

An [Fe-Fe]-Hydrogenase Mimic Immobilized on MCM-41 for the Photochemical Production of Hydrogen in Pure Water

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A composite proton-reducing catalyst Hy@MCM-41 was created by using a hydrophobic [Fe-Fe]-hydrogenase mimic (Hy) incorporated into the K⁺-exchanged molecular sieve MCM-41. Hy acts as the active site to generate H₂ by reducing H⁺, and MCM-41 provide a large surface area to maintain the dispersion of Hy and to prevent aggregation and precipitation. Hy@MCM-41 was successfully applied to the light-induced hydrogen production in pure water with an iridium compound [Ir(ppy)₂bpy]Cl and triethylamine (TEA) as the photosensitizer and the sacrificial electron donor, respectively, exhibiting good stability and catalytic activity. The present study provides a general strategy for the application of water-insoluble catalysts in pure water by using mesoporous molecular sieves.

Keywords energy conversion, hydrogen, hydrogenase, MCM-41, immobilization, photochemistry

Introduction

The requirement to solve the energy crisis and the climate change has stimulated new approaches to mimic natural photosynthesis in the conversion and storage of solar energy.^[1–3] Of these approaches, the photochemical production of hydrogen from water is at the forefront. In nature, the interconversion of protons and hydrogen is efficiently catalyzed by metalloenzymes known as hydrogenases, which exist in many microorganisms and rely on metals abundant on earth.^[4] Since the biological structures and the functionalities of the active sites of hydrogenases were proposed, chemists have made tremendous efforts to hydrogenase mimics for constructing hydrogen production systems.^[5–9] Water is believed to be an ideal solvent to construct these systems for many reasons including its non-toxic property as well as economic advantages.^[10] However, the proton reduction conducted on the hydrogenase mimics has been limited to organic solvents or a mixture of organic solvents and water because of the inherent insolubility of the majority of hydrogenase mimics in water. Developing new methods capable of realizing the functionality of hydrogenase mimics under aqueous conditions is of great importance for the application of hydrogenase mimics.

Over the past decades, only a handful of water-soluble hydrogenase mimics have been synthesized by introducing hydrophilic groups to the hydrogenase mimics. In 2004, Darensbourg and co-workers developed a water-soluble hydrogenase mimic by using a

substituent ligand PTA (PTA = 1,3,5-triaza-7-phosphaadamantane).^[11] Since then, other water-soluble groups, such as di-*N*-acetylated phosphotriazaadamantane (DAPTA) ligand,^[12] ether chains,^[13] sulfonate,^[14–16] functionalized sugars,^[17] protein,^[18] and peptide^[19,20] were also applied to enhance the water solubility of hydrogenase mimics. However, conventional synthetic processes for water-soluble [Fe-Fe]-hydrogenase mimics are labor-, time-, and energy-intensive. In comparison with the covalent method, the noncovalent methods display advantages such as tunability, simplicity and convenience, for improving the solubility of hydrogenase mimics in water. SDS,^[21] cyclodextrin^[22] and metal-organic framework (MOF)^[23] have been used to realize the application of water-insoluble hydrogenase mimics in water.

The ordered mesoporous molecular sieves display advantages such as tunable pore diameters (2–30 nm), narrow pore size distributions, high surface areas and electrostatic microenvironments, which have been widely used in ion exchange, separation, catalysis, sensor, biological molecular isolation and purification.^[24–35] The mesoporous molecular sieves with suitable size are able to accommodate the hydrogenase mimics, which can further conduct hydrogen production in water. Furthermore, the hydrogenase mimics immobilized into the mesoporous molecular sieves should be easily separated from the production system than from a micelle or a cyclodextrin inclusion complex. Herein, we report a [Fe-Fe]-hydrogenase mimic (Hy), which was incorporated into the ordered mesoporous K⁺-exchanged mo-

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molecular sieve MCM-41 to form an MCM-41-immobilized [Fe-Fe]-hydrogenase mimic (Hy@MCM-41). The studies on the photochemical production of hydrogen by Hy@MCM-41 demonstrate that immobilization into mesoporous molecular sieves is an effective way for application of hydrophobic hydrogenase mimics in pure water.

