

ChemComm

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: J. Sun, L. Jing, Y. Tian, F. Sun, P. Chen and G. Zhu, *Chem. Commun.*, 2018, DOI: 10.1039/C7CC09767K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Task-specific design of hierarchical porous aromatic framework as ultrastable platform for large-sized catalytic active site binding

Jin-Shi Sun,^a Li-Ping Jing,^a Yuyang Tian,^b Fuxing Sun,^a Peng Chen,^{*a} and Guangshan Zhu^{*b}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

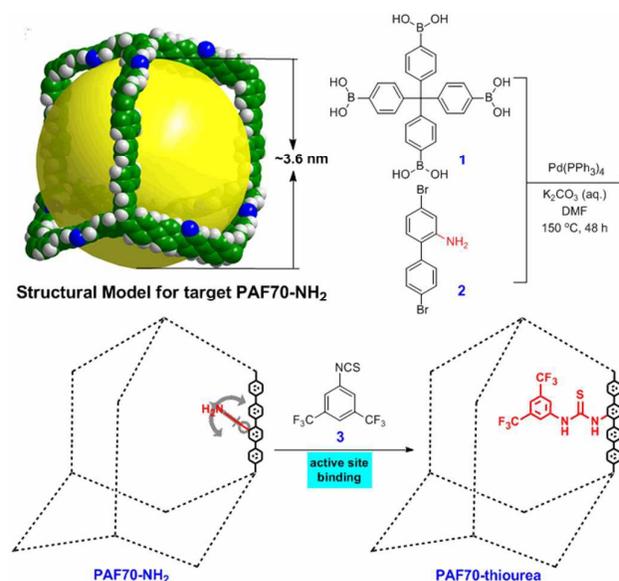
www.rsc.org/

An amine-tagged hierarchical porous aromatic framework PAF70-NH₂ with ultra-stability and narrowly distributed mesopores was synthesized. PAF70-NH₂ has high potential for covalently immobilizing relatively large-sized catalyst inside its pores. This work gave a perfect example of using PAF70-NH₂ as platform for completely recyclable heterogeneous organocatalysis.

Porous materials built entirely or partly from organic building blocks, such as metal organic frameworks (MOFs), covalent organic frameworks (COFs), and porous organic polymers (POPs), have attracted extensive interest.¹⁻⁸ As we all know, MOFs and COFs usually have highly flexible tunable and ordered pores but with low stability while POPs have high stability but usually with broadly distributed pores. Our group has reported a series of porous aromatic frameworks (PAFs) represented by **PAF-1**,⁹ which are constructed from rigid aromatic building blocks and featured by the high density of phenyl rings.^{1,10} The robust framework makes PAFs have narrowly distributed pores and good chemical stability. Hence, PAFs could combine exceptional features of MOFs, COFs and POPs^{10,11}. Increasing works using PAFs for diverse applications including adsorption,¹¹⁻¹⁷ separation,^{18,19} sensing^{20,21} and heterogeneous catalysis²²⁻²⁶ have been reported. Importantly, the lipophilicity of the pore in PAFs makes them very suitable to be used as platform for organocatalysis. Because of relatively large size of most organocatalysts, PAFs with mesopores which are large enough to accommodate diverse organocatalysts and various reaction substrates are highly desired. Since our seminal work of **PAF-1**, many attempts to construct mesoporous **PAF-1** analogues through increasing the numbers of benzene rings in edge of the diamondoid topology have been carried out, however no desired mesoporous PAFs

have been achieved.^{22,25-29} To date, synthesis of PAFs with narrowly distributed mesopores remains a major scientific challenge. In addition, in order to introduce organocatalytic site into porous material, pre-embedding amine anchor in the material is a good method. Generally, the most commonly used method to obtain amine-tagged PAFs is nitration of the phenyl ring in the framework followed by reduction of the nitro group.^{22,23,26} However, the above method faces a problem that the amine-group could not be precisely located or uniformly distributed in the materials. Using pre-modified monomers with amine-group to directly construct amine-tagged PAFs could solve this problem, but the corresponding research work is still rare. Herein, we developed a new pre-modification strategy to prepare an amine-tagged hierarchical PAF with narrowly distributed mesopores and studied its application as ultrastable platform for large-sized catalytic active site binding.

