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A water-based at room temperature synthesized ZIF-93, for CO₂ adsorption

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Zeolitic Imidazolate Framework ZIF-93 was synthesized from a stoichiometric mixture of metal-ligand in aqueous solutions at room temperature, yielding 80% of pure product. The characterization of the material confirmed the formation a material having the same properties to the one obtained previously by solvothermal method in DMF route. This method is very promising for efficient and environmentally friendly synthesis of ZIFs for CO₂ capture application, proved by breakthrough experiments of binary CO₂/N₂ mixtures.

Metal–Organic Frameworks (MOFs) have received considerable attention over the past decade, especially in the field of gas purification and storage as well as catalysis and drug delivery.¹ The first industrial production of MOFs with the ton-scale synthesis of aluminum fumarate (Basolite A520®), a promising candidate for methane storage and delivery, was carried out at BASF facilities.² As pointed out by Long et al. to date, the majority of research efforts related to MOFs for NG and H₂ storage have been directed toward the development of new materials exhibiting improved adsorption properties with little regard for material or production cost.³ Through a water-based route, they accomplished a shift to industrial production, increasing the production rates, whilst reducing both environmental impact and production costs. MOFs are not yet utilized in real life applications, but this drawback could be overcome using cheap starting materials and saving energy, increasing the sustainability of the synthesis procedure.² The largest proportion of the raw material costs derives from the solvent used, originating from the synthesis and purification procedures.³ Therefore, reduction of the amount of solvent and especially replacement by inexpensive and environmentally compatible water is a striking approach. Additionally, synthesis should be carried out at ambient temperature and pressure, avoiding solvothermal synthesis,

with a high energy consumption and pressure associated risks.⁴

Largely, MOF syntheses require high dilution factors which imply large amounts of organic solvents, low production rates and strong environmental impact. Consequently, usually space-time yields (STY) between 0.1 and 1 kg per m³ per day are reported for small-scale lab syntheses, remaining still the aim of a STY larger than 300 kg per m³ per day, through a reduction of solvent amount. Beyond this, the development of water-based routes for MOF synthesis would strongly facilitate their industrialization.^{5–6} An appropriate material for environmentally driven applications should show a low-emission and sustainable synthesis, besides demonstrating high efficiency. In order to quantify the required environmental impact of materials, recently Grande *et al* have introduced a standardized methodology, Life Cycle Assessment (LCA) assessing the environmental impact of CPO-27 synthesis.⁷

Among the diversity of MOFs, Zeolitic Imidazolate frameworks (ZIFs) constitute a subclass of MOFs that adopt zeolite structure types.^{8–10} ZIFs have better thermal and chemical stability than other MOFs families, more suitable for practical capture applications.¹¹ To date, mainly ZIF-8, Zn(mlm)₂, (and its cobalt metal equivalent, ZIF-67) has been synthesizing through hydro/solvothermal methods. Chen et al. reported for the first time, the synthesis in methanol and aqueous ammonia.¹² Synthesis in methanol at room temperature was also performed by Cravillon et al.¹³ The first synthesis of ZIF-8 in water at room temperature without using any additives was effective, but an excess amount of the ligand was needed.¹⁴ Another different synthesis strategies with the assistance of additives (such as triethylamine, sodium formate and *n*-butylamine) in the organic/water based solution system were developed to optimize preparation conditions and control over the morphology and size of ZIF-8.^{15–16} As an scarce example, ZIF-90 (Zn(lca)₂) was synthesized in an aqueous solution containing using polyvinylpyrrolidone (PVP) as an additive.¹⁷ To develop a method for high crystalline ZIFs preparation from stoichiometric ratio metal and ligand precursors in aqueous solution still remains a challenge.

