Chemistry
A European
Journal

Chemistry
Europe
European Chemical
Societies Publishing

Accepted Article

Title: Nanocomposite Hydrogel of Pd@ZIF-8 and Laponite®: Size-Selective Hydrogenation Catalyst at Mild Condition

Authors: Papri Sutar, Vasudeva Rao Bakuru, Pooja Yadav, Subhajit Laha, Suresh Babu Kalidindi, and Tapas Kumar Maji

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Chem. Eur. J.* 10.1002/chem.202004345

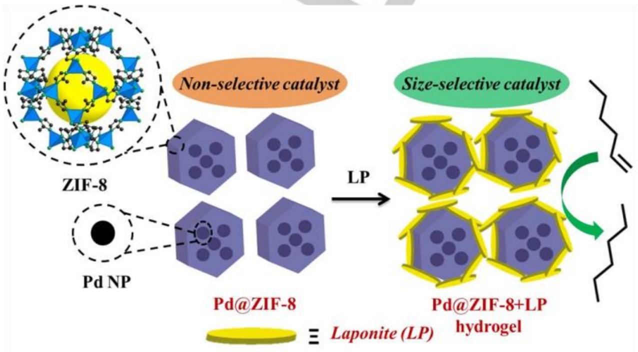
Link to VoR: https://doi.org/10.1002/chem.202004345

WILEY-VCH

Nanocomposite Hydrogel of Pd@ZIF-8 and Laponite®: Size-Selective Hydrogenation Catalyst at Mild Condition

Papri Sutar,[a] † Vasudeva Rao Bakuru, [a,c] † Pooja Yadav,[a] Subhajit Laha,[a] Suresh Babu Kalidindi*[b] and Tapas Kumar Maji*[a]

Abstract: *The composite hydrogel of the nanoscale metal-organic framework (NMOF) and nanoclay emerged as a new soft-material with advanced properties and applications. Here, we report a facile synthesis of a hydrogel nanocomposite by charge-assisted self-assembly of Pd@ZIF-8 nanoparticles with Laponite® nanoclay which coat the surface of Pd@ZIF-8 nanoparticles. Such surface coating significantly enhanced the thermal stability of the ZIF-8 compared to the pristine framework. Further, Pd@ZIF-8+LP hydrogel nanocomposite shows size-selective catalytic hydrogenation of olefins compared to bare Pd@ZIF-8 nanoparticles based on selective diffusion of the substrate.*



Scheme1. Schematic representation showing self-assembly of Pd@ZIF-8 and Laponite® to form Pd@ZIF-8+LP hydrogel nanocomposite that exhibits selective hydrogenation catalysis.

Metal-organic framework (MOF) based nanocomposites are the new class of hybrid materials that have attracted increasing research attention due to their synthetic diversities, unique functionalities, and architectures.[1] These nanocomposites usually consist of two integrated components; a nanoscale MOF (NMOF) and another one or more active ingredients such as graphene oxide,[2a-b] porous silica,[2c-d] organic polymers,[2e] inorganic clay,[2f-g,] and boron nitride[2h]. Such integration not only mitigates the shortcoming of the NMOF but also results in advanced properties that are notably different from the individual components. Therefore, MOF nanocomposites are widely explored as advanced materials that show promising applications in gas storage/separation,[2f-g] heterogeneous catalysis,[3a-e] drug delivery[3f-h] and sensing[3i-j]. Among different MOF nanocomposite reported to date, fabrication of 'soft' nanocomposite hydrogel from the supramolecular self-assembly of crystalline NMOF and another active component is rare. Recently, our group has reported an easy room-temperature synthesis of a nanocomposite hydrogel (ZIF-8+LP) by the charge-assisted self-assembly of ZIF-8 (zeolitic imidazolate framework) nanoparticles (ZIF-8 NPs) having a positive surface charge with organosilicate nanoclay, Laponite® (LP, a smectite clay, commercially available trademark product of BYK additives Ltd.) having negatively charged faces.[4] The surface coated of ZIF-8+LP nanoparticles showed a pH-controlled release of the encapsulated drug molecule. In general, MOFs are structurally fragile to high-temperature treatment compared to inorganic counterparts like zeolites, which limits their industrial application in heterogeneous catalysis. In this regard, we envisage that the surface coating of ZIF-8 with hard LP clay would increase the thermal stability of the hydrogel nanocomposite and provide an opportunity to study for size-selective heterogeneous catalysis using metal nanoparticles (MNPs) encapsulated ZIF-8.

