny displays that the quantity of N-5 higher than that of N-6 for all the samples, which is helpful for CO₂ adsorption according to the previous literature (Sánchez-Sánchez et al., 2014).

2.4. CO₂ adsorption properties

CO₂ uptake of these phenolic resin-based nitrogen-doped porous carbons are tested under 1 bar at 25 °C and 0 °C, respectively, with adsorption isotherms presented in Fig. 5. Under both test temperatures, the CO₂ adsorption abilities increase with the increasing pressure for all the sorbents. Furthermore, none of the samples shows sign of adsorption saturation under the test pressure of this study suggesting higher CO₂ adsorption abilities at elevated pressure. These N-integrated porous carbons possess exceptional CO₂ uptake, up to 5.01 and 7.47 mmol/g at 25 °C and 0 °C under ambient pressure. While at 0.15 bar, a typical CO₂ partial pressure in flue gas, the CO₂ uptakes can be up to 1.55 and 2.97 mmol/g at 25 °C and 0 °C, respectively. Compared with preceding reported CO₂ adsorption abilities, these capacities belong to the highest ones achieved

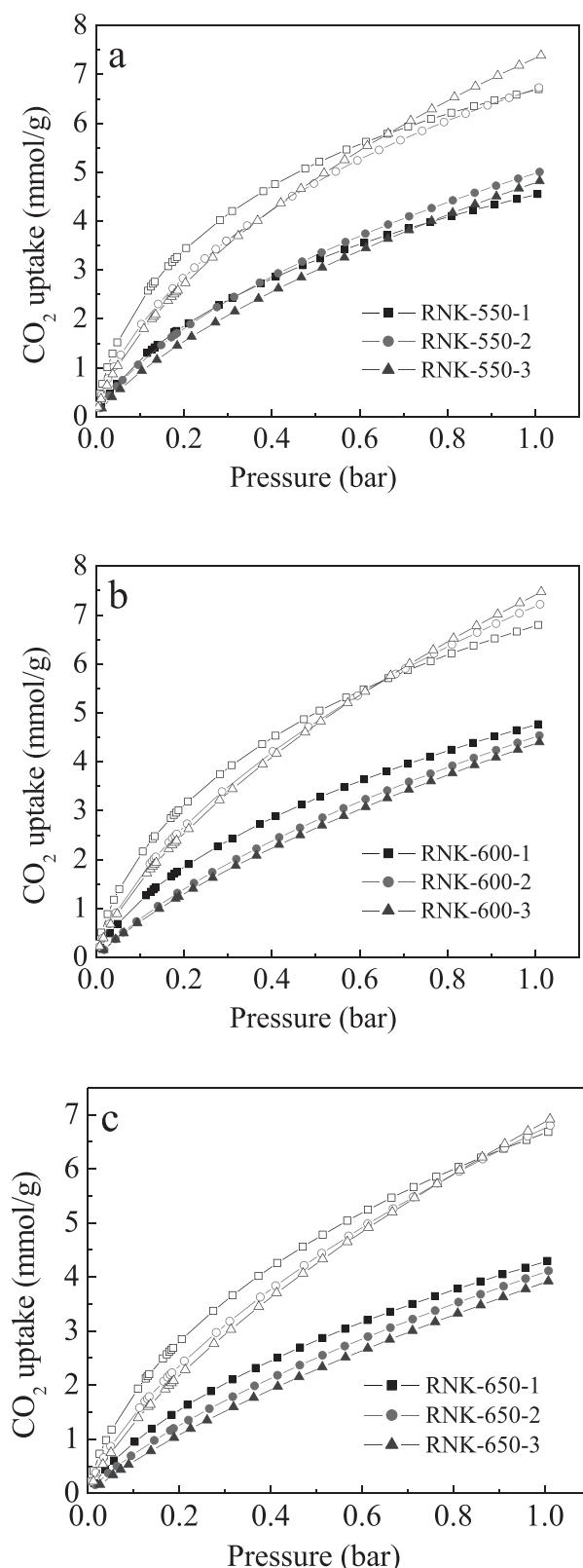


Fig. 5 – CO₂ adsorption isotherms at 25 °C (filled symbols) and 0 °C (empty symbols) for phenolic resin-based nitrogen-doped carbons prepared under different conditions.

