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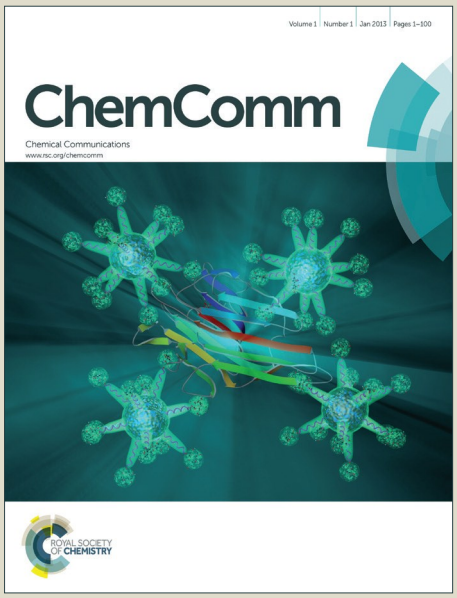




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View Article Online
DOI: 10.1039/C6CC06372A


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Communication



# Use of Steric Encumbrance to Develop Conjugated Nanoporous Polymers for Metal-free Catalytic Hydrogenation

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

DOI: 10.1039/x0xx00000x

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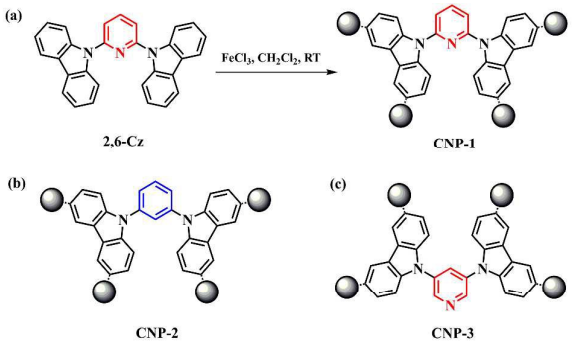
The design and synthesis of metal-free heterogeneous catalysts for efficient hydrogenation remains a great challenge. Here we report a novel approach to create conjugated nanoporous polymers with efficient hydrogenation activities toward unsaturated ketones by leveraging the innate steric encumbrance. The steric bulk of the framework as well as the local sterics of the Lewis basic sites within the polymeric skeleton result in the generation of the putative catalyst. This approach Opens up new possibilities for the development of innovative metal-free heterogeneous catalysts.

The use of advanced nanoporous materials for heterogeneous catalysis, driven by their facile recyclability and excellent chemical tunability, has inspired extensive development of novel nanoporous solids with readily accessible and highly designable active sites.[1] Conjugated nanoporous polymers (**CNPs**), formed by linking multidentate organic building blocks through covalent bonds, have recently come into the limelight as new versatile platforms for application in heterogeneous catalysis, due to the extent to which they can be synthetically tuned to enable molecular design of catalytic sites and access to diverse nano-pore regimes. Despite the large number of **CNPs** that have been studied in the context of heterogeneous catalysis,[2] the use of **CNPs** that enable metal-free hydrogenation of unsaturated substrates, like ketones, is rarely reported. Catalytic hydrogenation of unsaturated substrates is one of most fundamental transformations in chemistry and plays a crucial role in the chemical industry.[3] Conventional hydrogenation processes mediated by using metal-based catalysts also result in increased production costs and significant environmental pollution.[4] Herein, we report a novel approach to generating metal-free **CNP**-based catalysts by designing appropriately encumbered microenvironments capable of forming frustrated Lewis pairs (FLPs) within the supporting polymeric architecture. When loaded with an appropriate Lewis acid, these heterogeneous systems are prevented from forming traditional Lewis adducts due to the inherent framework structure, rather than through installation of bulky substituents surrounding the Lewis base, yet can cooperatively activate $H_2$ and facilitate the hydrogenation of ketones.




**Scheme 1.** One-pot synthesis route (a) and proposed frameworks (b, c) of **CNPs.**

We designed and synthesized a model **CNP-1** by a one-step $FeCl_3$-catalyzed oxidative reaction of 2,6-carbazole-substituted pyridine-based building block (**2,6-Cz**, **Scheme 1**). Carbazole serves as the substituted moiety for the reason that it is a highly reactive scaffold for the construction of porous rigid frameworks.[5] The persistence of Lewis-basic pyridine sites in the final framework material was verified by the solid state $^{13}C$ cross-polarization magic-angle spinning (CP/MAS) NMR (Figure S1). The peaks at 153 and 140 ppm arise from the aromatic carbons in pyridine ring, as has been determined previously.[6] Nitrogen adsorption-desorption isotherms exhibit a Type I adsorption profile (Figure S2), and the corresponding Brunauer-Emmett-Teller (BET) surface area was determined to be 1368 $m^2 g^{-1}$. To form the desired FLP microenvironment, we