Experimental

Materials

Reagents were purchased from Acros, Alfa Aesar, or Beijing Chemicals and were used without further purification unless otherwise noted. Mesoporous molecular sieve MCM-41 (mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3 \geq 20$, $\text{BET} \geq 900 \text{ m}^2/\text{g}$, $d = 3.5 \text{ nm}$) was purchased from Xian Feng Nano Company. HPLC-grade hexane was used for the preparation of Hy@MCM-41. Milli-Q deionized water (Millipore) was used in the light-driven hydrogen generation experiments and spectroscopy measurements. Acetonitrile and tetrahydrofuran were dried and distilled under N_2 atmosphere prior to use.

Instrumentation

^1H NMR (400 MHz) spectra were obtained from a Bruker Avance II-400 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer. MS spectra were obtained on MALDI-TOF (matrix assisted laser desorption ionization/time of flight) BI-FLEX III (Bruker Inc.) spectrometer. Absorption spectra were run on a Shimadzu UV-1601PC spectrometer. UV-Vis reflectance spectra were recorded on a Shimadzu UV-VIS-3100 spectrophotometer. ICP analysis was performed on a Varian 710-OES instrument. The analysis of hydrogen production was carried out on a Shimadzu GC-2014 with a TCD detector.

Preparation and characterization of Hy@MCM-41

The K^+ -exchanged molecular sieve MCM-41 (K-MCM-41) was prepared by mixing silica-alumina molecular sieve MCM-41 (5 g) with a potassium oxalate solution (0.25 mol/L, 50 mL) and stirring for 6 h at room temperature (fresh potassium oxalate solution was replaced each 2 h). The resulting white solid was filtered, washed with water, dried and activated at 120°C and 540°C for 3 h, respectively. The following procedure was used to prepare Hy@MCM-41 by incorporating Hy into K-MCM-41. A small amount of K-MCM-41 (150.0 mg) was suspended in the hexane solution of Hy ($4.0 \times 10^{-3} \text{ mol/L}$, 2 mL), which was stirred at ambient temperature overnight. The suspension was then centrifuged and the precipitate was dried at 40°C under vacuum. The amount of Hy immobilized into K-MCM-41 was determined by the absorbance change at 340 nm ($\epsilon = 1.4 \times 10^4 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$) of the 100-fold solution/supernatant dilutions before and after immobilization and the ICP analysis.

Photocatalytic H_2 generation

All experiments of photochemical production of H_2 were performed in a Pyrex reactor with 10 mL sample solution and a magnetic stir. The sample solutions were purged with nitrogen for 30 min prior to irradiation. A 300 W Xe lamp was used as the visible light source with filters cutting off the light below 400 nm and above 800 nm and a set of neutral density filters was used to adjust the irradiation intensity. The amount of H_2 was identified and quantified with a gas chromatograph equipped with a 5 Å molecular sieve column, N_2 carrier gas, and a thermal conductivity detector (TCD) with methane as an internal standard. The response factor of 1.52 for H_2/CH_4 was determined by calibration with known amounts of H_2 and CH_4 under the experimental conditions.

Results and Discussion

Preparation and characterization of Hy@MCM-41

A simple hydrogenase mimic [$\{(\mu\text{-SCH}_2)_2\text{N}(\text{CH}_2\text{-C}_6\text{H}_5)\}\text{Fe}_2(\text{CO})_5\text{P}(\text{Pyr})_3$] (Hy) was synthesized according to the literature.^[36] The details of the synthesis and the characterization of Hy are described in the Supporting Information. The structure of the Hy is depicted in Figure 1, which was characterized by ^1H NMR and IR spectroscopy as well as mass spectrometry (see the Supporting Information).

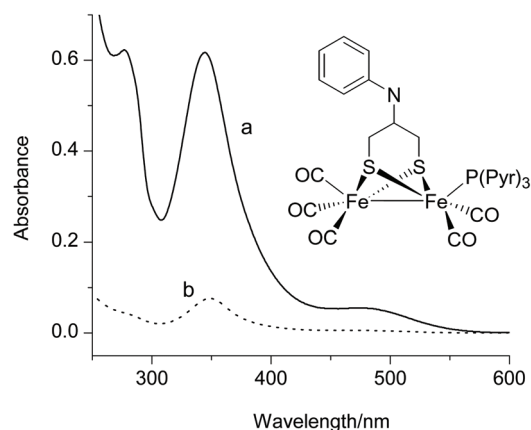


Figure 1 Absorption spectra of the 100-fold dilutions of Hy in hexane (a, $4.0 \times 10^{-5} \text{ mol/L}$) and the supernatant after addition of K-MCM-41 (150.0 mg) to 2 mL Hy solution (b). Inset: Schematic illustration of the structure of Hy.