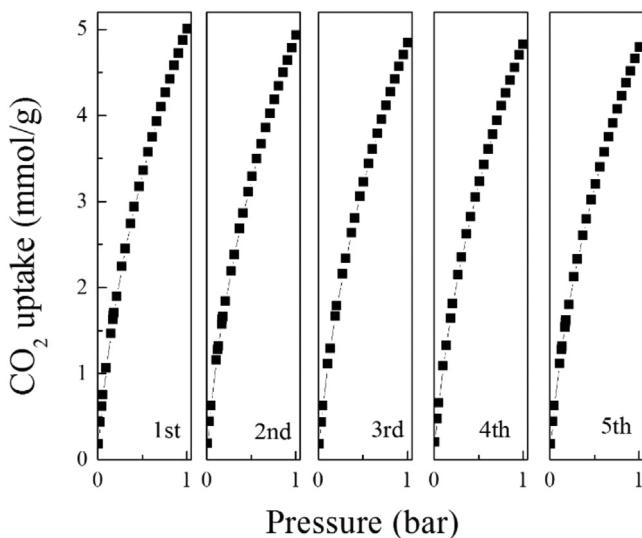


Fig. 6 – Cyclic study of CO₂ adsorption for RNK-550-2.

for carbons and greater than many typical porous solid sorbents such as zeolites (Bae et al., 2013), MOFs (Millward & Yaghi, 2005), COFs (Furukawa & Yaghi, 2009), PAFs (Ben et al., 2012), and porous polymers (Sun et al., 2015). To gain further insights on CO₂ adsorption, the effect of each porosity characteristic and N content on the CO₂ adsorption abilities was investigated, with correlation curves displayed in the Fig. S2 (supplementary materials). As illustrated in Fig. S2, no clear correlation between CO₂ uptake with any porosity characteristic or N content are established, representing that the CO₂ uptakes for these sorbents are unquestionably not determined by any sole feature described above. It has been widely reported in former literature that the synergistic effect of narrow micropores and N content decides the CO₂ adsorption ability of N-enriched carbonaceous adsorbents at ambient conditions (Liu et al., 2019b; Yang et al., 2015). This conclusion applies well for the results of this study. For example, among all the sorbents, RNK-550-2 has the third most nitrogen content but the third smallest V_n, but it has much higher CO₂ uptake than that of RNK-550-1 and RNK-650-3, which has the highest N content and V_n, respectively. The reason might be ascribed to the higher V_n of RNK-550-2 than RNK-550-1 and larger N content of RNK-550-2 than RNK-650-3, respectively. Same explanation works well when comparing any pair of sorbents of this work, indicating that the combined effect of N content and narrow microporosity determine the CO₂ adsorption abilities under ambient conditions for these adsorbents. It is worth to point out that RNK-550-2 has CO₂ uptake 30% higher than the control sample RUK-550-2, which illustrates the superiority of the two-step method used in this paper over the conventional carbonization-nitriding-activation three-step procedure in preparing nitrogen-doped porous carbonaceous CO₂ adsorbent.

For the potential applications, adsorbent stability and recyclability need to be considered. In order to test the recyclability, a five-time continuous CO₂ adsorption on RNK-550-2 was performed at 25 °C, with isotherms presented in Fig. 6. Prior to each test, RNK-550-2 was heated at 200 °C under vacuum for 6 h. It is found that only slight drop of CO₂ uptake ca. 5% was observed for RNK-550-2 after 5 cycles, indicating its excellent recyclability and stability.

Besides the adsorption capacity and recycling stability, the CO₂/N₂ selectivity is an essential factor for assessing an adsorbent. Here, the CO₂/N₂ selectivity for RNK-550-2 was calculated based on the CO₂ and N₂ adsorption isotherms, as shown in Fig. 7a. The N₂ uptake is about one tenth of CO₂ uptake for RNK-550-2, hinting a high selectivity towards CO₂. According to the ideal adsorbed

solution theory (IAST), (Myers & Prausnitz, 1965) the CO₂/N₂ selectivity of RNK-550-2 is 19 at a CO₂: N₂ ratio of 10: 90 at 25 °C and 1 bar, which is close to or greater than those of many carbon adsorbents produced previously (Hao et al., 2013; Hao et al., 2011; Ma et al., 2014; Zhao et al., 2011; Zhong et al., 2012).