Encapsulation of pre-synthesized MNPs in MOFs have been the subject of considerable research for the past few years because of their better efficiency in heterogeneous catalysis than free MNPs.[5] Owing to the high surface energy; free MNPs show fast aggregation that not only affects their intriguing properties but also hampers long-term storage, processing, and applications.[6,7] In this regard, Huo *et al*. described a strategy for controlled encapsulation of various polyvinylpyrrolidone (PVP)-modified Pt NPs within ZIF-8.[8] The Pt/ZIF-8 composite catalyzed organic reactions (hydrogenation and oxidation, etc.,) driven by the supported MNPs.[9] However, such MNPs/MOF composites could lack in catalytic selectivity due to the disintegration of MOF structure or change of stability of MNPs during the reaction at harsh conditions. The depletion of active centers in such composite system could inhibit their practical applications.[9i, 10] In this context, Jiang *et al.,* reported that surface hydrophobization of Pd/UiO-66 composite by a thin coating of polydimethylsiloxane (PDMS), improved catalytic selectivity towards hydrophobic reactants, as it facilitates the enrichment of hydrophobic substrates around the catalytic site.[11] However, the coating of PDMS on Pd/UiO-66 was carried out by a tedious chemical vapor evaporation technique. We envisioned that supramolecular self-assembly of LP nanoclay with Pd@ZIF-8 composite could be a facile and easy way to coat the surface of Pd@ZIF-8 through charge assisted assembly which could also facilitate the size-selective catalysis using hydrogel nanocomposite. In this communication, we report the synthesis and characterization of Pd@ZIF-8+LP nanocomposite hydrogel. Hydrogelation results uniform coating of LP onto the Pd@ZIF-8

---

[a] Dr. Papri Sutar, Dr. Vasudeva Rao Bakuru, Pooja Yadav, Subhajit Laha, and Prof. Dr. T. K. Maji
Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore -560 064, India.
E-mail: tmaji@jncasr.ac.in; http://www.jncasr.ac.in/tmaji
[b] Dr. Suresh Babu Kalidindi,
Inorganic and Analytical Chemistry Department, School of Chemistry, Andhra University, Visakhapatnam, India-530003.
E-mail: ksureshu@gmail.com
[c] Dr. Vasudeva Rao Bakuru,
Materials Science Division, Poornaprajna Institute of Scientific Research, Devanahalli, Bangalore Rural-562164, India. Manipal Academy of Higher Education, Manipal, 576 104, India

† These authors contributed equally.
Supporting information for this article is given via a link at the end of the document.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

NPs that results significantly high thermal stability and introduced selective hydrogenation for linear alkenes by controlled diffusion.