First, to obtain a mesoporous PAF, a framework with four



^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China. Email: pengchen@jlu.edu.cn

^b Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China. Email: zhugs100@nenu.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental details including synthesis and experimental method. See DOI: 10.1039/x0xx00000x

COMMUNICATION

Journal Name

benzene rings in the edge of the diamondoid topology was selected. As illustrated in Scheme 1, using monomers **1** and **2** (for the procedure details to prepare **1** and **2**, see ESI.†), the target amine-tagged **PAF70-NH₂** was directly synthesized employing Suzuki–Miyaura coupling reaction. Then, through the reaction of **PAF70-NH₂** and isothiocyanate **3**, a novel thiourea-containing **PAF70-thiourea** was obtained.

In order to verify if the above strategy successfully led to the desired PAF materials, fourier transform infrared (FT-IR) spectra were conducted. As shown in Fig. 1a, the FT-IR spectrum of **PAF70-NH₂** clearly showed disappearance of the characteristic peaks of boronic group in monomer **1** and C–Br bond (1068 cm⁻¹) in monomer **2**, indicating the successful coupling of phenyl-phenyl rings. Compared with **PAF70-NH₂**, in the FT-IR spectrum of **PAF70-thiourea**, the appearance of the characteristic peaks of thiourea unit and trifluoromethyl group (1279, 1178 and 1138 cm⁻¹), together with the changes in the region of 3300–3500 cm⁻¹ from two peaks of primary amine to mono peak of secondary amine, both directly proved the existence of thiourea unit.

The nitrogen adsorption–desorption isotherm of **PAF70-NH₂** (Fig. 1b) showed a combined isotherm of types I and IV. That is, the isotherms had a rapid uptake at low relative pressure and a pronounced hysteresis in the desorption branch, which indicated the coexistence of micropores and mesopores. The relatively sharp hysteresis in desorption branch is characteristic of mesoporous structure with narrowly distributed pore size. The Brunauer–Emmett–Teller (BET) surface area was 599 m² g⁻¹ for **PAF70-NH₂**. The non-local density functional theory (NLDFT) pore size distribution of **PAF70-NH₂** was shown in Fig. 1c. **PAF70-NH₂** had narrowly distributed mesopores with 3.8 nm diameter, which was in good agreement with the theoretical pore width (~3.6 nm) of the simulated structure (Scheme 1). Noteworthy, the amine anchor and mesopores in our hierarchical porous material make **PAF70-NH₂** have scientific and technological significant importance for further binding different active sites even with large sizes. After modification with thiourea, the corresponding sharp hysteresis in the desorption branch of **PAF70-NH₂** disappeared (Fig. 1b), demonstrating the absence of mesopores in **PAF70-thiourea**. The main pores of **PAF70-thiourea** with a NLDFT pore size distribution centered at about 1.5 nm width (Fig. 1c) could supply sufficient space for catalytic reaction. In addition, introducing thiourea unit led to a decrease of the BET surface area to 395 m² g⁻¹ for **PAF70-thiourea**.

Thermal stability of **PAF70-NH₂** was tested by thermogravimetric analysis (TGA). As shown in Fig. 1d, **PAF70-NH₂** (black curve) showed almost no weight loss below 300 °C, suggesting its high thermal stability. The decomposition of the framework started at about 400 °C and the decomposition became obvious when the temperature was above 500 °C. When the temperature reached 800 °C, there was still a 4.0 wt% residue for **PAF70-NH₂** ascribed to the residue of palladium species. Compared with **PAF70-NH₂**, **PAF70-thiourea** (red curve, Fig. 1d) showed a 24% weight loss between 180–400 °C, which was attributed to the decomposition of the thiourea