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Electronic Supplementary Information (ESI) available: Experimental section, Fig. S1-S9 and Table S1-S2. See DOI: 10.1039/x0xx00000x

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introduced a typical bulky Lewis acid, $B(C_6F_5)_3$, into the **CNP** scaffold through a facile wet impregnation technique (Details are provided in the supporting information). Powder x-ray diffraction (PXRD) patterns (Figure S3 and S4) reveal no residual characteristic peaks of $B(C_6F_5)_3$, indicating the molecular Lewis acid is highly dispersed within the hybrid material (**CNP-1/B**). A concomitant decrease in surface area was also observed for **CNP-1/B**, exhibiting negligible porosities which suggests extensive incorporation of sterically hindered Lewis acidic sites.

Our initial hydrogenation studies focused on the reduction of acetophenone (AP), as we sought to assess the activity of our **CNP**-based catalyst as well investigate the effects of the intrinsic steric hindrance on hydrogenation. **CNP-1/B** (0.2 mmol B) was combined with AP (2.5 mmol) and hexane (5 mL) in a high pressure hydrogenation vessel. Upon sealing, the reactor was charged to a pressure of 5 bar with $H_2$ and heated at 100 °C for 24 h. The use of hexane eliminates the potential for generating unintentional catalytic sites. Indeed, previous reports have demonstrated that catalytic hydrogenation of AP can be achieved by using $B(C_6F_5)_3$ in ethereal solvents.[7] After 24 h the conversion of AP to ethylbenzene (EB) on **CNP-1/B** reached as high as 36.7 %, almost tripling the 14% for the homogeneous FLP system reported under similar conditions.[7b] We also performed the hydrogenation of AP with the homogeneous 2,6-diphenyl pyridine/$B(C_6F_5)_3$.[8] After 24 h, the conversion of AP only reached 9.5% and the styrene and EB yield were 6.0% and 3.2%, respectively, while control reactions using either **CNP-1** or $B(C_6F_5)_3$ displayed no activity. Although inductively coupled plasma optical emission spectroscopy revealed 0.02 wt% of **CNP-1** was residual Fe from the framework synthesis, the absence of any appreciable catalyst activity in the aforementioned control experiment reveals the Fe is functionally innocent in the FLP-system.

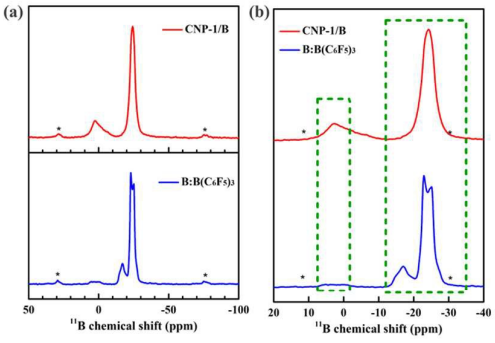


**Figure 1.** Solid-state $^{11}$BNMR of $B(C_6F_5)_3$ and **CNP-1/B**. (*:Spinning sideband)

In an effort to confirm the catalytic sites of **CNP-1/B**, we prepared an analogous material, **CNP-2,** where the pyridine strut was replaced by a benzylic group (**Scheme 1**). Despite loading with $B(C_6F_5)_3$ identically to the method described above, no catalytic activity was observed for **CNP-2/B**. From this we conclude formation of the active **CNP-1/B** catalyst requires inclusion of the pyridyl functionality inside the porous framework. We propose this Lewis basic site may act cooperatively with $B(C_6F_5)_3$ to form a favourable FLP microenvironment, capable of activating $H_2$ and inducing catalytic hydrogenation of AP.[9] To confirm this hypothesis, we performed solid state $^{11}$B NMR on the **CNP-1/B** catalyst and $B(C_6F_5)_3$. Different $^{11}$B quadrupolar lineshapes and chemical shifts were observed for these two samples (see **Figure 1**), similar to what has been shown in other $^{11}$B NMR work on borane-amine Lewis pairs.[10] These data may support the interaction between **CNP-1** and $B(C_6F_5)_3$ in the **CNP-1/B** system.

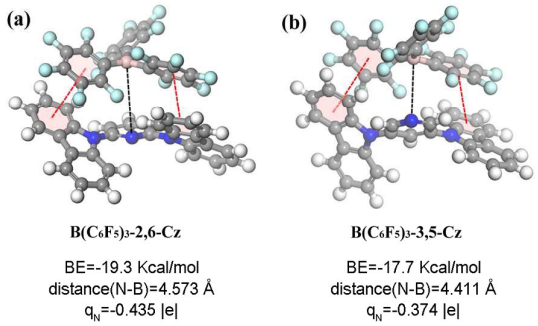


**Figure 2.** The complexes structures of **$B(C_6F_5)_3$-2,6-Cz** (a) and **$B(C_6F_5)_3$-3,5-Cz** (b). We mark π-π stacking with red dotted line. Color code: H, white; C, grey; N, blue; B, brown; F, cyan.