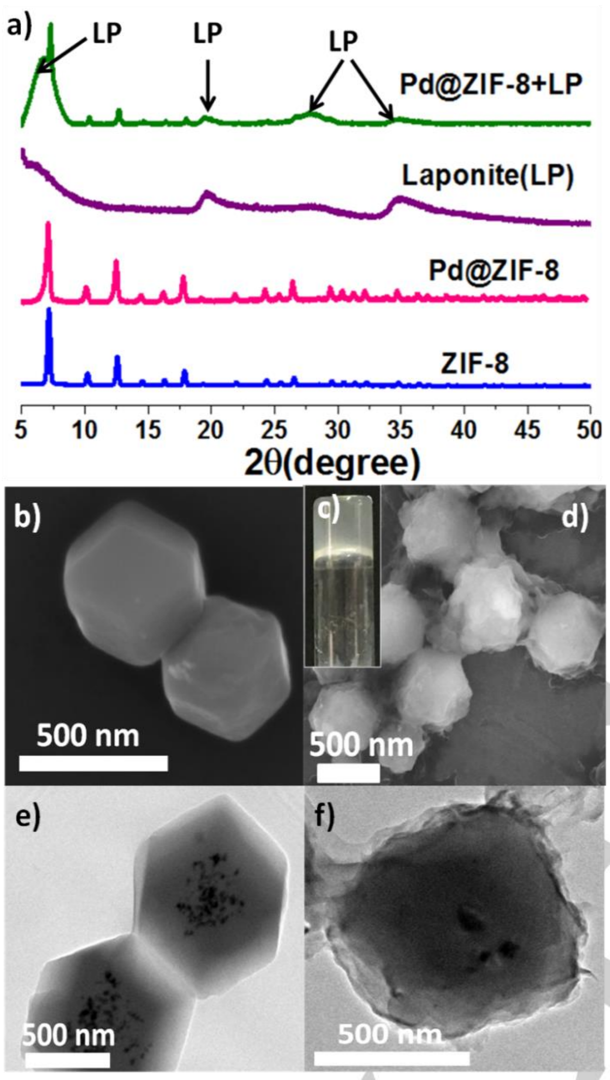


Figure 1. a) PXRD pattern of ZIF-8 (blue), Pd@ZIF-8 (pink), Laponite$^{®}$ (solid purple) and **Pd@ZIF-8+LP** (green), b) FESEM image of Pd@ZIF-8 showing formation of hexagonal particles, c) Picture of **Pd@ZIF-8+LP** hydrogel, d) FESEM image of **Pd@ZIF-8+LP** xerogel showing the wrapping of Laponite$^{®}$ over the hexagonal particles, e) High resolution TEM images of Pd@ZIF-8 NPs showing the encapsulated Pd NPs, and f) High resolution TEM image of **Pd@ZIF-8+LP** xerogel showing the encapsulated Pd NPs.

alkenes by controlled diffusion. The core-shell Pd@ZIF-8 nanoparticles were synthesized by modifying a previously reported procedure[4] (Supporting information) and characterized by powder X-ray diffraction pattern (PXRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analysis as shown Figure 1. The PXRD of Pd@ZIF-8 nanocomposite shows pattern to similar ZIF-8 NPs, suggesting structural integrity of ZIF-8 after incorporation of Pd NPs (Fig. 1a). The FESEM images of Pd@ZIF-8 NPs show the formation of mono-dispersed hexagonal nanoparticles with diameter in the range of 300-600 nm, similar to ZIF-8 NPs (Fig. 1b and Fig S3). The high-resolution TEM images of Pd@ZIF-8 confirm the formation of hexagonal core-shell nanoparticles with the Pd NPs well encapsulated by the ZIF-8 shell (Fig. 1e and Fig. S4). The N$_2$ adsorption isotherm at 77 K of desolvated Pd@ZIF-8 reveals lower N$_2$ uptake compared to pristine ZIF-8 NPs, and BET surface areas are determined to be 1384 and 1152 m^2/g for ZIF-8 and Pd@ZIF-8, respectively, and the pore-size distribution curves suggest that both materials in microporous nature (Fig. S5). Such a small decrease in surface area in Pd@ZIF-8 occurs due to mass occupation by nonporous Pd NPs. Energy-dispersive X-ray analysis (EDXA) of Pd@ZIF-8 indicates the presence of palladium in Pd@ZIF-8 NPs (Fig. S6). The palladium content in Pd@ZIF-8 NPs is determined to be 1.8 wt% by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. Zeta potential analysis of Pd@ZIF-8 NPs (a ζ potential of +55 mV) indicates the surface positive charge, resulting from the unsaturated Zn^{2+} sites at surfaces of Pd@ZIF-8 NPs (Fig. S7). Next, we have studied the self-assembly of Pd@ZIF-8 NPs with Laponite$^{®}$ (LP) nanoclay, similar to our previous report.[4] LP is well-known to have layered-platelet nanostructure with negatively charged faces. We envisioned that charge-assisted self-assembly of Pd@ZIF-8 NPs and LP could result in the composite hydrogel. Gelation experiments were performed in a water/MeOH mixture using various ratios of Pd@ZIF-8 NPs and LP. The formation of stable hydrogel (Pd@ZIF-8+LP) is realized when the dispersion of Pd@ZIF-8 (8 mg in 600 µl MeOH) was added into the aqueous solution of LP (10 mg in 1 ml water), and the homogeneous mixture (formed after sonication) was kept undisturbed at room temperature for 2-3 h. Pd@ZIF-8+LP hydrogel nanocomposite is transparent and remains stable upon inversion (Fig. 1c). The wt% of Pd@ZIF-8 and LP in Pd@ZIF-8+LP hydrogel is calculated to be 44.4% and 55.6%, respectively. PXRD analysis of Pd@ZIF-8+LP xerogel shows a pattern similar to ZIF-8 and Pd@ZIF-8, indicating the stability of Pd@ZIF-8 after hydrogel formation (Fig. 1a). The peaks corresponding to LP are also observed. To get insight into the morphology of the nanocomposite hydrogel, FESEM and TEM images were recorded. The FESEM images of Pd@ZIF-8+LP xerogel shows the formation of an interconnected network where the Pd@ZIF-8 particles are wrapped with layered LP clay matrix (Fig. 1d and Fig. S8). The EDX analysis of Pd@ZIF-8+LP xerogel indicates the presence of Pd along with C,

