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## ARTICLE TYPE

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### A novel nitrogen rich porous aromatic framework for hydrogen and carbon dioxide storage

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The nitrogen rich, p-phenylenediamine based, porous aromatic framework (NPAF) with 1790 m<sup>2</sup>/g BET surface area has been synthesized by using Yamamoto coupling technique. NPAF has shown hydrogen uptake of 1.87 and 0.33 wt. % at 77 K/1 atm and 298 K/80 bar, respectively. The CO<sub>2</sub> uptake and 10 selectivity of NPAF at 273 K/1 atm is 3.64 mmol/g and 48, respectively.

#### Introduction

Hydrogen storage<sup>1</sup> and carbon capture and storage  $(CCS)^2$  are the key technologies to mitigate the adverse effects of global warming induced by the anthropogenic CO<sub>2</sub> emission as a result 15 of an excessive fossil fuel consumption. According to the International Energy Agency, approximately two-thirds of the total CO<sub>2</sub> emission is due to generation of electricity and heat (41 %) and transportation (22 %) sectors.<sup>3</sup> Fossil fuel based power plants are considered as large CO<sub>2</sub> point sources and are suitable <sup>20</sup> sites for the application of the CCS technology.<sup>4</sup> Currently, stateof-the-art CCS technology relies on wet scrubbing by alkanolamines; however, high energy penalty of this process limits its widespread application.<sup>4, 5</sup> On the other hand, vehicles are considered as distributed CO<sub>2</sub> sources and application of the 25 CCS technology is neither practical nor economical.<sup>6</sup> Hence, significant reduction of CO<sub>2</sub> emission in the transportation sector can only be achieved by replacement of oil with alternative energy carriers such as hydrogen; however, hydrogen storage is the bottleneck in utilization of hydrogen as an energy carrier in <sup>30</sup> the mobile applications.<sup>7</sup> Therefore, novel materials and methods

that can satisfy the US Department of Energy (US DOE) hydrogen storage<sup>8</sup> and CCS<sup>9</sup> targets have yet to be discovered.

The last decade has witnessed expansive growth in the design and synthesis of novel porous materials such as MOFs<sup>10, 11</sup>. 35 COFs<sup>12, 13</sup>, porous polymers<sup>14-18</sup> and templated carbons<sup>19, 20</sup> for gas storage applications. Considering CCS technology, porous solid sorbents have the potential to lower the energy penalty of the alkanoalamine based carbon capture process since these materials can be regenerated simply by the pressure swing 40 adsorption and do not require high temperatures (100-140 °C for

- alkanoalamines<sup>4</sup>) for regeneration.<sup>5</sup> On the other hand, porous solid sorbents should have considerable CO<sub>2</sub> capacity (3 mmol/g) at flue gas exhaust temperature and pressure (50-75 °C at 1 bar) in the presence of water and other acidic impurities as well as
- 45 high selectivity towards CO<sub>2</sub> to be a viable alternative to alkanoalamines.4, 21, 22 Furthermore, an ideal hydrogen storage

material should have high gravimetric (55 g H<sub>2</sub>/kg system) and volumetric density (40 g H<sub>2</sub>/L system ) near ambient temperature.<sup>8</sup> Porous materials can only achieve high storage 50 capacity at cryogenic temperatures (77 K) because of the weak interaction (low adsorption enthalpy due to physisorption) of hydrogen molecules with the porous material. Hydrogen storage capacity of a material is a function adsorption enthalpy, pore size/volume and surface area.<sup>23, 24</sup> To achieve significant storage 55 capacity near room temperature, an optimal porous material should have an adsorption enthalpy of 15-20 kJ/mol H2.25, 26 Adsorption enthalpy can be tailored by optimizing the pore size (0.6-0.7 nm) and doping with impurity atoms such as nitrogen and boron.

