JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Enhanced H_2 Uptake in Solvents Confined in Mesoporous Metal–Organic Framework

Stephanie Clauzier,[†] Linh Ngoc Ho,[†] Marc Pera-Titus,[†,‡] Benoit Coasne,[§] and David Farrusseng*,[†]

[†]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS/Université de Lyon-1, 2, Av. A. Einstein, F-69626 Villeurbanne, France

[‡]Eco-efficient Products and Processes Laboratory (E2P2L), UMI 3464 CNRS/Rhodia, 3966 Jin Du Road, Xin Zhuang Industrial Zone, 201108 Shanghai, China

[§]Institut Charles Gerhardt Montpellier (ICGM), UMR 5253 CNRS/ENSCM/Université de Montpellier II, 8 rue de l'Ecole Normale, F-34296 Montpellier, France

Supporting Information

ABSTRACT: Hydrogen uptake at 298 K and 30 bar in hybrid sorbents consisting of *n*-hexane confined in MIL-101 is found to be 22 times larger than in sole *n*-hexane. The enhanced solubility in MIL-101, found to be 3 times larger than in mesoporous silica of similar pore size, highlights the key roles played by surface chemistry and accessible surface area.

Measuring and predicting the solubility of gases in liquids confined in porous solids (triphasic systems) has a high practical impact on a number of industrial processes.[1,2] These include heterogeneous catalytic systems (hydrogenation and oxidation reactions), as well as oil and shale gas extraction.[3] It is acknowledged that gas solubility in solvents, even when confined in macropore solids, follows the classical Henry's law, which establishes a linear relationship between the concentration of the solubilized gas and its pressure above the solvent (provided that the solvent does not chemically react with the gas and that the gas partial pressure is low enough).[4]

However, several groups have reported evidence of a striking increase of gas solubility in liquids confined in porous solids with pore size in the range of nanometers with respect to the values predicted by Henry's law. Luzar and Bratko[5,6] were among the first to predict an increase of gas (O_2, N_2, CO_2, and Ar) solubility in water confined in a hydrophobic environment. Using ^{1}H NMR, Miachon et al.[7] provided the first experimental evidence of enhanced hydrogen, methane, and ethane solubility in CCl_4 and CS_2 confined in mesoporous γ-alumina and silica. Using an adapted microvolumetric technique, H_2 oversolubilization was further demonstrated for a wide series of solvents ($CHCl_3$, *n*-hexane, water, and ethanol) and mesoporous solids (γ-alumina, pore diameter d = 10.9 nm; silica, d = 13.0 nm; MCM-41, d = 3.4 nm; MCM-41 with Si/Al = 1, d = 3.1 nm; SBA-15, d = 6.8 nm; silica aerogel, d = 8.6 nm).[8−10] In these studies, the apparent enhanced solubility was tentatively explained by the high amount of H_2 adsorbed at the nanoconfined gas/liquid interface. More recent studies focused on the enhanced CO_2 solubilities in nanoconfined solvents. Ho et al.[11−13] reported a 6-fold increase of CO_2 solubility in N-methyl-2-pyrrolydone (NMP) confined in MCM-41 (d = 3.2 nm). Molecular simulations carried out on the latter system revealed an underlying packing of solvent molecules where CO_2 is located near the pore surfaces to account for the apparent higher solubility. Finally, Soubeyrand-Lenoir et al.[14] reported recently a 5-fold increase of CO_2 uptake at 0.2 bar in water confined in Fe-MIL100 (d = 2.5−2.9 nm).

Based on measurements on different mesoporous silica and alumina-based materials, we have shown that the pore size is a key parameter in the enhanced solubility phenomena, the smallest mesoporous systems (MCM-41) exhibiting the largest uptake enhancement.[10] In contrast, no such study has been conducted to date on possible enhanced uptake effects with mesoporous MOFs. Such studies will make it possible to unravel the extent to which interfacial phenomena vs pore size affect gas solubility. To this aim, we have selected Cr-MIL101 and MCM-41, which exhibit similar pore size ($d \sim 3$ nm) but different surface chemistry and accessible surface area. The comparison is extended with a large micropore zeolite FAU (d = 1.2 nm) and with a mesoporous silica aerogel (d = 9.4 nm). We report here a dramatic increase of H_2 uptake in *n*-hexane and ethanol confined in Cr-MIL101.

Briefly, Cr-MlL101 was synthesized according to the protocol reported by Férey et al.,[15] affording an apparent BET surface area of 2612 m^2/g and a pore volume of 1.29 cm^3/g. The FAU sample was obtained commercially, with a BET surface area of 530 m^2/g and a pore volume of 0.17 cm^3/g. The silica aerogel and MCM-41 samples were prepared by sol−gel and hydrothermal synthesis, respectively, displaying BET surface areas of 799 and 948 m^2/g and pore volumes of 1.93 and 0.89 cm^3/g. Further details on the synthesis protocols and textural properties of the different materials can be found in the SI (see Table S1).