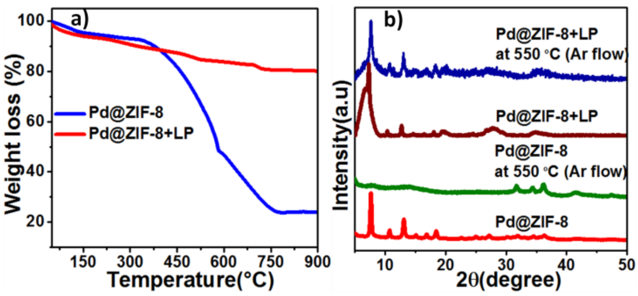


Figure 2. a) TGA of **Pd@ZIF-8** (blue) and **Pd@ZIF-8+LP** xerogel (red), b) PXRD of **Pd@ZIF-8** (red) and **Pd@ZIF-8+LP** xerogel (maroon) and their calcined products. Conditions: Calcinated at 550 ˚C under Ar for 1h.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

N, O, Li, Na, Mg and Zn (Fig. S9). The ICP-AES analysis of Pd@ZIF-8+LP confirms 0.85 wt% Pd content in the xerogel. TEM images of Pd@ZIF-8+LP xerogel clearly show that the hexagonal Pd@ZIF-8 particles are coated with LP clay layers which are mainly found at the edges of Pd@ZIF-8 NPs. The high-resolution TEM images reveal that Pd NPs are well-encapsulated by ZIF-8 and not leached out in Pd@ZIF-8+LP xerogel (Fig. 1f and Fig. S10). The unsaturated Zn^{2+} sites present at the surface of Pd@ZIF-8 interact electrostatically with the negative faces of LP and result in such wrapped nanostructures. The Pd@ZIF-8 shows thermal stability up to 420 °C as evident from thermogravimetric analysis (TGA) (Fig. 2a).[12] To our surprise Pd@ZIF-8+LP xerogel did not show any major weight loss step in TGA even above 550 °C that confirms our conjecture of LP coating would increase thermal stability. However, we observed a gradual weight loss of about 10 % till 550 °C, which can be attributed to dehydration of the clay. To further confirm the thermal stability, we annealed Pd@ZIF-8, Pd@ZIF-8+LP materials at 550 °C under Ar atmosphere for 1 h and recorded PXRD patterns (Fig. 2b). After annealing, Pd@ZIF-8 turns black and the PXRD pattern showed peaks corresponding to ZnO, indicating the decomposition of the ZIF-8 structure. However, under the same condition, Pd@ZIF-8+LP remains stable as evident from the PXRD pattern, showing peaks corresponding to ZIF-8 and LP. These observations highlight the important role of LP in enhancing the thermal stability (550 ˚C) of Pd@ZIF-8+LP and such observation is unprecedented in MOF chemistry. The N_2 adsorption isotherm at 77 K of Pd@ZIF-8+LP xerogel shows 190 m^2/g surface area which is less compared to Pd@ZIF-8. The low uptake of N_2 is mainly due to the mass occupation by nonporous LP clay (Fig. S5). Also, the pore-size distribution as calculated by NLDFT method, revealed that the material has a microporous nature with pore-size centered at 1.01 and 0.59 nm.

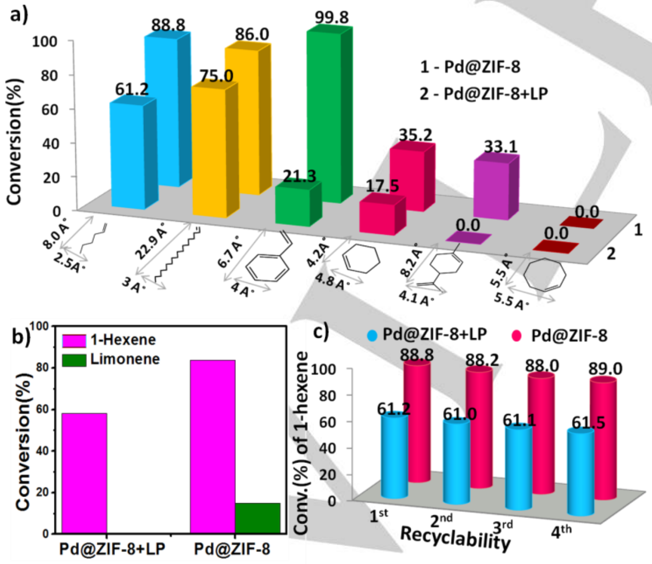


Figure 3. a) Hydrogenation of different substrates over **Pd@ZIF-8** and **Pd@ZIF-8+LP** catalysts, b) Hydrogenation of mixed 1-hexene and limonene substrates catalyzed by **Pd@ZIF-8** and **Pd@ZIF-8+LP** catalysts, and c) Recyclability test in the hydrogenation of 1-hexene over **Pd@ZIF-8** and **Pd@ZIF-8+LP** catalysts.