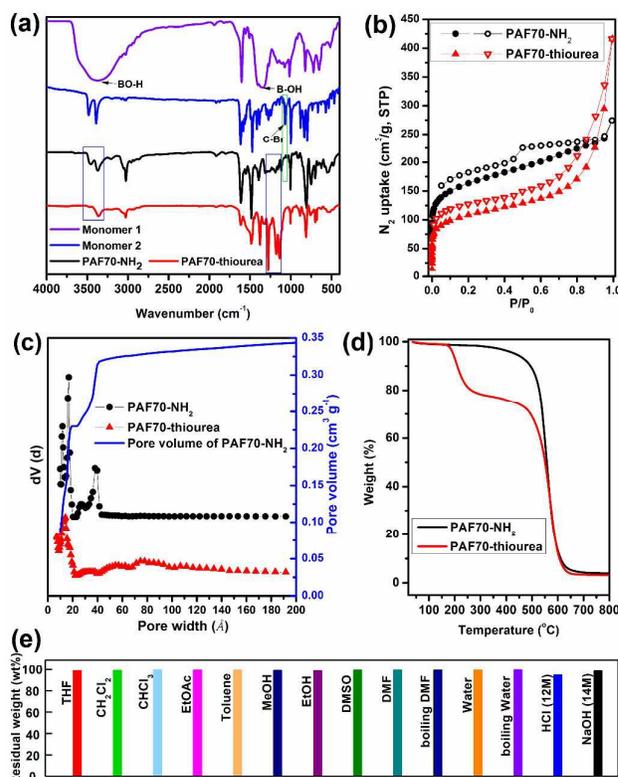


Fig. 1 (a) FT-IR spectra of **1**, **2**, **PAF70-NH₂** and **PAF70-thiourea**. (b) Nitrogen adsorption (solid symbols)–desorption (open symbols) isotherms measured at 77 K for **PAF70-NH₂** and **PAF70-thiourea**. (c) Pore size distributions calculated from NLDFT (N₂ at 77 K on carbon (slit pore)) of **PAF70-NH₂** and **PAF70-thiourea**. (d) TGA plots of **PAF70-NH₂** and **PAF70-thiourea** at air condition with a heating rate of 10 °C min⁻¹. (e) Residue weight percentage of **PAF70-NH₂** after treatment for one week in different solvents.

unit and was consistent with the sulfur content (3.1 wt%) determined by elemental analysis. Further obvious decomposition of the framework started at 450 °C and there was a 3.2 wt% palladium species residue which came from the preparation process of **PAF70-NH₂**. Although **PAF70-thiourea** showed lower thermal stability which mainly resulted from the intrinsic property of the catalytic unit, the decomposition temperature (180 °C) was high enough to meet the need of the overwhelming majority of organic reactions.

To conclude, the above characterization of the materials clearly proved the successful preparation of **PAF70-NH₂** and **PAF70-thiourea**.

Furthermore, considering the high potential of **PAF70-NH₂** for diverse applications through binding different active sites in the pores, we then focused on investigating the chemical stability of **PAF70-NH₂**. As shown in Fig. 1e, **PAF70-NH₂** could not be dissolved or decomposed in almost all common solvents (all >99 wt% residue after treatment with these solvents for one week) such as tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), ethyl acetate (EtOAc), toluene, methanol (MeOH), ethanol (EtOH), dimethyl sulfoxide (DMSO), dimethylformamide (DMF) and water. Furthermore, **PAF70-NH₂** could not be dissolved or decomposed even in harsh conditions, such as boiling water

(>99 wt% residue), boiling DMF (>99 wt% residue), strong acid (12 mol/L HCl aqueous solution, 95 wt% residue) and strong base (14 mol/L NaOH aqueous solution, 99 wt% residue). These results demonstrated that **PAF70-NH₂** possesses chemical ultra-stability. The stability and mesoporous features make **PAF70-NH₂** have high potential for diverse post-functionalizations.