Nitrogen rich porous polymers are highly desirable for both hydrogen storage and CCS applications. Basic nitrogen groups can enhance the interaction of acidic CO<sub>2</sub> gas with the porous polymer matrix.<sup>27-29</sup> On the other hand, increased nitrogen content can increase the adsorption enthalpy of hydrogen as 65 shown by theoretical and experimental studies.<sup>30-33</sup> To date, hydrogen and CO2 storage characteristics of various porous polymers such as hypercrosslinked polymers<sup>14, 15, 34-37</sup>, polymers of intrinsic porosity<sup>38</sup>, porous aromatic frameworks (PAF)<sup>39, 40</sup> covalent organic polymers with borazine<sup>41-45</sup>, and 70 benzimidazole<sup>46-50</sup>, triazine<sup>51-57</sup> and porphyrin<sup>58, 59</sup> building blocks as well as functionalized porous polymer networks<sup>60-67</sup> with post synthetic modifications<sup>29, 65, 68-74</sup> were reported.

Herein, we have investigated for the first time the hydrogen storage and CCS characteristics of p-phenylenediamine based 75 nitrogen rich porous aromatic framework (NPAF) at low and high pressure.

#### **Experimental details**

#### Chemicals

Starting material 1,4-Bis(diphenylamino)benzene (1), reagents 80 for Yamamato coupling. 1,5-Cyclooctadiene, Bis(1.5cyclooctadiene)nickel(0) and 2,2'-Bipyridyl, and anhydrous solvents tetrahydrofuran (THF) and N,N-Dimethylformamide (DMF) were purchased from Sigma-Aldrich and used without further purification. All materials were handled in an argon filled glove box in which oxygen and water levels were below 0.1 ppm.

#### 5 Synthesis

Synthesis of, N, N, N', N'-Tetrakis(4-bromophenyl)-pphenylenediamine, compound **2**, was accomplished by a procedure similar to the one reported previously.<sup>75</sup> Briefly, 4.66 g (29 mmol) of bromine dissolved in 50 ml of CHCl<sub>3</sub> added <sup>10</sup> dropwise to a 3 g (7.3 mmol) of 1,4-Bis(diphenylamino)benzene dissolved in 50 ml of CHCl<sub>3</sub>. After refluxing the solution for 20 min, the hot solution was filtered. Upon cooling to room temperature compound **2** was precipitated, and the product was washed with cold CHCl<sub>3</sub> (white powder, yield: 2.92 g, 55%).

- Synthesis of **NPAF** was carried out in an argon filled glove box at room temperature. Briefly, 1.2 g (1.65 mmol) of compound **2**, 1.03 g (6.6 mmol) of 2,2'-Bipyridyl, 0.72 g (6.6 mmol) of 1,5-Cyclooctadiene and 1.65 g (6.6 mmol) of Bis(1,5cyclooctadiene)nickel(0) were added to a 60 ml THF / 90 ml
- <sup>20</sup> DMF solution and stirred overnight. After removing the flask from the glove box, 4 M HCl (100 ml) was added slowly to the solution to dissolve the nickel atoms. After filtering the solution, product was washed with CHCl<sub>3</sub>, THF and water (yellow powder, yield: 0.61 g, 90%). As discussed in results and discussion <sup>25</sup> section, to remove the Cl<sup>-</sup> ions from NPAF, 0.6 g of NPAF was refluxed in 100 ml of triethanolamine (TEA) for 8 h. Upon cooling to room temperature, TEA treated NPAF was filtered and washed with copious amount of water.