The presence of Pd nanoparticles inside a matrix of ZIF-8 allows sieving of reactant molecules based on their molecular sizes for hydrogenation of alkenes.[7k, 8] In Pd@ZIF-8+LP xerogel, the presence additional layer of LP over Pd@ZIF-8 could offer further disparity in the diffusion of reactant molecules leading to fine sieving of reactants. To explore this, both Pd@ZIF-8 and Pd@ZIF-8+LP materials were evaluated for the hydrogenation of a wide variety of alkenes with different molecular sizes. All the reactions were carried out under 1 bar H_2 at 50 °C over 0.21 mol % (Pd content) catalyst for 1h. As evident from Figure 3a, the presence of LP offered an additional sieving effect; the conversions are low over Pd@ZIF-8+LP compared to Pd@ZIF-8 due to longer diffusion (slow rate) substrate pathways offered by the catalyst (Table S1). This is very much apparent for the substrates containing cyclic C_6 rings in their structure. For a simple linear 1-hexene (2.5 Å X 8.0 $Å^2$) Pd@ZIF-8 and Pd@ZIF-8+LP catalysts showed a conversion of 88.8 % and 61.2 %, respectively(Fig. S12). On the other hand, for styrene (4.0 Å X 6.7 $Å^2$), the catalysts showed conversions of 99.8% and 21.3%, respectively. In the case of 1-limonene (8.2 Å X 4.1 $Å^2$), the Pd@ZIF-8+LP catalyst did not show any conversion, whereas Pd@ZIF-8 showed a conversion of 33.1 %. This suggests that LP offered a high diffusion barrier to 1-limonene. For, large-size cyclooctene (5.5 Å X 5.5 Å) both Pd@ZIF-8+LP and Pd@ZIF-8 did not show any conversion. Further, mixtures of alkenes were subjected to hydrogenation over both catalysts as shown in Figure 3b. Hydrogenation of 1-hexene and 1-limonene mixture was carried out under the above-mentioned reaction conditions over Pd@ZIF-8+LP and Pd@ZIF-8, separately. As expected, over Pd@ZIF-8+LP, only 1-hexene underwent hydrogenation to hexane with 58.2 % conversion, no detectable conversion of 1-limonene was observed. On the other hand, Pd@ZIF-8 showed 83.7 % 1-hexene and 15.0 % of 1-limonene conversions under the same reaction conditions. Therefore, Pd active sites in Pd@ZIF-8+LP are accessible to only 1-hexene unlike Pd@ZIF-8 wherein Pd sites are accessible to both substrates (though to a different degree). We have also carried out the hydrogenation of 1-hexene and styrene mixture over both catalysts (Fig. S13). Again, reinforcing the excellent sieving effect imposed by LP, the conversions were 63.5 % and 30.2 % over Pd@ZIF-8+LP and 91.2 %, 99.9 % over Pd@ZIF-8, for 1-hexene and styrene, respectively. Overall, these results suggest that Pd@ZIF-8+LP can fine sieve the reactants by bringing additional disparity in diffusion. As this material has characteristic microporous nature (~1 nm), the linear alkene molecules can easily diffuse into the Pd@ZIF-8+LP material. Such reduction in pore size introduces size-selective hydrogenation.

We have also tested the stability of Pd@ZIF-8+LP and Pd@ZIF-8 catalysts by carrying out recyclability tests (Fig. 3c). We did not notice any significant changes in the conversions of 1-hexene over both catalysts after 4 cycles. Moreover, no significant change in the PXRD pattern of the Pd@ZIF-8+LP after 4 catalytic cycles suggesting high stability of the hydrogel composite (Figure S15). Further, hot filtration tests were carried out by isolating the catalysts during the reaction (Fig. S14). After removal of catalyst from the reaction mixtures, no further progress of the reactions was observed. These observations suggest that the hydrogenation reaction was heterogeneous and no leaching of Pd has taken place.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

In summary, we have demonstrated the facile synthesis of a nanocomposite hydrogel (Pd@ZIF-8+LP) by charge-assisted self-assembly of Pd@ZIF-8 NPs with LPs nanoclay. In Pd@ZIF-8+LP, the wrapping of LP layers over Pd@ZIF-8 NPs not only enhances its thermal stability but also introduces fine-tuning on size-selective diffusion of substrates, leading to selectivity in hydrogenation catalysis. The Pd@ZIF-8+LP is quite stable and maintained significant activity up to four cycles, no considerable change in the conversion of 1-hexene was observed. Overall, the demonstrated results suggest that the versatility of the metal@MOF+clay nanocomposite materials for fine-tuning size-selective catalysis and this kind of approach stimulates further research in this direction.