Next, the catalytic properties of **PAF70-thiourea** was studied. *N*-Bromosuccinimide (NBS)-mediated oxidation of alcohols was selected as model reaction.³⁰⁻³² First, 1-phenylethanol (**1a**) listed in **Table 1**) was selected as the model substrate to screen the reaction conditions. Among various screened temperatures it was found that at -35 °C **PAF70-thiourea** (5 mol%) could smoothly catalyze the needed oxidation reaction in CH₂Cl₂ with almost no side reactions (71% conversion, Table S1, entry 1, ESI.†). Then, some control experiments were conducted at -35 °C (Table S1, entry 2, ESI.†). Second, **PAF70** without amine groups, which was synthesized through the same strategy with **PAF70-NH₂** (for preparation details, see ESI.†) and has a 4.6 wt% Pd residue, absolutely had no catalytic activity (Table S1, entry 3, ESI.†), indicating that Pd residue has no catalytic activity for this reaction. Third, **PAF70-NH₂** with free amines could react with NBS rapidly under the same condition (Table S1, entry 4, ESI.†), making the catalyst's mass greatly increase. To further demonstrate this phenomenon, 2-aminobiphenyl (**4** in table S1) was used in the same reaction, obtaining a complicated system in which a series of bromination products could be detected by mass spectrum (Table S1, entry 5, ESI.†). Therefore, **PAF70-NH₂** is obviously not suitable as catalyst for the current reaction. Fourth, a molecule (**5** in table S1) with the same thiourea unit itself could not react with any reactants in the current reaction. Furthermore, as a homogeneous catalyst, **5** could catalyze this oxidation reaction and gave a 60% conversion under the same conditions (Table S1, entry 6, ESI.†). This obviously proved that thiourea unit is indeed effective catalytic site for the current reaction. Compared with the homogeneous counterpart, **PAF70-thiourea** exhibited preferable catalytic activity. This is due to that the immobilized thiourea catalysts in the pores could efficiently avoid self-quenching which is a self-assembly behavior of thiourea molecules through intermolecular hydrogen bonding interactions between the Brønsted acid site and Lewis base site.³³ Fifth, when the catalyst loading increased from 5 mol% to 10 mol%, the reaction could become slightly faster (71% to 79% conversion, Table S1, entries 1 and 7, ESI.†). Sixth, the supernatant liquid of the CH₂Cl₂ suspension of **PAF70-thiourea** showed no catalytic activity for the reaction (Table S1, entry 8, ESI.†), indicating no leakage of catalytically active species from **PAF70-thiourea** in the catalysis process. The above control experiments demonstrated that the thiourea unit is efficient catalytic site for the current **PAF70-thiourea** catalyzed reaction and this reaction proceeds via a heterogeneous process.

As a narrowly distributed porous material immobilized catalyst, the size selectivity is an important factor. Hence, the size selectivity of **PAF70-thiourea** was tested using a series of

Table 1 **PAF70-thiourea** catalyzed NBS-mediated oxidation of alcohols.^a

| entry | alcohol | product | T [°C] | time | Yield ^b |
|-------|---------|---------|--------|------|--------------------|
| 1 | | | -35 | 3d | 78% |
| 2 | | | -35 | 7d | 62% |
| 3 | | | -20 | 20h | 90% |
| 4 | | | -20 | 20h | 28% |

^a Reaction condition: a solution of 0.335 mmol **1a-4a**, 0.50 mmol NBS and 35 mg **PAF70-thiourea** in 1 mL of CH₂Cl₂ was stirred at the indicated temperature for the indicated time. ^b Isolated yield.

alcohols as the reaction substrates at a 10 mol% catalyst loading. Compared with entry 1 of Table 1, the substrate **2a** (Table 1, entry 2) which is similar to **1a** but has larger size, reacted slowly than **1a** under the same conditions. Then, to further investigate this size selectivity, a contrast test using **3a** and **4a** with different sizes was performed. Compared with that **3a** could smoothly transform to **3b** in 90% yield (Table 1, entry 3), the larger-sized **4a** reacted more slowly under the same conditions (Table 1, entry 4, in the same time, only 28% yield), obviously indicating that the catalytic reaction could occur inside the pores of the PAF-based catalyst. This size selectivity further confirmed the existence of the narrowly distributed mesopores in **PAF70-NH₂**, in which the thiourea unit was introduced and the organocatalysis occurred.

The recyclability of **PAF70-thiourea** was tested by subjecting it to 36 cycles of the oxidation reaction of **1a**. The reaction was driven to react for the same time in each cycle. As shown in Fig. 2 and Table S2 (ESI.†), in the first 5 cycles **PAF70-thiourea** showed a slow increase of the catalytic activity, which might