#### Characterization

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- <sup>30</sup> The powder X-ray diffraction (XRD) of the samples was carried out by a custom-built air tight stainless steel sample holder<sup>76</sup> using a Philips X'pert diffractometer with CuK $\alpha$  radiation of  $\lambda$ =1.54060 Å. The samples were prepared inside the glove box and sealed with Kapton<sup>®</sup> film. Scanning electron microscopy <sup>35</sup> (SEM), Hitachi S800, with energy dispersive X-rays (EDX) attachment was utilized to investigate the chemical composition of the elements. The <sup>13</sup>C cross-polarization magic-angle spinning nuclear magnetic resonance (CP/MAS NMR) experiment was performed on a Bruker DSX 300 spectrometer operating at a
- <sup>40</sup> magnetic field strength of 7.0 T. The resonance frequencies for <sup>1</sup>H and <sup>13</sup>C at this field strength are 300.13 MHz and 75.47 MHz, respectively. A Bruker 4 mm MAS probe was used to acquire <sup>13</sup>C CP/MAS NMR spectra at 7.5 kHz spinning. The chemical shifts were externally referenced to adamantane for <sup>13</sup>C. The
- <sup>45</sup> gravimetric weight loss and melting point were analyzed by a TA Instrument's SDT-Q600, and the data was analyzed with a TA Universal Analysis 2000 software. All low pressure ( $P \le 1$  atm) adsorption and desorption isotherms of hydrogen, nitrogen and CO<sub>2</sub> were measured by a Quantachrome AS1C. The measurement
- <sup>50</sup> accuracy and repeatability of the Quantachrome AS1C were verified with the Quantachrome standard reference material (SARM-2012) before the measurements. The test value was within the reproducibility limit ( $\pm$  5 %) of the expected value. The adsorption data was analyzed by a Quantachrome AS1Win
- 55 software. The specific surface area (SSA) of the samples was calculated from nitrogen adsorption at 77 K using the Brunauer-Emmett-Teller (BET) equation. The pore size distribution (PSD)
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and pore volume of NPAF was calculated by the non-local density functional theory (NLDFT). The high pressure hydrogen and CO<sub>2</sub> pressure-concentration-temperature (PCT) isotherms were collected with Setaram-HyEnergy PCTPro 2000, Sievert's type apparatus. The sample loading was 1.5 g or more to limit the uncertainty of the high pressure measurements. The uncertainties

associated with the hydrogen storage measurements are <sup>65</sup> thoroughly discussed in our previous work.<sup>77</sup>

#### **Results and discussion**

## Synthesis of NPAF and its structural, spectroscopic and thermal characteristics

Synthetic route for the synthesis of NPAF is given in Scheme 1. <sup>70</sup> Successful sythesis of compound **2** is confirmed by TGA and FTIR. The melting point of commpound **2** is 298 °C which is in accordance with the reported value (Fig. S1, ESI†).<sup>75</sup> Moreover, FTIR analysis showed strong C-Br stretching peak around 500-600 cm<sup>-1</sup> (Fig. S2, ESI†). The synthesis of NPAF was accomplished by Yamamoto coupling which was proved to be an effective method for synthesizing high surface area porous polymers.<sup>78, 79</sup> The structure of NPAF was probed by <sup>13</sup>C CP/MAS NMR experiment. <sup>13</sup>C CP/MAS NMR spectrum of NPAF is given in Fig. 1, and in good agreement with the <sup>80</sup> predicted spectrum, showing that cross-coupling reaction was succesful under the given conditions. The peaks around 30 and 230 ppm are due to spinning side bands.



85 FTIR analysis showed C-Br peaks in NPAF also, indicating unreacted Br upon Yamamoto coupling. SEM-EDX analysis confirmed the residual Br impurities, less than 0.1 at. %; in Published on 16 September 2013. Downloaded by University of Calgary on 17/09/2013 14:10:05

addition, showed Cl impurities due to HCl washing (Fig. S3, ESI<sup>†</sup>). Chlorine ions can interact with the electron rich nitrogen atoms; therefore, can limit the NPAF's CO<sub>2</sub> and hydrogen uptake. To remove Cl<sup>-</sup> ions, NPAF was refluxed in triethanolamine <sup>5</sup> (TEA). Indeed, both hydrogen and CO<sub>2</sub> uptakes were increased around 10% upon TEA treatment (Fig. S4, ESI<sup>†</sup>).



Fig. 1. Experimental and predicted <sup>13</sup>C NMR spectra of NPAF.