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Electronic Supplementary Information (ESI) available: Details of characterization analyses of ZIF-93 crystals, adsorption and breakthrough experiments; SEM pictures, TGA profile, N₂ isotherms at 77K. See DOI: 10.1039/x0xx00000x

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In this study, we studied ZIF-93,¹⁸ Zn(mlm)₂, with a RHO structure, that possess the same metal ion Zn²⁺ and same organic ligand 4-methyl-5-imidazolecarboxaldehyde as SIM-1, but different topologies, since SIM-1 has a SOD structure.¹⁹⁻²⁰ The original synthesis is carried out with zinc acetate in DMF.¹⁸ Liu et al. employed a hydrothermal procedure to prepare ZIF-93 nanocrystals. However, they used an excess of ligand in a very diluted mixture (1:8:1000) and MeOH for the purification procedure. A synthesis in water with sodium formate as additive was reported for a microfluidic mixed matrix membrane fabrication.²¹

Capture CO₂ from post-combustion flue gases using MOFs is one of the promising approaches for CO₂ capture and sequestration.²² One of the advantages of MOFs is the ability to systematically modulate the pore dimensions and surface chemistry within their framework, allowing tailoring sorbent materials for effective CO₂ capture.²³ Currently, implementation of CO₂ capture can be accomplished by using either liquid amine-based chemical adsorbents or cryogenic technology; but both of these solutions are energy-intensive and expensive. To overcome their drawbacks, porous adsorbents that can reversibly capture and release CO₂ by means of pressure swing adsorption-desorption cycles (PSA) are currently under investigation. Eddaoudi and cols. introduced a unique and novel multistep experimental testing protocol based on cyclic breakthrough experiments and regeneration step by temperature or vacuum swing. The application of this screening methodology allows the assessment of MOF powders based on relevant indicators quantitative performance indicators, CO₂ uptake at 0.1 bar, CO₂/N₂ selectivity, resistance to poisoning and energy of regeneration.²⁴ As stressed by the company Johnson Matthey and others in the frame of MOF development for adsorbents, beyond stability and performances, the cost of the adsorbent shall be considered as well when aiming at commercial application.^{3, 25}

Herein, we report for the first time, a rapid, easy to scale up, high yield and eco-friendly strategy for the synthesis of ZIF-93 under stoichiometric and concentrated aqueous conditions, with ammonia as additive. In addition, we performed breakthrough experiments giving a proof that the resultant material can separate CO₂ from N₂ in a fixed-bed adsorption column. The costing analysis of industrial scale production of ZIF-93 is beyond the scope of this study.

In our synthesis, 1.0456 g of zinc nitrate hexahydrate and 0.8808 g of 4-methyl-5-imidazolecarboxaldehyde are dissolved in 56 mL of distilled water. Then, a solution of 480 µL of NH₄OH in 40 mL of water is added dropwise under vigorous stirring onto the former one. The suspension was then stirred for additional 18 hours at room temperature. Overall, the metal:ligand:base:H₂O molar ratios were 1:2:1:135. Formation of precipitated occurred within seconds when the base solution was poured into the stirred ligand-metal solution. The white solid was isolated by centrifugation and washed three times with water. The resultant solid was dried overnight at 120°C. The synthesis yield is 79% based on zinc. Expressed in kg per m³ per day (STY), the industrially pertinent unit, the

space-time yield of the water based synthesis is 14 kg per m³ per day, considerably higher than those for small-scale lab syntheses.

This preparation shows several improved, perceptible and different features from the reported cases of ZIF synthesis in aqueous synthesis. First of all, we achieved crystalline ZIF-93 with a stoichiometric metal and ligand precursor ratio (1:2), while others reported ZIFs syntheses need more amount of ligand. In the aqueous synthesis of ZIF-8, Pan et al. required an amount of 2-methylimidazole 70 times the amount of zinc nitrate.¹⁴ Jia and cols. studied, among other synthesis conditions, the effect of molar ratio mlm/Zn on the crystallization process of ZIF-8 particles in a water based system. They found that molar ratios of mlm/Zn ≥ 35 were required to generate pure ZIF-8 phase when using zinc nitrate (along with others salts). Peaks related to ZIF-8 disappeared in XRD results, showing unknown peaks and the products exhibited a 2D leaf-layered structure. They hypothesized that the unexplored product could be immature ZIF-8 particles with some by-products such as Zn(OH)₂ compounds.²⁶ Up to date, the only report of water based synthesis of ZIF-93 nanocrystals required an amount of ligand used of 8 equivalent of metal ions on order to obtain a pure phase. However, only a yield of 45% is reached.²⁷