The H_2 uptake measurements were performed by partially filling the pore volume with the solvent via wet impregnation, to obtain what is referred to as "hybrid sorbents" in this work. The experimental procedure was adapted from one developed previously[8] and described in the SI. The preparation of a 60% *n*-hexane loaded Cr-MIL101 hybrid sorbent (i.e., 60%hybrid) is given. A volume of 0.22 cm^3 of *n*-hexane (140 mg) was impregnated in 0.2806 g of Cr-MIL101, corresponding to 0.36

Received: August 16, 2012
Published: October 8, 2012

cm^3 of the pore volume. The hybrid sorbent was then placed in a high-pressure cell and gently evacuated to remove absorbed air. The H_2 uptake was measured from 1 to 60 bar at 298 K using a PCT Pro volumetric apparatus from Setaram. As a comparison, H_2 adsorption measurements were also carried out on the bare evacuated solids and on the bulk solvents. The H_2 uptake in the triphasic system (gas/liquid/solid) was expressed as the number of moles of H_2 uptake divided by the porous volume of the evacuated solid.[11,12] We checked by weighing the samples that the amount of solvent confined in the porous solid remained constant prior to and after evacuation of air and also after H_2 uptake. The reproducibility of the experiments was confirmed by at least three consecutive measurements (Figure S1).

Figure 1 compares the H_2 uptake at 298 K and 30 bar for *n*-hexane, the different bare solids, and the corresponding 60% hybrids. Results for ethanol can be found in the SI (Figure S2). No significant variation is observed for the H_2 uptake upon *n*-hexane and ethanol confinement in the FAU porosity. In contrast, under mesoporous confinement (i.e., MCM-41, Cr-MIL101, and silica aerogel), the H_2 uptake is larger than that measured for bulk *n*-hexane and ethanol and for the bare solids. When *n*-hexane is confined in Cr-MIL101, the solubility increases by a factor of 22.2 compared to that of the *n*-hexane alone. Such an enhanced solubility effect is much larger than those observed for silica aerogel and MCM-41 (3.1 and 15.9 times larger than the bulk, respectively). Despite the partial filling of the pores by the solvent, the H_2 uptake in the hybrid sorbents is about twice the value of the bare solids (×1.9 for Cr-MIL101, ×3.1 for MCM-41, and ×2 for aerogel). Similar enhanced H_2 uptakes are observed for ethanol (SI). The results show that the greatest H_2 uptake enhancement is achieved with porous solids exhibiting small mesopores. For microporous zeolites ($d < 1.2$ nm) and larger mesoporous systems ($d > 9.4$ nm), very modest enhancements are observed.

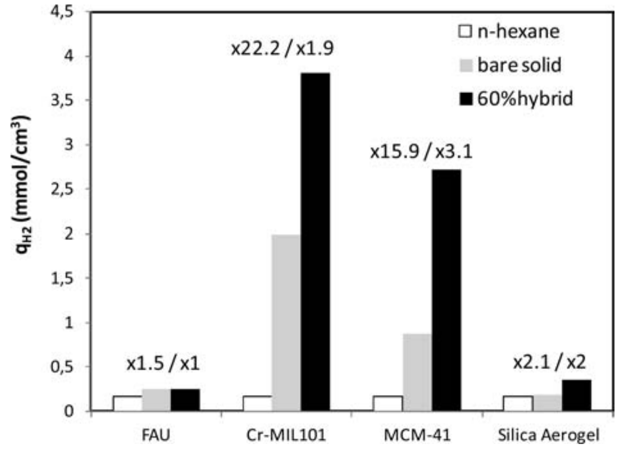

Figure 1. H_2 uptake on *n*-hexane (white), on the bare solids (gray), and on 60% hybrids based on *n*-hexane (black) confined in FAU, Cr-MIL101, MCM-41, and silica aerogel. The H_2 uptake enhancement factors *a*/*b* are given with respect to bulk *n*-hexane and the bare solid, respectively.

Figure 2 shows the H_2 uptake as a function of applied pressure at 298 K for *n*-hexane confined in Cr-MIL101 and in MCM-41. For comparison, results for the bulk solvent and bare Cr-MIL101 and MCM-41 are also shown. Similar trends have been obtained for ethanol (Figure S3). A very large H_2 uptake, which is well above the values attainable with bare Cr-MIL101 and bare or hybrid MCM-41, is observed at high pressure for the MOF-based hybrid sorbent.