Thermal stability of NPAF was tested by thermogravimetric <sup>10</sup> analysis (TGA) (Fig. S5, ESI<sup>†</sup>). TGA shows that NPAF is highly stable and starts to decompose around 550 °C under nitrogen flow. Moreover, as mentioned in the introduction, solid sorbent for CCS technology should be stable under moisture since flue gas includes 5% water vapour. After storing NPAF under ambient <sup>15</sup> air over a month we did not observe any noticeable change in the surface area, and hydrogen and CO<sub>2</sub> uptakes (not shown). On the other hand, X-ray diffraction (XRD) analysis revealed the amorphous nature of the NPAF material (Fig. S6, ESI<sup>†</sup>).

#### Porous structure of NPAF

- <sup>20</sup> Figure 2 shows the nitrogen isotherm of NPAF at 77 K which is of type IV isotherm indicating a micro-/mesoporous material according to IUPAC classification.<sup>80</sup> Significant nitrogen uptake at high relative pressures (i.e.,  $P/P_o > 0.1$ ) and the broad hysteresis in the desorption branch are distinctive features of the <sup>25</sup> porous polymers, and can be attributed to the swelling of the
- polymer matrix and the presence of mesopores and intraparticle voids.<sup>80, 81-82</sup> Brunauer–Emmett–Teller (BET) surface area of NPAF is 1790 m<sup>2</sup>/g, and the relative pressure range for BET surface area calculation was determined using the consistency <sup>30</sup> criteria (Fig. S7, ESI<sup>+</sup>).<sup>82-84</sup>
- Pore size distribution of NPAF was probed by nitrogen at 77 K and CO<sub>2</sub> at 273 K, and was calculated by NLDFT based on a carbon material kernel. The pore size distribution of NPAF is given in Fig. 3. The nitrogen isotherm at 77 K was fitted using <sup>35</sup> hybrid slit/cylindrical pore model (i.e., slit pore geometry for pores < 2nm and cylindrical pore geometry for pores > 2nm) since it resulted in better fit to the experimental data as compared to using either one alone; whereas, CO<sub>2</sub> isotherm was fitted using slit pore geometry (Fig. S8, ESI<sup>†</sup>). Utilizing CO<sub>2</sub> at 273 K was
- <sup>40</sup> shown to be useful in determination of the very narrow pores due to diffusional limitations of nitrogen at 77 K.<sup>85</sup> Indeed, CO<sub>2</sub> at 273 K revealed pores as small as 0.3, 0.6 and 0.8 nm being the





Fig. 2. Nitrogen adsorption and desorption isotherms of NPAF at 77 K.

The proposed ideal structure of NPAF given in Scheme 1 is further studied using Spartan software. The pore size of the <sup>50</sup> optimized geometry is found to be 1.05 nm which is in good agreement with the experimental pore size. The smaller pores revealed from the experimental data should be related to the deviation from the ideal structure given in Scheme 1 (i.e., pores formed by cross coupling of three building blocks instead of four <sup>55</sup> and/or Br atoms attached to the ortho- or meta- positions instead of the para- position in the benzene ring).



The micropore and total pore volumes of NPAF were <sup>60</sup> calculated by NLDFT from the nitrogen adsorption isotherm at 77 K using the ranges  $P/P_o < 0.1$  and  $P/P_o < 0.99$ , respectively. The micropore, mesopore and total pore volumes of NPAF are 1.21, 0.77 and 1.98 cc/g, respectively. The mesopore size distribution of NPAF is also given in Fig. S9, ESI<sup>†</sup>.