To obtain a better understanding regarding the influence of framework sterics on hydrogenation performance, we further prepared **CNP-3** ($S_{BET}$ = 1538 $m^2$ $g^{-1}$) from 3,5-carbazole-substituted pyridine (**3,5-Cz, Scheme 1**) and tested it for AP hydrogenation. Despite a lower conversion of AP to EB (17.2%) with **CNP-3/B**, it was nevertheless superior to the activity of the analogous homogeneous system.[7b] We then performed density functional theory (DFT) calculations to model the interaction between carbazolic-substituted pyridines (**2,6-Cz** and **3,5-Cz**) and $B(C_6F_5)_3$, with results displayed in **Figure 2**, to further investigate the effects of sterics on the hydrogenation activity in **CNP** catalyst systems (calculation details are provided in the supporting information). Our initial expectation had been that the difference in activity was due to the accessibility of the pyridyl nitrogen in **CNP-3**, with carbazole substituents at the 3 and 5 positions oriented to afford unimpeded access to the nitrogen. In contrast, the **CNP-1** is much more encumbered, with the carbazole ligands forming a cleft of 60° with the pyridine located at the vertex. However, in contrast to our previous hypothesis, the calculated structures display association of $B(C_6F_5)_3$ roughly orthogonal to the plane of the pyridyl group, and indicate π-π stacking dominates the non-bonding interaction between carbazolic moieties and $B(C_6F_5)_3$. Inspection of the structures

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displayed in **Figure 2** reveals a significantly greater torsion angle of the carbazole substituents when bound at the 3,5 positions as compared to the 2,6 positions, while the distances between positive boron and negative pyridinic nitrogen atoms are about 4.5 Å for both structures. Finally, the absolute value of the binding energy (|BE|) for **B($C_6F_5$)$_3$-2,6-Cz** is 1.6 kcal/mol higher than that of **B($C_6F_5$)$_3$-3,5-Cz**, implying that **CNP-1** is more favourable for binding B($C_6F_5$)$_3$ than **CNP-3**. Taken cumulatively, these results indicate the catalytic activity of the **CNP** material is correlated with the ability of the carbazole-pyridine strut to achieve optimal interactions with the B($C_6F_5$)$_3$ while experiencing minimal structural distortion. The B-N interaction may dominate the formation of a FLP microenvironment, and while the bond length is similar in both instances, it requires greater structural distortion in the case of the **B($C_6F_5$)$_3$-3,5-Cz**. The non-optimal electronic structure resulting from these distortions would be expected to deleteriously affect catalytic activity, and indeed the atomic charge on nitrogen in **B($C_6F_5$)$_3$-2,6-Cz** (-0.435|e|) is much more negative than that in **B($C_6F_5$)$_3$-3,5-Cz** (-0.374|e|), suggesting a more favourable environment for hydrogenation.[11] Accordingly, both the intrinsic sterically-frustrated framework and the local innate steric hindrance on pyridine sites in **2,6-Cz** play a crucial role in achieving efficient AP hydrogenation on **CNP-1/B**. As such, both need be considered simultaneously when designing new **CNP**-based metal-free catalysts for hydrogenation.

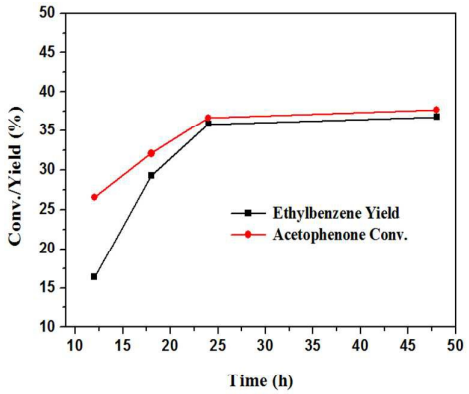
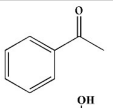
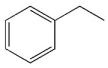
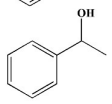
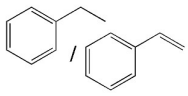
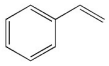
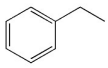
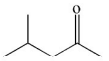
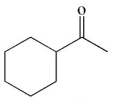
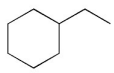
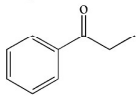
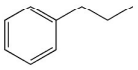
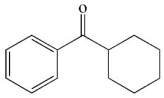
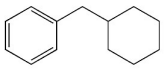
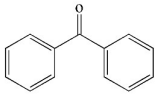
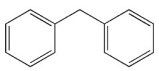