Apart from possessing high adsorption ability, stable recyclability and good CO₂/N₂ selectivity, an efficient adsorbent used in actual CO₂ capture systems must also possess rapid adsorption kinetics. The CO₂ adsorption kinetics property of RNK-550-2 was examined at 25 °C. The kinetics curve is displayed in Fig. 7b. A very rapid CO₂ adsorption rate was found for RNK-550-2, i.e. 95% adsorption saturation is achieved in about 4 mins. This result points out that this phenolic resin-derived carbon can efficiently cut the cyclic time in the process of CO₂ capture, and thus reduce the expenses, which is highly promising for potential applications.

The isosteric heat of adsorption (Q_{st}), which reveals the interaction strength between adsorbate and sorbent, is crucial to formulate and design new carbonaceous CO₂ sorbents as well. Q_{st} of CO₂ adsorption for some representative samples was achieved using CO₂ adsorption isotherms at 0 and 25 °C based on the Clausius-Clapeyron equation (Kaye & Long, 2005) (Fig. 7c). The Q_{st} for these carbonaceous adsorbents varied within the range 31–40 kJ/mol at nearly zero CO₂ loading, which is greater than formerly described data for some porous carbons (Qian et al., 2014; Sevilla et al., 2012; Sevilla & Fuertes, 2011; Xia et al., 2011). The higher Q_{st} implies stronger interaction between adsorbents and CO₂, which has an enhanced behavior for the CO₂ separation from diluted streams. But an excessive Q_{st} denotes high energy penalty associated with adsorbent regeneration, which is unfavorable in the realistic application. The values of Q_{st} for these phenolic resin-based sorbents are in the scope of 16–40 kJ/mol, typical for a physisorption process indicating the easiness of adsorbent regeneration.

In the actual CO₂ capture process, the flue gas continuously flows out at a high flow rate. Under this circumstance, the dynamic CO₂ capture capacity for an adsorbent is the key to accomplish the CO₂ separation from the flue gas. Here, dynamic breakthrough separation experiments were carried out under conditions that mimic a flue gas, which contains CO₂ of 10 v% in a N₂ stream. As shown in Fig. 7d, the CO₂ breakthrough takes place at nearly 10 mins for RNK-550-2. By integration of this breakthrough curve, the dynamic CO₂ uptake of this sample is calculated to be 1.04 mmol/g. This superb dynamic CO₂ capture capacity proposes its great prospective in the CO₂ capture from the flue gas.

3. Conclusions

In this paper, N-incorporated porous carbons were produced using low cost commercial phenolic resin as the raw materials. Unlike the common carbonization-nitridation-activation three-step procedure, this work explores a facile two-step preparation process to obtain N-doped porous carbonaceous adsorbents. First, the mixture of phenolic resin and urea was pyrolyzed to form the nitrogen-enriched precursor, then the nitrogen-incorporated porous carbons were achieved by following KOH activation at various reaction conditions. This strategy combines carbonization and nitridation into one reaction step and therefore greatly reduce the adsorbent synthesis cost. The as-obtained carbonaceous adsorbents have well developed porous structure as well as high N amount. Superior CO₂ adsorption capacities were found for these phenolic resin-based adsorbents, with maximum CO₂ uptake of 5.01 and 7.47 mmol/g at 25 and 0 °C under ambient pressure, respectively. Detailed studies indicate that the synergistic effects of N content and narrow microporosity of the adsorbents determine their CO₂ uptake under 25 °C and atmospheric pressure. Besides high CO₂ adsorption ability, these samples also possess many extra excellent CO₂ adsorption properties like excellent recyclability.