#### 65 Low pressure CO<sub>2</sub>, hydrogen and nitrogen uptake of NPAF

Low pressure hydrogen, CO2 and nitrogen uptakes of NPAF are

given in Fig. 4. Hydrogen uptake of NPAF at 1 atm and 77 K is 212 cc/g (1.87 wt. %) which is one of the highest for porous polymers reported so far (Table S1, ESI†).<sup>63, 86</sup> Hydrogen uptake did not reach saturation at 1 atm and 77 K, so it possible to store <sup>5</sup> more hydrogen at elevated pressures. At 1 atm, CO<sub>2</sub> uptake of NPAF is 81.5 cc/g (3.64 mmol/g) and 52.3 cc/g (2.32 mmol/g) at 273 K and 298 K, respectively. The CO<sub>2</sub> uptake of NPAF also surpasses most of the porous polymers reported so far (Table S1, ESI†).<sup>34</sup>



Fig. 4. Hydrogen (at 77 K), CO<sub>2</sub> (at 273 K and 298 K) and nitrogen (at 273 K and 298 K) uptakes of NPAF.

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Effect of nitrogen density on gas uptake and adsorption enthalpy of NPAF

- <sup>15</sup> As mentioned in the introduction, one of the motivations behind this work was to synthesize a nitrogen rich porous polymer. Similar nitrogen rich polymers have been reported previosuly, triphenylamine based JUC-Z2 is the most notable one.<sup>87</sup> One of the advantages of NPAF over JUC-Z2 is; NPAF has two nitrogen <sup>20</sup> atoms per five benzene rings, whereas JUC-Z2 has one nitrogen atom per three benzene rings in its building block. Therefore, NPAF has a higher nitrogen atom density per benzene ring. In addition, NPAF has narrower pores (1.05 nm) as compared to JUC-Z2 (1.2 nm). Comparing the hydrogen uptake values (77 K <sup>25</sup> and 1 atm) of JUC-Z2 (1.62 wt. %) and NPAF (1.87 wt. %) with
- nitrogen free triphenylbenzene based COP-3<sup>51</sup> (1.4 wt. %) porous polymer, all of which have very similar surface areas, further proves the favorable effect of nitrogen content on small gas uptake. Hence, NPAF's higher nitrogen atom density and <sup>30</sup> narrower pores should be responsible for its superior CO<sub>2</sub> and hydrogen uptake as compared to JUC-Z2 and COP-3.

The hydrogen and  $CO_2$  adsorption enthalpies of NPAF were calculated by using Clausius-Clapeyron equation from hydrogen isotherms at 77 K and 87 K, and CO2 isotherms at 273 K and 298

- <sup>35</sup> K, respectively. Isotherms were fitted by dual site Langmuir Freundlich (DSLF) equation which was shown to be appropriate in fitting experimental nitrogen, hydrogen and CO<sub>2</sub> isotherms (Fig S10-12 and Table S2, ESI<sup>†</sup>).<sup>51, 88</sup> Both hydrogen (5.2 kJ/mol) and CO<sub>2</sub> (19 kJ/mol) adsorption enthalpies of NPAF are <sup>40</sup> relatively low compared to the other porous polymers as shown in
- Fig 5. Considering hydrogen storage at 77 K, adsorption enthalpy claimed to be the most effective parameter at low loadings.<sup>23</sup> It is

worthwhile to note that NPAF has a significant hydrogen uptake at 1 atm and 77 K although it has a lower adsorption enthalpy <sup>45</sup> than most of the other porous polymers reported so far.



Fig. 5. (A) CO<sub>2</sub> and (B) hydrogen adsorption enthalpy of NPAF.

#### CO<sub>2</sub>/N<sub>2</sub> selectivity of NPAF

The CO<sub>2</sub>/N<sub>2</sub> selectivity is an important parameter in evaluating a solid sorbent for CCS applications. Ideal adsorption solution theory (IAST) has shown to be accurate in calculating the multi component adsorption isotherm of a mixture based on the single component adsorption isotherms of the components.<sup>51, 89</sup> The selectivity of NPAF, 0.15/0.85 mole fraction ratio of CO<sub>2</sub>/N<sub>2</sub>, at 273 K decreases gradually with increasing pressure (48 at 1 atm), whereas at 298 K selectivity of NPAF (88 at 1 atm) is relatively constant up to 1 atm as shown in Fig. 6.



