

Supporting information

Transformation of single MOF nanocrystals into single nanostructured catalysts within mesoporous supports: platform for pioneer Fluidized-Nanoreactor Hydrogen Carriers

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Chemicals

ZrOCl₂·8H₂O, 2-aminoterephthalic acid (H₂BDC(NH₂)), salicylaldehyde, carbazole, N-ethylcarbazole, dibromomethane, 1,3-dibromopropane and bis(acetonitrile)dichloropalladium(II), were used as received from Sigma-Aldrich without further purification. Triethylamine (TEA), chloroform (CHCl₃) and methanol (MeOH) were of analytical grade (Sigma-Aldrich). SBA-15 was prepared according to the published procedure [1]. Silica(A) was kindly provided by our commercial partner. Mesoporous silicas were previously evacuated at 120 °C under vacuum for 24h.

Synthesis of the [PdCl-SI-(Zr)UiO-66(NH₂)/SBA-15] precursor

[PdCl-SI-(Zr)UiO-66(NH₂)/SBA-15] precursor was prepared via solid-state synthesis by following this general procedure: 1) multi-step incipient wetness impregnation of MOF precursor solutions on SBA-15, 2) treatment at specific conditions, 3) general washing treatment, 4) vapor phase post-synthesis functionalization, and 5) liquid phase post-synthesis metalation. All [M₂-Z-(M₁)MOF/MPM] precursors can be prepared by following this general procedure with slight modifications described in our previous work [2]. Monometallic [(M₁)MOF/MPM] precursors are prepared by following only the three first steps (1-3).

1) Multi-step incipient wetness impregnation (IWI) of MOF precursor solution on SBA-15

First, a ligand salt precursor solution (TEA)₂BDC(NH₂) was prepared by dissolving H₂BDC(NH₂) (1.5 g) and TEA (2.5 mL) in 35 mL of water. Second, 10 g of evacuated SBA-15 (evacuated overnight under vacuum at 120 °C) were impregnated with the (TEA)₂BDC(NH₂) solution and then dried at 50 °C under vacuum in a rotavapor for 2 h. Subsequently, the resulting dry intermediate [(TEA)₂BDC(NH₂)/SBA-15] was placed in a fluidized bed reactor where it was first treated with a nitrogen flow saturated with concentrated HCl (37%) for 2 hours at room temperature and eventually purged with a nitrogen flow for 2 h to remove the excess of HCl. Afterwards, the metal salt precursor solution prepared by dissolving 2.5 g of ZrOCl₂·8H₂O in 30 mL of water was used to impregnate the [H₂BDC(NH₂)/SBA-15] intermediate. The resulting [ZrOCl₂/H₂BDC(NH₂)/SBA-15] solid was finally dried at 50 °C under vacuum in a rotavapor for 2 h. All the impregnation steps were done via incipient wetness impregnation.

2) Treatment at specific conditions:

The dry solid intermediate [ZrOCl₂/H₂BDC(NH₂)/SBA-15] together with an additive (15 wt.% of H₂O) was placed either in a scintillation vial or Pyrex glass bottle capped with a Teflon tap and heated in an oven at 120 °C for 2 h.

3) *General washing procedure:*

After cooling, the resulting [(Zr)UiO-66(NH₂)/SBA-15] precursor containing 18.6 wt.% of (Zr)UiO-66(NH₂) nanocrystals was thoroughly washed with distilled water in a filtration funnel. Subsequently, the material was further washed overnight in a Soxhlet extractor with MeOH. All materials were activated overnight at 120 °C under vacuum.

4) Vapor-phase post-synthesis functionalization

The evacuated precursor [(Zr)UiO-66(NH₂)/SBA-15] (1 gram) and a tube containing salicylaldehyde (1 mL) were separately placed into a Schlenk. The Schlenk was subsequently closed under vacuum and heated at 100 °C overnight in an oven. The color of the material shifts from pale yellow to orange upon exposure to salicylaldehyde vapor, which indicates the formation of the imine covalent bond between MOF and salicylaldehyde leading to a solid containing salicylideneimine groups (or Schiff base, SI). This material corresponds to the intermediate [SI-(Zr)UiO-66(NH₂)/SBA-15].

5) Liquid-phase post-synthesis metalation

The metal cation was chelated to the intermediate material containing the Schiff base [SI-(Zr)UiO-66(NH₂)/SBA-15] by soaking for 2-3 hours at room temperature in a solution containing PdCl₂(CH₃CN) (200 mg) in THF (5mL). Afterwards the material was washed with MeOH and dried at 80 °C under vacuum to obtain the precursor [PdCl-SI-(Zr)UiO-66(NH₂)/SBA-15] containing 1.5 wt.% of Pd and 5.3 wt.% of Zr, according to XRF. In the same way, several other metal cations can be incorporated into the Schiff base intermediate [SI-(Zr)UiO-66(NH₂)/SBA-15], such as Au, Pt, Ag, Cu or Ni. (See some more examples in Table S1).