Acknowledgements

PS is thankful to the Council of Scientific and Industrial Research (CSIR). BVR thanks to DST and TRC-JNC/4612 for providing fellowship. SBK thanks DST-inspire for the grant (IFA-12/CH-166). TKM is grateful to the DST (SERB, DST, project no. CRG/2019/005951), Govt. of India, and the JNCASR for financial support.

Keywords: •Metal-Organic Frameworks (MOFs) •Nanocomposite hydrogel • Catalysis • Selective hydrogenation

[1] (a) S. Li, F. Huo, *Nanoscal.* **2015**, *7*, 7482−7501; (b) Q.-L. Zhu, Q. Xu, *Chem. Soc. Rev.*, **2014**, *43,* 5468−5512; (c) I. Ahmed, S. H. Jhung, *Mater. Today*. **2014**, *17*, 136−146; (d) X. Lian, Y. Fang, E. Joseph, Q. Wang, J. Li, S. Banerjee, C. Lollar, X. Wang, H. − C. Zhou, *Chem. Soc. Rev.* **2017**, *46*, 3386−3401.

[2] (a) R. Kumar, K. Jayaramulu, T. K. Maji, C. N. R. Rao, *Chem. Commun.* **2013**, *49*, 4947-4949; (b) L. Yang, B. Tang, P. Wu, *J. Mater. Chem. A*, **2015**, *3*, 15838-15842; (c) L. Chen, J. Zhang, X. Zhou, S. Yang, Q. Zhang, W. Wang, Z. You, C. Peng, C. He, *Acta Biomater*. **2019**, *86*, 406–415; (d) X. Yan, X. Hu, S. Komarneni, *RSC Adv*. **2014**, *4*, 57501-57504; (e) T. Kitao, Y. Zhang, S. Kitagawa, B. Wang, T. Uemura, *Chem. Soc. Rev*. **2017**, *46*, 3108—3 133; (f) A. Chakraborty, A. Achari, M. Eswaramoorthy, T. K. Maji, *Chem. Commun*. **2016**, *52*, 11378-11381; (g) A. Chakraborty, S. Roy, M. Eswaramoorthy, T. K. Maji, *J. Mater. Chem. A*, **2017**, *5*, 8423-8430; (h) P. Wang, H. Li, Q. Gao, P-Z. Li, X. Yao, L. Bai, K. T. Nguyen, R-Q. Zou, Y. Zhao, *J. Mater. Chem. A,* **2014**, *2*, 18731–18735.

[3] (a) H. L. J. Q. Yang, Q. Xu, *Chem. Soc. Rev*. **2017**, *46*, 4774–4808; (b) L. Zhu, X. Q. Liu, H. L. Jiang, L. B. Sun, *Chem. Rev*. **2017**, *117*, 8129–8176; (c) G. Huang, Q. Yang, Q. Xu, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2016**, *55*, 7379; (d) M. Jahan, Q. Bao, K. P. Loh, *J. Am. Chem. Soc.* **2012**, *134*, 6707-6713; (e) S. Aguado, J. Canivet, D. Farrusseng, *Chem. Commun*. **2010**, *46*, 7999-8001; (f) F. Ke, Y. –P. Yuan, L. –G. Qiu, Y. –H. Shen, A. –J. Xie, J. –F. Zhu, X. –Y. Tian, L. –D. Zhang, *J. Mater. Chem*. **2011**, *21*, 3843-3848; (g) H. Li, N. Lv, X. Li, B. Liu, J. Feng, X. Ren, T. Guo, D. Chen, J. F. Stoddart, R. Gref and J. Zhang, *Nanoscale*, **2017**, *9*, 7454-7463; (h) H. –X. Zhao, Q. Zou, S. –K. Sun, C. Yu, X. Zhang, R. –J. Li, Y. –Y. Fu, *Chem. Sci*., **2016**, *7*, 5294-5301; (i) Y. Liu, L. He, Y. Liu, J. Liu, Y. Xiong, J. Zheng and Z. Tang, *Angew. Chemie - Int. Ed*. **2013**, *52*, 3741–3745; (j) S. Kempahanumakkagari, K. Vellingiri, A. Deep, E. E. Kwon, N. Bolan, K.-H. Kim, *Coord. Chem. Rev*. **2018**, *357*, 105-129.