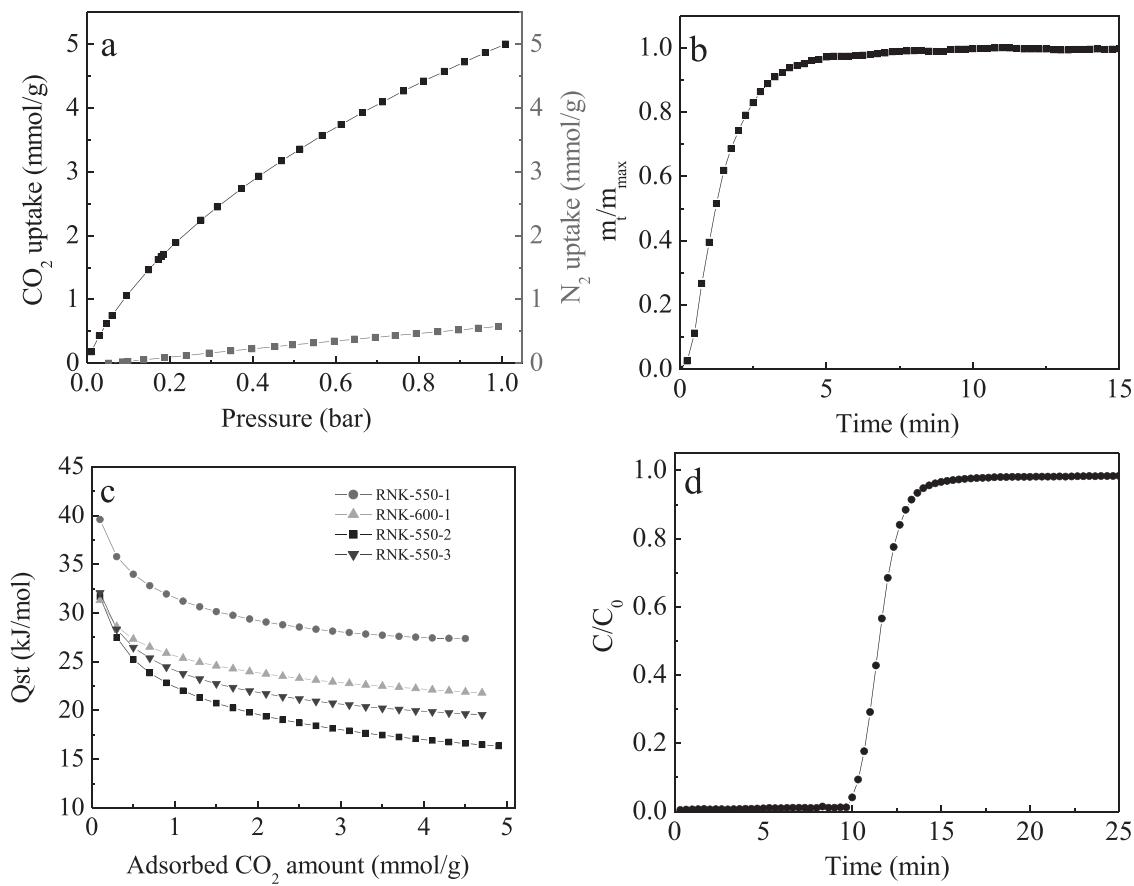


Fig. 7 – (a) CO₂ and N₂ adsorption isotherms of RNK-550-2 at 25 °C and 1 bar (b) adsorption kinetic of CO₂ at 25 °C for RNK-550-2 (c) isosteric heat of CO₂ adsorption on selected sorbents calculated from the experimental adsorption isotherms at 0 and 25 °C and (d) breakthrough curves of RNK-550-2 (adsorption temperature: 25 °C, gas flow rate: 10 mL/min, inlet CO₂ concentration: 10 vol.%, gas pressure: 1 bar).

ity, rapid adsorption kinetics, medium heat of adsorption, excellent CO₂/N₂ selectivity and great dynamic CO₂ uptake. These results specify that the phenolic resin-based carbons of this work are promising as the CO₂ adsorbents.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jes.2020.04.006](https://doi.org/10.1016/j.jes.2020.04.006).

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