The second enhanced feature is the amount of water needed, certainly concentrated in contrast with the high diluted published procedures, being at least one order of magnitude lower. Regarding to water based ZIF-8 synthesis, reports included a high consumption of water, with molar ratios of 2255,¹⁶ 1238¹⁴ and 1280.²⁶ Once more, the reported water based synthesis of ZIF-93 by Liu et al. is based on a diluted mixture, with a molar ratio Zn/water of 1000, an order of magnitude higher than in this work.²⁷ Comparing with ZIF-8 aqueous synthesis with supplementary additive, He et al. needed a molar ratio of 2:32 (ligand:NH₄OH) to avoid the formation of an almost amorphous phase.²⁸ Similarly, Gross et al. claimed that higher triethylamine (TEA) than a 2:1 ligand:TEA molar ratio is required to deprotonate the zinc-methyl imidazole complex, obtaining their best results with a ratio metal:ligand:TEA of 1:16:16.¹⁶ Finally, synthesis yield in this work is comparable to the ones reported for water based synthesis of ZIF-8, but higher than the only report on ZIF-93. An overall comparison and contrast with the reported water based ZIFs synthesis with the most similar and close procedure conditions show that our approach overreaches any other strategy. Concerning ZIF-8, the approach of He et al. coincides with ligand and water amount, but diverges in the quantity of NH₄OH as additive, where an equivalent of 32 is required, since a lower amount leads to an amorphous phase.²⁸ For ZIF-93, the closer water based synthesis involved an equivalent of 8 and 1000, for ligand and water, respectively. And, although no additive is necessary, only a 45% of yield is achieved.²⁷

Figure 1. PXRD pattern of as-synthesized ZIF-93 and the simulated one from ZIF-93 crystal structure data.

The X-ray diffraction (XRD) patterns for the synthesized material agrees with the known patterns from syntheses with ZIF-93 as shown in Fig. 1.¹⁸ All peaks index to a RHO structure and show excellent agreement with peak positions calculated from the known crystal structures. The N₂ adsorption measurement (Fig. S4, †ESI) shows a type I isotherm in the micropore region and type II at high relative pressure. It indicates that the material has a microporous structure, made out of small particles that produces an uptake at high relative pressure in the inter particles space.²⁹ BET surface areas is 604 m²·g⁻¹, a little bit lower to the value reported from ZIF-93 sample prepared solvothermally in DMF.¹⁸ The size of the as-synthesized crystals was ca. 1-2 mm according to SEM analysis (Fig. S2, †ESI) where rhombic dodecahedra with distinct facets can be recognized. Figure S3 (†ESI) shows the thermal gravimetric analysis (TGA) of the water based synthesized ZIF-93 samples performed under air flow. The TGA curve is similar to that reported previously,^{21, 27} exhibiting a gradual weight-loss step of 7% up to ca. 100°C, corresponding to the removal of guest molecules (H₂O) from the cavities or unreacted species. A plateau was shown in the temperature range of 100-350°C, indicating high thermal stability of the sample.

Figure 2. CO₂ isotherms up to 1 bar and 30 bar (insert image, same axes) at 303 K of the material synthesized in aqueous solution (close symbol) compared with ZIF-93 solvothermally synthesized in DMF reported by Morris *et al* (open symbol).¹⁸

For the industrially relevant process of post-combustion CO₂ capture from flue gas, adsorbents must be able to effectively separate CO₂. Consequently, the CO₂ uptake for the material was first assessed in the high-pressure region up to 30 bar by analysis of the isotherms measured at 303 K, as shown in the insert in Figure 2. Despite the difference in surface area, ZIF-93 synthesized in water medium in this work shows a similar uptake in the whole region of pressures as ZIF-93 prepared solvothermally in DMF, 180 and 35 cm³ (STP)·g⁻¹ at 30 and 1 bar, respectively. Furthermore, it is also noted that there is almost no adsorption of N₂ (Fig. S6, †ESI), indicating the water based ZIF-93 highly preferentially adsorbs CO₂ over N₂, which makes ZIF-93 potentially promising material for the removal of CO₂ from its binary mixture CO₂/N₂.