[4] A. Chakraborty, P. Sutar, P. Yadav, M. Eswaramoorthy, T. K. Maji, *Inorg. Chem*. **2018**, *57*, 14480- 14483.

[5] (a) Q. Yang, Q. Xu, H.-L. Jiang, *Chem. Soc. Rev.* **2017**, *46*, 4774-4808; (b) C. Rösler, S. Dissegna, V. L. Rechac, M. Kauer, P. Guo, S. Turner, K. Ollegott, H. Kobayashi, T. Yamamoto, D. Peeters, Y. Wang, S. Matsumura, G. van Tendeloo, H. Kitagawa, M. Muhler, F. X. Llabrés I Xamena, R. A. Fischer, *Chem.Eur. J.* **2017**, *23*, 3583–3594; (c) C. Rösler, R. A. Fischer, *CrystEngComm.* **2015**, *17*, 199–217; (d) V. R. Bakuru, S. B. Kalidindi, *Chem. Eur. J.* **2017**, *23*, 16456; (e) D. Chen, W. Yang, L. Jiao, L. Li, S. H. Yu, H. L. Jiang, *Adv. Mat.* **2020**, *32*, 2000041; (f) L. Li, W. Yang, Q. Yang, Q. Guan, J. Lu, S. H. Yu, H. L. Jiang, *ACS Catal.* **2020**, *10*, 7753-7762; (g) Y. Z. Chen, B. Gu, T. Uchida, J. Liu, X. Liu, B. J. Ye, Q. Xu, H. L. Jiang, *Nat. comm.* **2019**, *10*, 1-10; (h) J.D. Xiao, L. Han, J. Luo, S.H. Yu, H. L. Jiang, *Angew. Chem. Int. Edit.* **2018**, *57*, 1103-1107.

[6] M. Zhao, K. Yuan, Y. Wang, G. Li, J. Guo, L. Gu, W. Hu, H. Zhao, Z. Tang, *Nature*, **2016**, *539*, 76- 80.

[7] (a) M. Meilikhov, K. Yusenko, D. Esken, S. Turner, G. Van Tendeloo, R. A. Fischer, *Eur. J. Inorg. Chem*. **2010**, 3701–3714; (b) V. R. Bakuru, B. Velaga, N. R. Peela, S. B. Kalidindi, *Chem. Eur. J.* **2018**, *24*, 15978–15982; (c) H. Q. Wu, L. Huang, J. Q. Li, A. M. Zheng, Y. Tao, L. X. Yang, W. H. Yin, F. Luo, *Inorg. Chem*. **2018**, *57*, 12444–12447; (d) M. Zhao, K. Deng, L. He, Y. Liu, G. Li, H. Zhao, Z. Tang, *J. Am. Chem. Soc*. **2014**, *136*, 1738−1741; (e) K. M. Choi, K. Na, G. A. Somorjai, O. M. Yaghi, *J. Am. Chem. Soc.* **2015**, *137*, 7810–7816.; (f) Y. Chen, O. Sakata, Y. Nanba, L. S. R. Kumara, A. Yang, C. Song, M. Koyama, G. Li, H. Kobayashi, H. Kitagawa, *Comm. Chem.* **2018**, *1*, 61; (g) P. Hu, J. V. Morabito, C. K. Tsung, *ACS Catal.* **2014**, *4*, 4409–4419; (h) V. R. Bakuru, D. Davis, S. B. Kalidindi, *Dalt. Trans.* **2019**, *48*, 8573-8577; (i) H. Kobayashi, Y. Mitsuka, H. Kitagawa, *Inorg. Chem.* **2016**, *55*, 7301–7310; (j) Y. Jiang, X. Zhang, X. Dai, Q. Sheng, H. Zhuo, J. Yong, Y. Wang, K. Yu, L. Yu, C. Luan, H. Wang, Y. Zhu, X. Duan, P. Che, *Chem. Mater.* **2017**, *29*, 6336–6345; (k) Q. Yang, Q. Xu, S.-H. Yu, H.-L Jiang, *Angew. Chem. Int. Ed.* **2016**, *55*, 3685–3689.

[8] G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, Y. Wang, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp, F. Huo, *Nat. Chem*. 2012, **4**, 310–316.