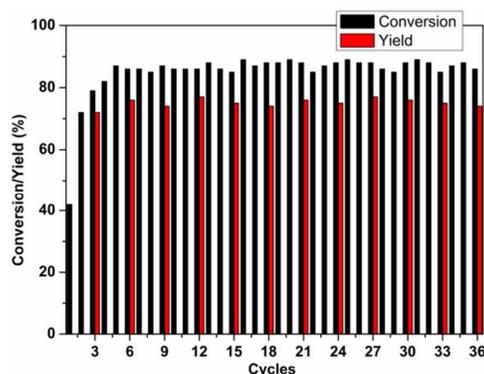


Fig. 2 The recycle test of **PAF70-thiourea** catalyzed NBS-mediated oxidation of 1-phenylethanol. Conversion was determined by ¹H NMR of the crude reaction mixture and yield is the isolated yield of **1b**.

be due to the gradual disappearance of some guest molecules in the pores of the PAF. After 5 cycles, the catalytic activity of **PAF70-thiourea** became very stable. Surprisingly, after 36 cycles, there was absolutely no loss of catalytic activity of the catalyst. Notably, the FT-IR spectra (Fig. S8, ESI.†) and nitrogen adsorption-desorption isotherms (Fig. S9, ESI.†) of the fresh **PAF70-thiourea** and the recycled catalyst after 36 cycles were almost the same, indicating that **PAF70-thiourea** remained unchanged after 36 cycles. In other words, as catalyst in the current system, **PAF70-thiourea** is completely recyclable and reusable. Considering the complexity of the reaction system, this complete recyclability is very rare and exciting.

In conclusion, an amine-tagged hierarchical PAF material (**PAF70-NH₂**) was task-specifically designed and successfully obtained. It had narrowly distributed mesopores. Benefitting from the intrinsic stability of the very robust framework, **PAF70-NH₂** showed ultra-stability, which together with the amine-anchor in the large enough mesopores endow **PAF70-NH₂** with high potential for binding large-sized active sites through post-functionalization. Then, by binding to the amine anchor, the relatively large-sized thiourea unit was easily covalently introduced into the pores of **PAF70-NH₂**, affording **PAF70-thiourea**. **PAF70-thiourea** could catalyze NBS-mediated oxidation of alcohols and showed higher catalytic activity than its homogeneous counterpart. More importantly, **PAF70-thiourea** demonstrated complete recyclability, that is, it could undergo at least 36 cycles without any activity loss in the current catalysis system. In addition, the size selectivity of our catalysis system further confirmed the existence of the narrowly distributed mesopores in **PAF70-NH₂**. This study fully demonstrates the advantages of PAF materials and presents an enticing prospect of using mesoporous PAFs as ultrastable platform for immobilizing organocatalysts usually with relatively large sizes. The work using **PAF70-NH₂** for additional applications such as immobilization of organometallic catalysts and molecular switches is ongoing. It is expected that our study will further promote the development of mesoporous PAF materials and their application in catalysis and other fields.

This work was supported by National Basic Research Program of China (973 Program, grant no. 2014CB931804) and National Natural Science Foundation of China (NSFC Project, grant nos. 21302061 and 21531003).

Conflicts of interest

There are no conflicts to declare.

Notes and references

- X. Zou, H. Ren and G. Zhu, *Chem. Commun.*, 2013, **49**, 3925-3936.
- Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012-8031.
- S. Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548-568.
- Q. Sun, Z. Dai, X. Meng and F.-S. Xiao, *Chem. Soc. Rev.*, 2015, **44**, 6018-6034.

- Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng and F. S. Xiao, *J. Am. Chem. Soc.*, 2015, **137**, 5204-5209.
- Q. Sun, B. Aguila, G. Verma, X. Liu, Z. Dai, F. Deng, X. Meng, F.-S. Xiao and S. Ma, *Chem*, 2016, **1**, 628-639.
- S. Das, P. Heasman, T. Ben and S. Qiu, *Chem. Rev.*, 2017, **117**, 1515-1563.
- W. Zhang, B. Aguila and S. Ma, *J. Mater. Chem. A*, 2017, **5**, 8795-8824.
- T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **48**, 9457-9460.
- C. Pei, T. Ben and S. Qiu, *Mater. Horiz.*, 2015, **2**, 11-21.
- S. Demir, N. K. Brune, J. F. Van Humbeck, J. A. Mason, T. V. Plakhova, S. Wang, G. Tian, S. G. Minasian, T. Tyliczszak, T. Yaita, T. Kobayashi, S. N. Kalmykov, H. Shiwaku, D. K. Shuh and J. R. Long, *ACS Cent. Sci.*, 2016, **2**, 253-265.
- K. Konstas, J. W. Taylor, A. W. Thornton, C. M. Doherty, W. X. Lim, T. J. Bastow, D. F. Kennedy, C. D. Wood, B. J. Cox, J. M. Hill, A. J. Hill and M. R. Hill, *Angew. Chem. Int. Ed.*, 2012, **51**, 6639-6642.
- B. Li, Y. Zhang, R. Krishna, K. Yao, Y. Han, Z. Wu, D. Ma, Z. Shi, T. Pham, B. Space, J. Liu, P. K. Thallapally, J. Liu, M. Chrzanowski and S. Ma, *J. Am. Chem. Soc.*, 2014, **136**, 8654-8660.
- B. Li, Y. Zhang, D. Ma, Z. Shi and S. Ma, *Nat Commun*, 2014, **5**, 5537.
- C. H. Lau, K. Konstas, C. M. Doherty, S. Kanehashi, B. Ozcelik, S. E. Kentish, A. J. Hill and M. R. Hill, *Chem. Mater.*, 2015, **27**, 4756-4762.
- Z. Yan, Y. Yuan, Y. Tian, D. Zhang and G. Zhu, *Angew. Chem. Int. Ed.*, 2015, **54**, 12733-12737.
- B. Li, Y. Zhang, D. Ma, Z. Xing, T. Ma, Z. Shi, X. Ji and S. Ma, *Chem. Sci.*, 2016, **7**, 2138-2144.
- H. Zhao, Z. Jin, H. Su, J. Zhang, X. Yao, H. Zhao and G. Zhu, *Chem. Commun.*, 2013, **49**, 2780-2782.
- C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill and M. R. Hill, *Angew. Chem. Int. Ed.*, 2015, **54**, 2669-2673.
- C. Gu, N. Huang, J. Gao, F. Xu, Y. Xu and D. Jiang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4850-4855.
- N. Sang, C. Zhan and D. Cao, *J. Mater. Chem. A*, 2015, **3**, 92-96.
- E. Merino, E. Verde-Sesto, E. M. Maya, A. Corma, M. Iglesias and F. Sánchez, *Appl. Catal. A: Gen.*, 2014, **469**, 206-212.
- Y. Zhang, B. Li and S. Ma, *Chem. Commun.*, 2014, **50**, 8507-8510.
- A. Maximov, A. Zolotukhina, L. Kulikov, Y. Kardasheva and E. Karakhanov, *Reac. Kinet. Mech. Cat.*, 2016, **117**, 729-743.
- E. Rangel-Rangel, E. Verde-Sesto, A. M. Rasero-Almansa, M. Iglesias and F. Sánchez, *Catal. Sci. Technol.*, 2016, **6**, 6037-6045.
- E. Verde-Sesto, E. Merino, E. Rangel-Rangel, A. Corma, M. Iglesias and F. Sánchez, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1078-1084.
- M. Rose, N. Klein, W. Böhlmann, B. Böhringer, S. Fichtner and S. Kaskel, *Soft Matter*, 2010, **6**, 3918.
- Y. Yuan, F. X. Sun, H. Ren, X. F. Jing, W. Wang, H. P. Ma, H. J. Zhao and G. S. Zhu, *J. Mater. Chem.*, 2011, **21**, 13498-13502.
- H. J. Jeon, J. H. Choi, Y. Lee, K. M. Choi, J. H. Park and J. K. Kang, *Adv. Energy Mater.*, 2012, **2**, 225-228.
- C. G. Stuckwisch, G. G. Hammer and N. F. Blau, *J. Org. Chem.*, 1957, **22**, 1678-1680.
- J.-C. Fan, Z.-C. Shang, J. Liang, X.-H. Liu and Y. Liu, *J. Phys. Org. Chem.*, 2008, **21**, 945-953.
- C. B. Tripathi and S. Mukherjee, *J. Org. Chem.*, 2012, **77**, 1592-1598.
- Y. Luan, N. Zheng, Y. Qi, J. Tang and G. Wang, *Catal. Sci. Technol.*, 2014, **4**, 925-929.

Journal Name

COMMUNICATION

Published on 16 January 2018. Downloaded by University of Reading on 16/01/2018 15:38:55.

ChemComm Accepted Manuscript