General methods

ATR absorption spectroscopy measurements were performed in the range of 4000–400 cm^{-1} with a Perkin Elmer Spectrum 100 FTIR spectrometer.

XRD patterns were recorded using a Panalytical Empyrean X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=1.54778 \text{ \AA}$). The samples were prepared by filling the holder with the dry powder.

N_2 sorption isotherms were performed in a Micromeritics ASAP at 77K (Accelerated Surface Area and Porosimetry) 2020 System. A multi-point BET surface area was determined from 6 measurements at relative pressures (P/P_0) ranging from 0.050 to 0.300. Single point adsorption total pore volume was measured near saturation pressure ($P_0 \approx 770 \text{ mmHg}$).

XRF analysis were performed in a ARL Thermo Scientific (Ecublens, Switzerland) Perform'X Wavelength-Dispersive X-ray Fluorescence (WDXRF) equipped with an X-ray tube 5GN-type Rh target with ultra-thin 30 μm Be window to maximize light element response. 4000 W power supply for 60 kV max or 120 mA max with two detectors (flow proportional and scintillation) and seven analyzer crystals to achieve a broad elemental range.

Transmission electron microscopy (TEM) experiments were performed in a JEOL JEM-2000FX S/TEM microscope with LaB6 emitter at 200kV with a 120 μm condenser lens aperture and 80 μm objective lens aperture inserted.

GC/MS analysis was performed using an Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer with electron impact ionization.

NMR Spectra of the liquid phase was recorded with an AVANCE 600 MHz spectrometer (Bruker, Germany) in CDCl_3 at room temperature.