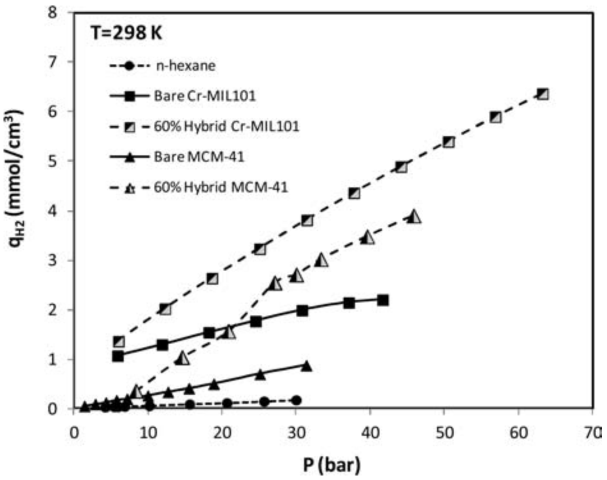

Figure 2. H_2 uptake as a function of applied pressure in bare Cr-MIL101, in bare MCM-41, and in 60% hybrids consisting of *n*-hexane in Cr-MIL101 and MCM-41.

We have shown that exceptionally large H_2 uptakes can be obtained at high pressures using hybrid adsorbents consisting of mesoporous MOF partially filled with solvents. This study clearly shows that the pore size is not the only factor governing the phenomena. In particular, the hybrid sorbent made up of *n*-hexane in Cr-MIL-101, which shows H_2 solubility from ~10 to ~22 times larger than the bulk depending on pressure, is much more efficient than MCM-41 with a similar pore size. The experimental results also demonstrate the important role of the surface chemistry and accessible surface area in the effect of enhanced solubility. For instance, the H_2 uptake enhancement with respect to bulk solvent increases with increasing BET surface area of the solids. However, no simple quantitative correlation can be established for the enhancement factor with respect to the bare solid. We believe that this finding will enable the design of a new type of solid/liquid adsorbents and hydrogenation catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Material preparation, elementary analysis, the reproducibility of the experiments, and the adsorption measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

david.farrusseng@ircelyon.univ-lyon1.fr

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Dr. A. Tuel for providing MCM samples. Thanks to scientific services of IRCELYON. This work is supported by a grant from the Région Rhône-Alpes (Cluster 7/ARC) for a doctoral fellowship.

REFERENCES

(1) Carberry, J. J. *Chemical and Catalytic Reaction Engineering*; Dover Publications, Inc.: New York, 2001.

(2) Xu, X. C.; Song, C. S.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W. *Energy Fuels* **2002**, *16*, 1463−1469.

(3) Beenackers, A. A. C. M. In *Handbook of Heterogeneous Catalysis*; Ertl, G., Knözinger, H., Weitkamp, J., Eds.; Wiley-VCH, Inc.: Weinheim, 1997; pp 1444−1464.

(4) Henry, W. *Philos. Trans. R. Soc. London* **1803**, *93*, 29−274.

(5) Luzar, A.; Bratko, D. *J. Phys. Chem. B* **2005**, *109*, 22545−22552.

(6) Bratko, D.; Luzar, A. *Langmuir* **2008**, *24*, 1247−1253.

(7) Miachon, S.; Syakaev, V. V.; Rakhmatullin, A.; M. Pera-Titus, M.; Caldarelli, S.; Dalmon, J.-A. *ChemPhysChem.* **2008**, *9*, 78−82.

(8) Pera-Titus, M.; El-Chahal, R.; Rakotovao, V.; Miachon, S.; Dalmon, J.-A. *ChemPhysChem* **2009**, *10*, 2082−2089.

(9) Pera-Titus, M.; Miachon, S.; Dalmon, J.-A. *AIChE J.* **2009**, *55*, 434−441.

(10) Rakotovao, V.; Ammar, R.; Miachon, S.; Pera-Titus, M. *Chem. Phys. Lett.* **2010**, *485*, 299−303.

(11) Ho, N. L.; Porcheron, F.; Pellenq, R. J.-M. *Langmuir* **2010**, *26*, 13287−13296.

(12) Ho, N. L.; Perez, P. J.; Porcheron, F.; Pellenq, R. J.-M. *Langmuir* **2011**, *27*, 8187−8197.

(13) Ho, N. L.; Perez, P. J.; Porcheron, F.; Pellenq, R. J.-M. *J. Phys. Chem. C* **2012**, *116*, 3600−3607.

(14) Soubeyrand-Lenoir, E.; Vagner, C.; Yoon, J. W.; Bazin, P.; Ragon, F.; Hwang, Y. K.; Serre, C.; Chang, J.-S.; Llewellyn, P. L. *J. Am. Chem. Soc.* **2012**, *134*, 10174−10181.

(15) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040−2042.