[9] (a) M. Wan, X. Zhang, M. Li, B. Chen, J. Yin, H. Jin, L. Lin, *small*. **2017**, 1701395; (b) H. Yin, J. Choi, A. C. K. Yip, *Catal. Today.* **2016**, *265*, 203-209;(c) H. L. Jiang, B. Liu, T. Akita, M. Haruta, H. akurai, Q. Xu, *J. Am. Chem. Soc.* **2009**, *131*, 11302–11303; (d) W. Wang, Y. Li, R. Zhang, D. He, H. Liu, S. Liao, *Catal. Comm.* **2011**, *12*, 875–879;(e) B. Xia, N. Cao, H. Dai, J. Su, X. Wu, W. Luo, G. Cheng, *ChemCatChem*., **2014**, *6*, 2549–2552; (f) X. Jia, S. Wang, Y. Fan, *J. Catal.* **2015**, *327*, 54–57; (g) Q. Liu, Z. X. Low, L. Li, A. Razmjou, K. Wang, J. Yao, H. Wang, *J. Mater. Chem. A*. **2013**, *1*, 11563; (h) P. Z. Li, K. Aranishi, Q. Xu, *Chem. Commun.* **2012**, *48*, 3173–3175; (i) Y. Feng, G. Yan, T. Wang, W. Jia, X. Zeng, J. Sperry, Y. Sun, X. Tang, T. Lei, L. Lin, *Green Chem.,* **2019**, *21*, 4319; (j) F. Pang, M. He, J. Ge, *Chem. Eur. J.* **2015**, *21*, 1–10;; (k) T. T. Dang, Y. Zhu, J. S. Ngiam, S. C. Ghosh, A. Chen, A. M. Seayad, *ACS Cat.* **2013**, *3*, 1406-1410; (l) C. J. Stephenson, J. T. Hupp, O. K. Farha, *Inorg. Chem*. **2016**, *55*, 1361–1363.

[10] (a) Q. Yang, F. Yao, Y. Zhong, F. Chen, X. Shu, J. Sun, L. He, B. Wu, K. Hou, D. Wang, X. Li, *Part. Part. Syst. Charact.* **2019**, *1800557*, 1–19; (b) B. Rungtaweevoranit, J. Baek, J. R. Araujo, B. S. Archanjo, K. M. Choi, O. M. Yagh,I G. A. Somorjai, *Nano Lett*. **2016**, *16*, 7645–7649; (c) Z. Li, A. W. Peters, A. E. P. Prats, J. Liu, C. W. Kung, H. Noh, M. R. D. Stefano, N. M. Schweitzer, K. W. Chapman, J. T. Hupp, O. K. Farha, *J. Am. Chem. Soc.* **2017**,*139*, 15251−15258.

[11] G. Huang, Q. Yang, Q. Xu, S. Yu and H. Jiang, *Angew. Chem. Int. Ed*. **2016**, *5*, 7379–7383.

[12] (a) Q. Yang, H.-Yu. Zhang, L. Wang, Y. Zhang, Jiquan Zhao, *ACS Omega*. **201**8, *3*, 4199−4212; (b) Y. Zhu, Y.-M. Wang, P. Liu, Y.-L. Wu, W. Wei, C.-K. Xia, J.-M. Xie, *New J. Chem.* **2015**, *39*, 2669-2674.

Accepted Manuscript

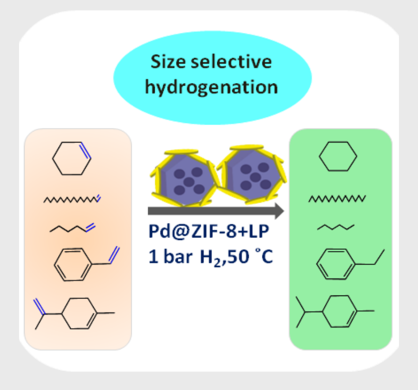
WILEY-VCH

This article is protected by copyright. All rights reserved.

Entry for the Table of Contents

COMMUNICATION

We have demonstrated here a preparation of a hydrogel nanocomposite by charge-assisted self-assembly of Pd@ZIF-8 nanoparticles with Laponite® nanoclay and the resulting Pd@ZIF-8+LP nanocomposite showed efficient and size selective catalytic hydrogenation of olefins.



Papri Sutar,[a] † Vasudeva Rao Bakuru [a,c] †, Pooja Yadav,[a] Subhajit Laha,[a] Suresh Babu Kalidindi[b] and Tapas Kumar Maji*[a]*

Page No. – Page No.

Nanocomposite Hydrogel of Pd@ZIF-8 and Laponite®: Size-Selective Hydrogenation Catalyst at Mild Condition

WILEY-VCH
Accepted Manuscript

This article is protected by copyright. All rights reserved.