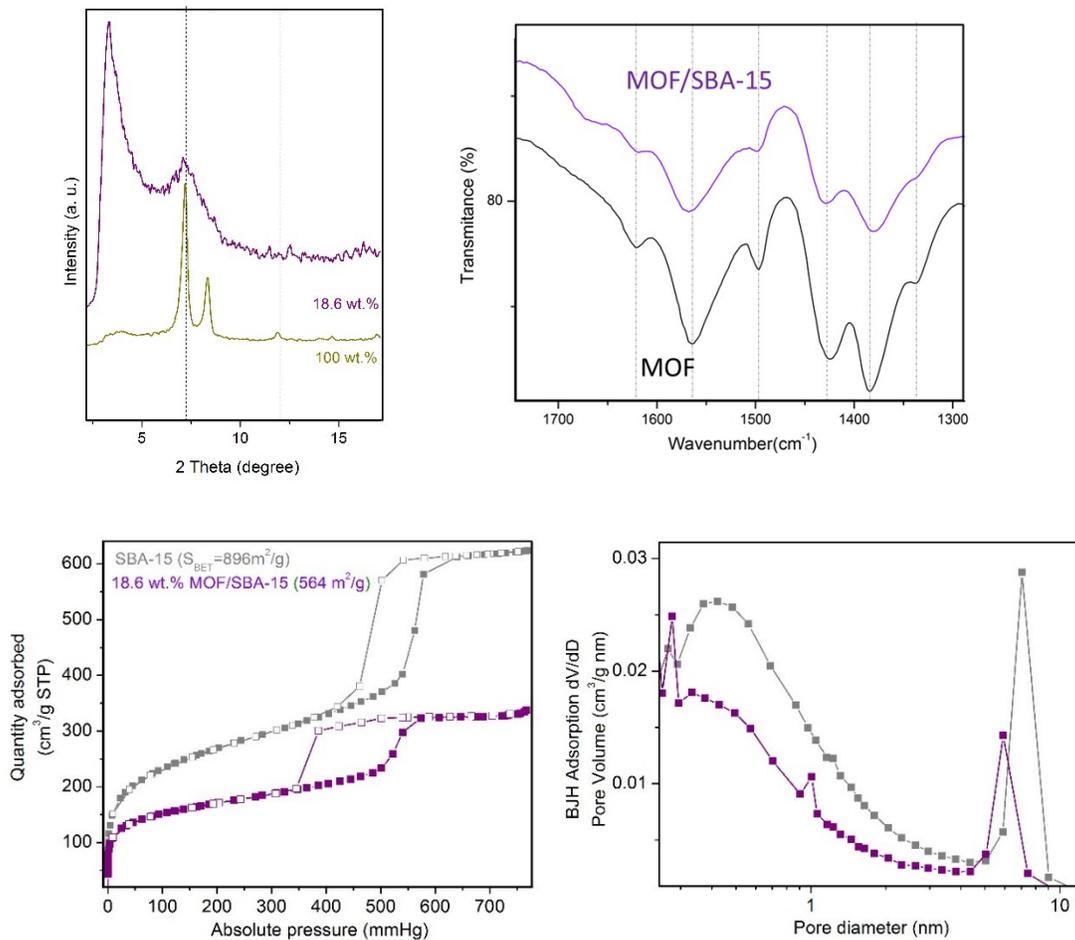


Figure S1. Typical characterization routine for [(Zr)UiO-66(NH₂)/SBA-15] precursor material: XRD, FTIR, N₂ sorption isotherms and pore distribution plot. See our previous work for more details [2].

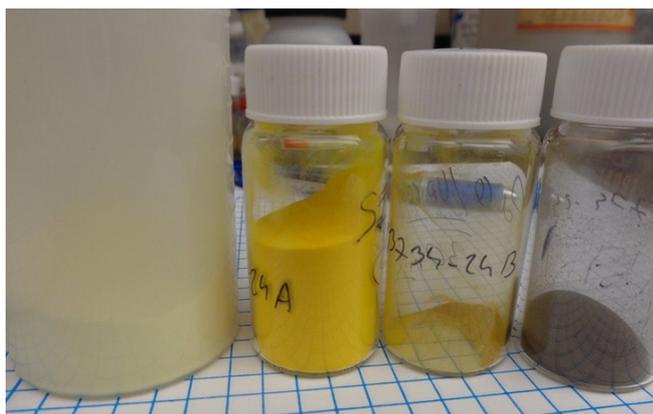


Figure S2. Pictures of the materials (from left to right): (Zr)UiO-66(NH₂)/SBA-15, SI-(Zr)UiO-66(NH₂)/SBA-15, PdCl-SI-(Zr)UiO-66(NH₂)/SBA-15 and PdZrO₂/SBA-15 (pyrolyzed at 650 °C under N₂).

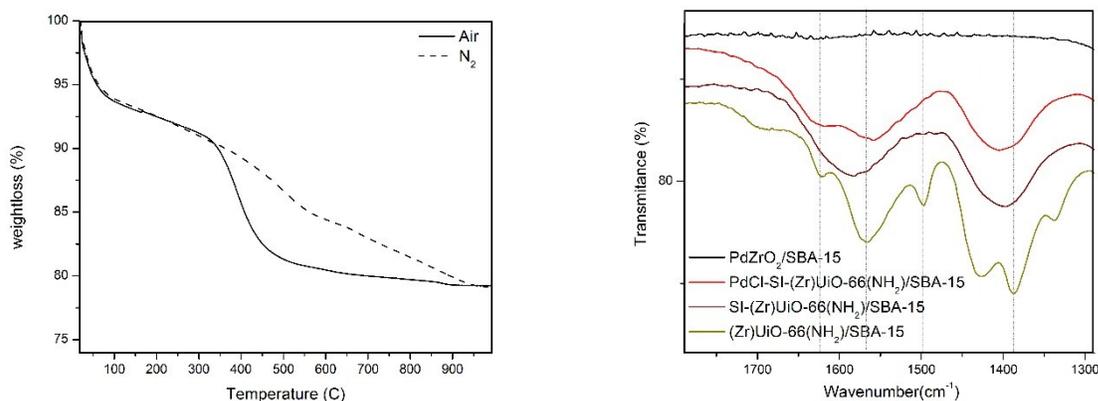


Figure S3. (left) TGA profiles for sample PdCl-SI-(Zr)UiO-66(NH₂)/SBA-15 calcined under air (solid line) and pyrolyzed under nitrogen (dashed line). (right) FTIR spectra of consecutive steps for the preparation of PdZrO₂/SBA-15 sample via pyrolysis under nitrogen at 900 °C, as shown in Figure 1 in manuscript.

Table S1. Example of mono metallic and bimetallic catalysts prepared via ‘single MOF nanocrystals to single nanostructured catalyst’ approach. All the MOF/SiO₂ hybrids were prepared according to our previous publication [2].