The K^+ -exchanged MCM-41 (K-MCM-41) was prepared according to a reported method by using potassium oxalate as the K^+ source.^[37] K-MCM-41 was further used to immobilize Hy to give the Hy@MCM-41 composite. The adsorption of Hy into K-MCM-41 was conducted by addition of K-MCM-41 (150.0 mg) to the solution of Hy in hexane (2 mL, $4 \times 10^{-3} \text{ mol/L}$). The quantity of Hy immobilized into K-MCM-41 was $43.0 \mu\text{mol/g}$ by evaluating the absorb-

ance change of the 100-fold Hy-solution/supernatant dilutions before and after immobilization (Figure 1), which is in agreement with the result obtained from the ICP analysis ($44.6 \mu\text{mol/g}$). The loading of Hy into K-MCM-41 makes the color of K-MCM-41 change from white to orange (Figure 2a). The firmness of Hy loaded into K-MCM-41 was examined by stirring the suspension of Hy@MCM-41 in water at room temperature overnight. No leakage of Hy from Hy@MCM-41 was observed by analyzing absorption spectrum of the supernatant, which indicated that Hy was tightly incorporated into K-MCM-41.

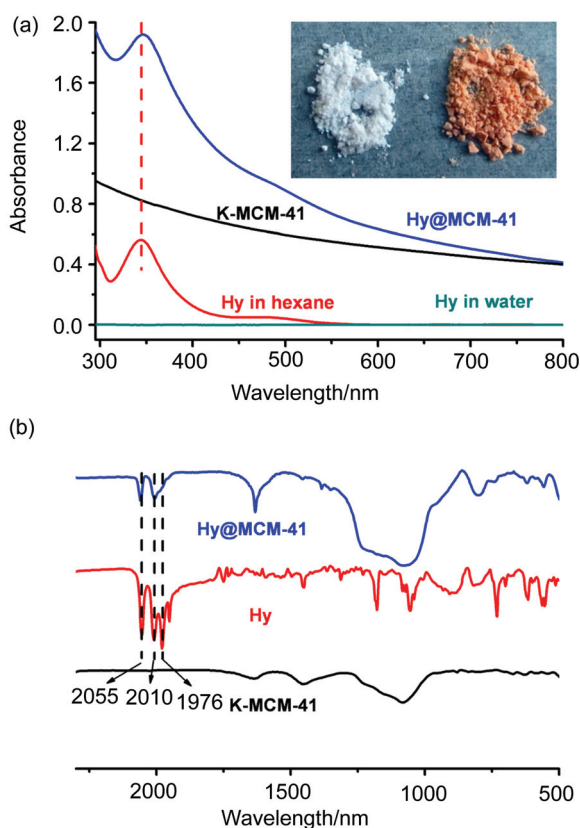


Figure 2 (a) Absorption spectra of the suspensions of Hy@MCM-41 (3.0 mg, loading: $75.2 \mu\text{mol/g}$, blue line) in water, Hy ($4 \times 10^{-5} \text{ mol/L}$, red line) in hexane, K-MCM-41 (3.0 mg, black line) and Hy (3.0 mg, cyan line) in 5 mL water. Inset: photographs of K-MCM-41 (left) and Hy@MCM-41 (right). (b) FTIR spectra of K-MCM-41 (black line), Hy (red line) and Hy@MCM-41 (blue line).

The Hy@MCM-41 was characterized by UV-Vis, DRS-UV-Vis and FTIR spectroscopy. The absorption spectrum of the Hy@MCM-41 suspension in water is similar to the sum of those of Hy and K-MCM-41 with absorption band at 344 nm characteristics of Hy (Figure 2a). The diffuse reflectance spectrum of Hy@MCM-41 also exhibits the absorption band of Hy (see Figure S4 in the Supporting Information). Three prominent bands of the CO stretching vibration at 2055, 2010, and 1976 cm^{-1} attributed to Hy are observed in the FTIR spectra of Hy@MCM-41 (Figure 2b). The characterization re-

sults validate the reality of the immobilization of Hy into K-MCM-41. The FTIR spectrum of Hy@MCM-41 is smoother than that of the Hy, which can be ascribed to the bad light transmission of the K-MCM-41-adulterated KBr tablet.