**Figure 3.** Effect of reaction time on the AP conversion to EB catalyzed by **CNP-1/B** at 100 °C.

Inspired by these promising results, we proceeded to carefully investigate the effects of reaction time on AP conversion and ethylbenzene (EB) yield in the presence of **CNP-1/B**. After 12 h, the conversion of AP reached 26.6% while the yield of styrene and EB were 10.2% and 16.4%, respectively, as evidenced by GC-MS (**Figure 3**). Both AP conversion and EB yield increased continuously during the following 12 h, with minimal styrene observed. After 24 h, the final conversion of AP was as high as 36.7%, with the corresponding EB yield of 35.8%. Extending the reaction time to 48 h, AP conversion and EB increased modestly to 37.7% and 36.8%, respectively. We further investigated the hydrogenation of 1-phenylethyl alcohol and styrene with **CNP-1/B**. After 24 h under the same conditions, the hydrogenation of styrene completely yielded EB and 1-phenylethyl alcohol gave EB and styrene in 76.3% and 23.7% yield, respectively. These results are summarized in **Table 1** (Entry 2,3).

We reasoned that the presence of $H_2O$ might have a potent inhibitory effect on this homogeneous hydrogenation system.[7b] To investigate this possibility, stoichiometric $H_2O$ (relative to AP) was added with **CNP-1/B** at the beginning of the reaction. To our delight, an 35.7% conversion of AP to EB obtained after 24 h, clearly demonstrating that **CNP-1/B** is an efficient water-tolerant heterogeneous system for metal-free hydrogenation of AP.

**Table 1.** The catalytic hydrogenation of ketones and other substrates by **CNP-1/B**.[a]

| Entry | Substrate | t / h | Pruduct | Conv. / % | Yield / % |
|---|---|---|---|---|---|
| 1 |  | 24 |  | 36.7 | 35.8 |
| 2 |  | 24 |  | 100 | 76.3 / 23.7 |
| 3 |  | 24 |  | 100 | 100 |
| 4 |  | 72 |  | 47.8 | 46.6 |
| 5 |  | 72 |  | 44.8 | 42.6 |
| 6 |  | 24 |  | 9.6 | 7.3 |
| 7 |  | 24 |  | 29.1 | 27.4 |
| 8 |  | 24 |  | 12.7 | 12.7 |
| 9 |  | 24 |  | 50.7 | 50.7 |

[a] Reaction conditions: 2.5 mmol of substrates, 0.20 g of catalyst (0.2 mmol B), 5 bar $H_2$, T = 100 °C, and in 5 mL of hexane. Conversion and yield estimated by GC-MS.

As recyclability has been considered to be one of most advantageous features of heterogeneous catalysts over to homogeneous catalysts, the reuse of **CNP-1/B** was also assessed. When simply collected by filtration, dried, and added

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to a new reaction, the recovered catalyst displayed a significant drop in activity, achieving 8.6% conversion, while maintaining the yield of EB at 8.2%. This is due to the partial dissolution and subsequent removal of $B(C_6F_5)_3$, supported by the decrease of F within the framework (12.2 vs 2.2 at%), as determined by X-ray photoelectron spectroscopy. Accordingly, restoration of the catalytic activity was facilely achieved through the addition of $B(C_6F_5)_3$ (Table S2).[9] Following this approach, the recycled catalyst can consistently give high conversion of AP (29.4%) and EB yield (28.1%), even after as many as four recycles.

Seeking to probe the generality of our **CNP-1/B** heterogeneous catalyst, we investigated the hydrogenation of a range of other ketone substrates, such as three alkyl ketones (**Table 1**, Entry 4-6) and three benzyl ketone (Entry 7-9). As displayed in Table 1, these reactions generally afford conversion to the desired hydrogenation products, clearly demonstrating the accessibility of bulky substrates within the pore structure of the **CNP-1/B** system and the diversity of this novel heterogeneous FLP catalyst.

## Conclusions

In conclusion, we have developed a novel heterogeneous system for efficient, metal-free, and water-tolerant hydrogenation using the steric encumbrance within conjugated nanoporous polymers. Analysis of structurally related variants demonstrate the intrinsic steric hindrance from the framework is what effects formation of a favourable hydrogenation microenvironment, while computational results indicate the local sterics surrounding the Lewis base also play a significant role in the charge distribution and thus the resulting catalytic activity. As the struts for these assemblies can be rationally designed and synthetically controlled through conventional organic techniques, we anticipate that this innovative new class of materials will enable new areas of catalysis research, and the successful pursuit of more challenging hydrogenation reactions.

## Acknowledgements

The research was supported financially by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US Department of Energy. The NMR experiments were performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL).

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