Fig. 6. CO<sub>2</sub>/N<sub>2</sub> (0.15/0.85 mole fraction) selectivity of NPAF at 273 K and 298 K.

#### High pressure $\ensuremath{\text{CO}}_2$ and hydrogen uptake of NPAF

The high pressure hydrogen and CO<sub>2</sub> storage capacities of porous polymers are important for real world applications but seldom reported in the literature.<sup>18, 49, 51, 59</sup> NPAF has a 28.7 mmol/g CO<sub>2</sub> <sup>65</sup> uptake at 57.2 bar and 298 K which surpasses BILP-10<sup>49</sup>; however, less than PPN-4 as shown in Fig. 7(a) (Table S1, ESI†).<sup>18</sup> On the other hand, hydrogen storage capacity of NPAF at 80 bar and 298 K is 0.33 wt. % which is too low for practical applications, Fig. 7(b). The absolute CO<sub>2</sub> and hydrogen <sup>70</sup> gravimetric capacities of NPAF were also calculated using real gas equation of state<sup>90, 91</sup>, and are given in Figs. S13 and S14, respectively (ESI†).

The volumetric capacity of the porous materials is especially important for mobile applications (i.e., hydrogen storage 75 systems). The absolute (i.e., skeletal) density of NPAF was Published on 16 September 2013. Downloaded by University of Calgary on 17/09/2013 14:10:05

determined by a helium adsorption test and found to be 1.05 g/cc, whereas the tap density of NPAF was 0.07 g/cc. The significant difference (i.e., 15 fold) between the absolute and tap densities indicates the inefficient packing of NPAF particles; in addition, s this difference poses engineering challenges in designing system

level hydrogen storage systems and reactors for  $CO_2$  capture applications.



Fig. 7. (A) High pressure CO<sub>2</sub> uptake of NPAF at 273 K and 298 K and (B) high pressure hydrogen uptake of NPAF at 298 K.

The volumetric hydrogen storage capacity of NPAF was determined using the absolute density of NPAF. The calculated volumetric capacities of NPAF at 298 K/80 bar and 77 K/1 atm are 3.48 g/L and 20.01 g/L, respectively. However, volumetric <sup>15</sup> capacity of NPAF is significantly lower than the 2015 US DOE target of 40 g H<sub>2</sub>/L system. One should note that, this is the highest attainable volumetric storage capacity of NPAF and the actual volumetric storage capacity (i.e., after packing) of NPAF will be lower than the reported value here. In other words, actual <sup>20</sup> density of NPAF after packing will be in between the absolute (i.e., skeletal) and tap densities. Packing efficiency of 90% was reported for MIL-101<sup>92</sup>; however, packing efficiency of NPAF needs to be further studied to determine the actual volumetric storage capacity of NPAF.

#### 25 Conclusions

Overall, we have prepared a novel nitrogen rich porous aromatic framework (NPAF), and investigated its performance for hydrogen storage and CCS applications. The relatively high  $CO_2$  uptake (3.64 mmol/g) and selectivity (48) at 273 K and 1 atm

- <sup>30</sup> make NPAF one of the promising materials for CCS applications. On the other hand, hydrogen uptake of NPAF at 77 K and 1 atm (1.87 wt. %) is among the highest in porous polymers. However, room temperature hydrogen storage capacity (0.33 wt. %) of NPAF is far below the US DOE targets to be practical. The
- <sup>35</sup> hydrogen storage and CCS performance of NPAF can be enhanced further by post synthetic modifications. Further work is required to understand the effect of moisture on CO<sub>2</sub> capture performance of NPAF.

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- <sup>45</sup> collecting the <sup>13</sup>C NMR spectrum.

#### Notes and references

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: [BET consistency plot, TGA, FTIR, XRD, DSLF fits to CO<sub>2</sub>, nitrogen and hydrogen uptakes, and excess and absolute gravimetric
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Nitrogen rich porous polymer showed enhanced hydrogen and CO<sub>2</sub> storage capacities as compared to similar porous polymers with lower nitrogen content.