The adsorption of Ps into K-MCM-41 was further studied by comparing the absorption spectra of the aqueous solution of $\text{Ir}(\text{ppy})_2\text{bpyCl}$ (Ps, $2.5 \times 10^{-4} \text{ mol/L}$) and the supernatant after addition of Hy@MCM-41 (4.5 mg, Hy loading: $43.0 \mu\text{mol/g}$) and K-MCM-41 (4.5 mg) to 10 mL $\text{Ir}(\text{ppy})_2\text{bpyCl}$ solution (Figure S5). Both supernatants show typical absorption characteristics of $\text{Ir}(\text{ppy})_2\text{bpyCl}$, but the absorption intensities are *ca.* 15% lower than the corresponding aqueous solution of $\text{Ir}(\text{ppy})_2\text{bpyCl}$. These indicate that Ps can be partially adsorbed into K-MCM-41. Similar intensity of both supernatants suggests that the adsorption of Hy into K-MCM-41 with loading $43.0 \mu\text{mol/g}$ does not affect further adsorption of Ps.

Application of Hy@MCM-41 to hydrogen production

The catalytic activity of Hy@MCM-41 for light-driven hydrogen production was examined by using $[\text{Ir}(\text{ppy})_2\text{bpy}]\text{Cl}$ and triethylamine (TEA) as the photosensitizer (Ps) and the sacrificial electron donor, respectively (Figure 3). Pure water was used to solubilize or disperse all the components. Irradiation of the Hy@MCM-41 catalytic system with visible light resulted in the production of hydrogen. Control experiments indicated that Ps, Hy and TEA are all essential for production of H_2 , and the absence of any of them led to no detectable photochemical production of H_2 . Moreover, the molecular sieve K-MCM-41 is also essential for the H_2 production in pure water and there is no detectable H_2 production by using an aqueous dispersion of Hy when other conditions are identical. The performance of the photocatalyst system was dramatically affected by the reaction conditions, such as the concentrations of Ps and TEA, and the Hy loading of Hy@MCM-41.

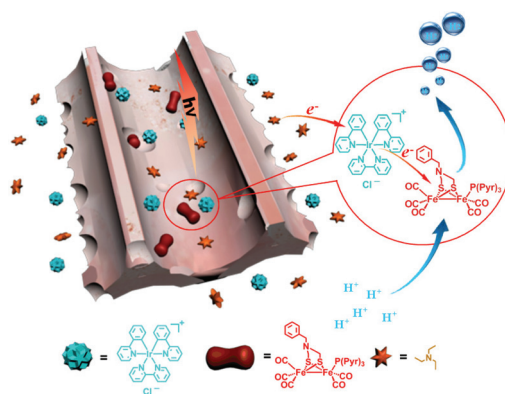


Figure 3 Schematic illustration of the photochemical production of H_2 by Hy@MCM-41.

To optimize the experiment condition, light-induced hydrogen production was conducted by using Hy@MCM-41 with varied loading of Hy in pure water at different concentrations of Ps and TEA upon the visible light irradiation (Figure 4). The influence of the Ps concentration on the photoinduced H_2 production was examined first when all the other conditions were kept identical (Figure 4a). The higher concentration favors the hydrogen production. When the concentration of Ps increases from 0.063 to 0.25 mmol/L, the amount of hydrogen in initial 1 h increases from 6.1 to 64.2 μL . The concentration of TEA also produces an effect on the catalytic performance. The best catalytic activity of the catalytic system was accomplished at the concentration of TEA to be 0.28 mol/L with same amount of Hy@MCM-41 (4.5 mg Hy@MCM-41 with loading of 43.0 $\mu\text{mol/g}$) and same concentration of Ps (0.25 mmol/L) in pure water, giving the turnover number (TON) calculated from the amount of H_2 molecules versus the number of Hy molecules to be 18.3. The less catalytic activity of the catalytic system at higher and