The efficient adsorption properties of ZIF-93 synthesized in aqueous medium are confirmed by dynamic breakthrough experiments carried out on a CO₂/N₂ mixture, as related to practical industrial processes. In these experiments, an adsorbent material is exposed to a mixed gas stream to estimate the time in which the material can selectively hold CO₂ while the other gas components pass through. A longer resulting CO₂ retention time indicates a greater dynamic separation capacity. Figure 3 shows the breakthrough curves of a mixture of CO₂/N₂ (25:75) through a column filled with 0.4 g of ZIF-93 at 298 K and 1 atm. After the first seconds, nitrogen breaks through the ZIF-93 column. The exclusion of nitrogen in the ZIF-93 column is consistent with the absence of adsorption of nitrogen observed in volumetric measurements. During the first 2 min, the adsorbent retains CO₂ and the outlet stream contains pure nitrogen. We used H₂ as reference and inert gas (†ESI) and its profile in the breakthrough curve shows us the shape of the profile is not due to the adsorption effect but to dynamics of the fix bed. As H₂ and N₂ first momentum is the same, we can say that N₂ adsorption is close to negligible. After 12 min, the concentration of the outlet gas reflects the feed gas composition, indicating the saturation of ZIF-93.

Figure 3. Breakthrough curves of a CO₂/N₂ mixture (25:75), 12 cm³ (STP)/min at 298 K on 0.4 g of ZIF-93.

Another important issue in industrial separation application is the regeneration process, being necessary low energy consumption and time efficiency. For the case of our water

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based ZIF-93, regeneration was fully realized under He flow at ambient temperature (Fig. S8, †ESI). Within 2 min, adsorbed CO₂ was purged from the bed, much faster than for another ZIFs.³⁰ That shows us that, besides a noticeable separation of CO₂ and N₂, a weak CO₂ adsorption leads to a very quick regeneration time.

Following the protocol for evaluating porous adsorbents as prospective CO₂ adsorbent from flue gas proposed by Eddaoudi,²⁴ we compared the CO₂ adsorption results on our material with some preselected candidate materials. We tracked the criteria for material selection, that is to say CO₂ uptake, CO₂/N₂ selectivity, energy of regeneration and tolerance to moisture and other impurities. Regarding to CO₂ uptake at 0.1 bar, water-based ZIF-93 is comparable to (NDC)-fcu-MOF, isorecticular to UiO-66 but with a reduced pore-aperture size and pore volume (0.19 cm³·g⁻¹). Even ZIF-93 has a larger pore volume (0.46 cm³·g⁻¹), the presence of aldehyde moieties plays a role on the affinity of this material for carbon dioxide.³¹ Correspondingly, breakthrough time is similar for both materials (around 10 min·g⁻¹) and lower than other elected materials, as NbOFFIVE-1-Ni, SIFSIX-3-Cu, zeolite 13X, and UTSA-16 (55, 65, 70 and 45 min·g⁻¹, respectively). Additional experiments, as breakthrough experiments at 328 K (flue gas temperature after desulfurization step) and recyclability would give us further information to compare with benchmark materials. If we consider the associated isosteric heat of adsorption (Q_{st}), we would expect a reduction of performance at 328 K due to the moderate energy of interaction between CO₂ molecules and the framework (29 kJ mol⁻¹) as attested with UTSA-16. The reported protocol revealed that NbOFFIVE-1-Ni displays all the essential properties to deal with the challenging postcombustion carbon capture.

As said before, in order to smooth the progress of industrialization of water-based routes for MOF synthesis, a higher reduction of solvent amount is still required, to aim a STY larger than 300 kg per m³ per day. As a hint that there is still room for improvement regarding to synthesis conditions, a change in water amount and synthesis time is applied to the synthesis. Decreasing water amount four times up to a molar ratio of 1:2:1:33 and decreasing synthesis time from 18 to 2 h, leads to an increase of STY up to 175 kg per m³ per day. Remarkably, the resultant material keeps the same quality in terms of crystallinity and porosity as the material synthesized in a more diluted synthesis mixture and for a synthesis time of 18h (Fig. S1 and S5, †ESI). To our best knowledge this the highest STY value reported for ZIFs water base synthesis, which demonstrate the great potential of the synthetic method reported here.