lower concentration of TEA may be rationalized by the decomposition of the photosensitizer and the lower concentration of electron donor, respectively.^[38] The photochemical production of hydrogen by Hy@MCM-41 with different loading was examined in pure water, and the results are shown in Figures 4c and 4d. Keeping the optimal conditions of $[\text{Ps}] = 0.25 \text{ mmol/L}$ and $[\text{TEA}] = 0.28 \text{ mol/L}$, an obvious improvement in photochemical H_2 production was observed when the Hy loading of Hy@MCM-41 was successively increased from 13.5 to 119.5 $\mu\text{mol/g}$. However, the activity of Hy@MCM-41 decreases when the loading is increased. The growth of H_2 evolution in initial 10 min vs. the loading (13.5–119.5 $\mu\text{mol/g}$) shows a parabolic-like trend when all the other conditions are kept identical. The less catalytic activity of the catalytic system at higher Hy loading of Hy@MCM-41 may be attributed to the gradual decomposition of Hy because Hy can absorb light during the illumination.^[5]

In order to figure out the reason for the cease of hydrogen production, parallel experiments were carried

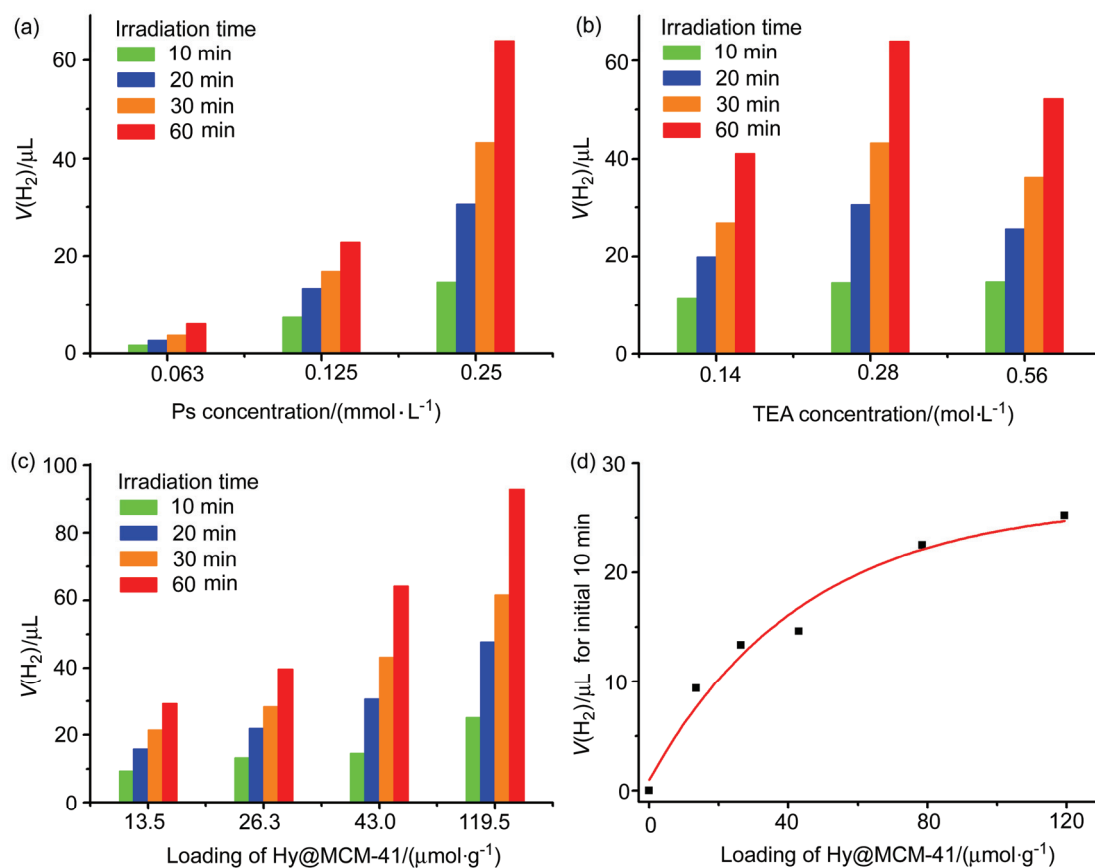


Figure 4 Influence of the concentrations of Ps and TEA, and the Hy loading of Hy@MCM-41 on the photoinduced H_2 evolution. (a) H_2 evolution with various concentrations of Ps in pure water (10 mL). $[\text{Hy@MCM-41}] = 4.5 \text{ mg}$ (loading: 43.0 $\mu\text{mol/g}$), $[\text{TEA}] = 0.28 \text{ mol/L}$. (b) H_2 evolution with various concentrations of TEA in pure water (10 mL). $[\text{Hy@MCM-41}] = 4.5 \text{ mg}$ (loading: 43.0 $\mu\text{mol/g}$), $[\text{Ps}] = 0.25 \text{ mmol/L}$. (c) Photochemical evolution of H_2 catalyzed by Hy@MCM-41 with different loading in pure water (10 mL). $[\text{Ps}] = 0.25 \text{ mmol/L}$, $[\text{TEA}] = 0.28 \text{ mol/L}$, $[\text{Hy@MCM-41}] = 4.5 \text{ mg}$. (d) H_2 evolution vs. the Hy loading of Hy@MCM-41 in initial 10 min. $[\text{Ps}] = 0.25 \text{ mmol/L}$, $[\text{TEA}] = 0.28 \text{ mol/L}$, $[\text{Hy@MCM-41}] = 4.5 \text{ mg}$.