Conclusions

We have shown for the first time that high quality ZIF-93 can be produced in water at room temperature. The product shows excellent thermal and chemical stabilities, and improved hydrothermal stability. The material demonstrates a comparable CO₂ adsorption uptake than the one prepared

solvothermally in DMF, and hence, less environmental friendly. We believe this green and facile synthesis strategy can be widely-applicable in large-scale production of ZIF-93. Furthermore, we present the separation and removal of CO₂ from its binary CO₂/N₂ mixture by fixed-bed adsorption, establishing the feasibility of water based ZIF for their potential applications in this important industrial and environmental process.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.
- M. Gaab, N. Trukhan, S. Maurer, R. Gummaraju and U. Müller, *Microporous Mesoporous Mater.*, 2012, **157**, 131-136.
- D. DeSantis, J. A. Mason, B. D. James, C. Houchins, J. R. Long and M. Veenstra, *Energy Fuels*, 2017, **31**, 2024-2032.
- H. Reinsch, *Eur. J. Inorg. Chem.*, 2016, **2016**, 4290-4299.
- A. Czaja, E. Leung, N. Trukhan and U. Müller, in *Metal-Organic Frameworks*, Wiley-VCH Verlag GmbH & Co. KGaA, 2011, pp. 337-352.
- T. Didriksen, A. I. Spjelkavik and R. Blom, *J. Flow Chem.*, 2017, **7**, 13-17.
- C. A. Grande, R. Blom, A. Spjelkavik, V. Moreau and J. Payet, *Sustainable Materials and Technologies*, 2017, **14**, 11-18.
- R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 3875.
- R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939.
- K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. D. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186-10191.
- A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2009, **43**, 58-67.
- X.-C. Huang, Y.-Y. Lin, J.-P. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2006, **45**, 1557-1559.
- J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, **21**, 1410-1412.
- Y. Pan, Y. Liu, G. Zeng, L. Zhao and Z. Lai, *Chem. Comm.*, 2011, **47**, 2071-2073.
- J. Cravillon, R. Nayuk, S. Springer, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2011, **23**, 2130-2141.
- A. F. Gross, E. Sherman and J. J. Vajo, *Dalton Transactions*, 2012, **41**, 5458-5460.
- F.-K. Shieh, S.-C. Wang, S.-Y. Leo and K. C. W. Wu, *Chemistry – A European Journal*, 2013, **19**, 11139-11142.
- W. Morris, B. Leung, H. Furukawa, O. K. Yaghi, N. He, H. Hayashi, Y. Houndonougbo, M. Asta, B. B. Laird and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 11006-11008.
- S. Aguado, J. Canivet and D. Farrusseng, *J. Mater. Chem.*, 2011, **21**, 7582-7588.
- FR09/04488 Pat., FR09/04488, 2009.

Journal Name

COMMUNICATION

21. F. Cacho-Bailo, G. Caro, M. Etxeberria-Benavides, O. Karvan, C. Tellez and J. Coronas, *Chem. Comm.*, 2015, **51**, 11283-11285.
22. J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.
23. K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724-781.
24. K. Adil, P. M. Bhatt, Y. Belmabkhout, S. M. T. Abtab, H. Jiang, A. H. Assen, A. Mallick, A. Cadiau, J. Aqil and M. Eddaoudi, *Adv. Mater.*, 2017, **29**, 1702953-1702963.
25. S. Hindocha and S. Poulston, *Faraday Discuss.*, 2017, **201**, 113-125.
26. M. Jian, B. Liu, R. Liu, J. Qu, H. Wang and X. Zhang, *RSC Advances*, 2015, **5**, 48433-48441.
27. X. Liu, Y. Li, Y. Ban, Y. Peng, H. Jin, W. Yang and K. Li, *Mater. Lett.*, 2014, **136**, 341-344.
28. M. He, J. Yao, Q. Liu, K. Wang, F. Chen and H. Wang, *Microporous Mesoporous Mater.*, 2014, **184**, 55-60.
29. M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K. S. W. Sing, *Pure Appl. Chem.*, 2015, **87**, 1051-1069.
30. N. T. T. Nguyen, H. Furukawa, F. Gándara, H. T. Nguyen, K. E. Cordova and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2014, **53**, 10645-10648.
31. H. Amrouche, S. Aguado, J. Pérez-Pellitero, C. Chizallet, F. Siperstein, D. Farrusseng, N. Bats and C. Nieto-Draghi, *The Journal of Physical Chemistry C*, 2011, **115**, 16425-16432.

ZIF-93 synthesized in water medium at room temperature with high yield for CO₂/N₂ separation