out after the H_2 evolution ceased (*ca.* 160 min). The deactivation of the system might be caused by the decomposition of Ps and/or the Hy@MCM-41 catalyst because a huge excess amount of TEA exists in the photocatalyst system. The experiment with re-addition of Hy@MCM-41 (4.2 mg, loading: $119.5 \mu\text{mol/g}$) to the system showed no more hydrogen production under irradiation and another experiment with re-addition of Ps ($1.25 \mu\text{mol}$) demonstrated a recovered activity for the photochemical H_2 generation (Figure 5), which indicated that the deactivation of the catalytic system is mainly due to the decomposition of Ps. Moreover, the decomposition of Hy@MCM-41 also accounts for the decrease in the H_2 production, because re-addition of Ps does not fully recover the catalytic activity of the system for H_2 production.

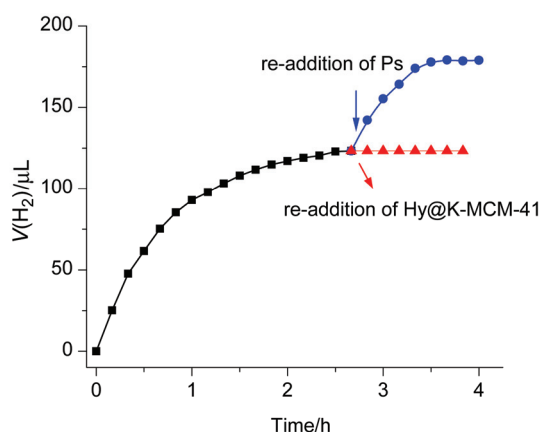


Figure 5 The plot of H_2 production from 10 mL aqueous solution vs. irradiation time with re-addition of Ps ($1.25 \mu\text{mol}$, blue line) and Hy@MCM-41 (4.2 mg, loading: $119.5 \mu\text{mol/g}$, red line) to the photocatalytic system after 160 min irradiation. Initial sample concentration: Hy@MCM-41 (4.2 mg, loading: $119.5 \mu\text{mol/g}$), Ps (0.25 mmol/L) and TEA (0.28 mol/L).

Conclusions

A hydrophobic [Fe-Fe] hydrogenase mimic Hy was immobilized into the mesoporous molecular sieve K-MCM-41 to form a composite Hy@MCM-41. The immobilized hydrogenase mimic has been successfully applied to the photochemical production of hydrogen in pure water by using $[\text{Ir}(\text{ppy})_2\text{bpy}]\text{Cl}$ as the photosensitizer and TEA as the sacrificial electron donor. The results of photochemical production of hydrogen demonstrate that the immobilization of Hy into mesoporous molecular sieve is a way to disperse hydrophobic hydrogenase mimics in water. The present study provides a general strategy for applying hydrophobic artificial catalysts in pure water by using mesoporous molecular sieves.

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