MOF precursor	treatment	MPM	M ₁	M ₂	formula
(Ru)HKUST-1	N ₂ , 900°C	Silica(A)	Ru	-	Ru/Silica(A)
(Co)MOF-74	N ₂ , 900 °C	SBA-15	Co	-	Co/SBA-15
(Ni)MOF-74	N ₂ , 900 °C	SBA-15	Ni	-	Ni/SBA-15
(Zr)UiO-66(NH ₂)	N ₂ , 900 °C	Silica(A)	Zr	-	ZrO ₂ / Silica(A)
(Fe)MIL-100	N ₂ , 500 °C	Silica(A)	Fe	-	FeC/ Silica(A)
(Fe)MIL-100	O ₂ , 500 °C	Silica(A)	Fe		Fe ₃ O ₄ / Silica(A)
(V)MIL-101(NH ₂)	N ₂ , 900°C	Silica(A)	V		VO _x / Silica(A)
PdCl-SI-(Zr)UiO-66(NH ₂)	O ₂ , 500 °C	SBA-15	Zr	Pd	PdZrO ₂ /SBA-15
PdCl-SI-(Zr)UiO-66(NH ₂)	N ₂ , 900 °C	SBA-15	Zr	Pd	PdZrO ₂ /SBA-15
PdCl-SI-(Zr)UiO-66(NH ₂)	H ₂ , 200 °C	SBA-15	Zr	Pd	Pd/SI-(Zr)UiO-66(NH ₂)/SBA-15
RuCl ₂ -SI-(Zr)UiO-66(NH ₂)	N ₂ , 900 °C	Silica(A)	Zr	Ru	RuZrO ₂ / Silica(A)
IrCl ₂ -SI-(Zr)UiO-66(NH ₂)	N ₂ , 900 °C	Silica(A)	Zr	Ir	IrZrO ₂ / Silica(A)
RhCl ₂ -SI-(Zr)UiO-66(NH ₂)	N ₂ , 900 °C	Silica(A)	Zr	Rh	RhZrO ₂ / Silica(A)
PdCl-SI-(Al)MIL-53(NH ₂)	N ₂ , 900 °C	Silica(A)	Al	Pd	PdAl ₂ O ₃ / Silica(A)
AuCl ₂ -SI-(Ti)MIL-125(NH ₂)	N ₂ , 900 °C	Silica(A)	Ti	Au	AuTiO ₂ / Silica(A)

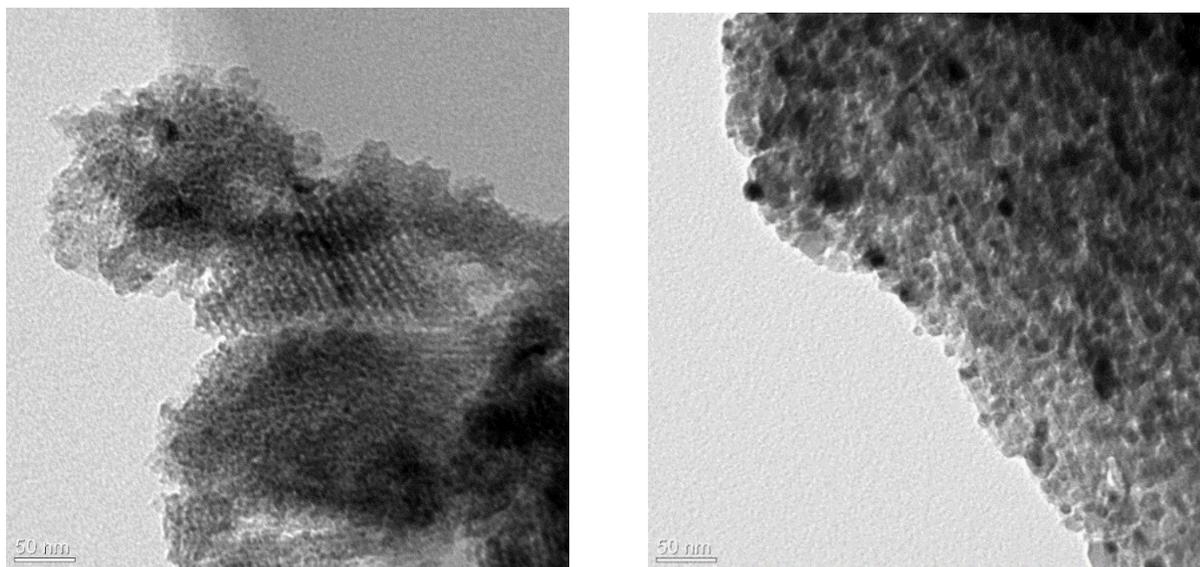


Fig S4. TEM of Ni/SBA-15 (left) and Co/SBA-15 (right) prepared from (Ni)MOF-74/SBA-15 and (Co)MOF-74/SBA-15, respectively.

FNHCs compared to state-of-art hydrogen storage systems.

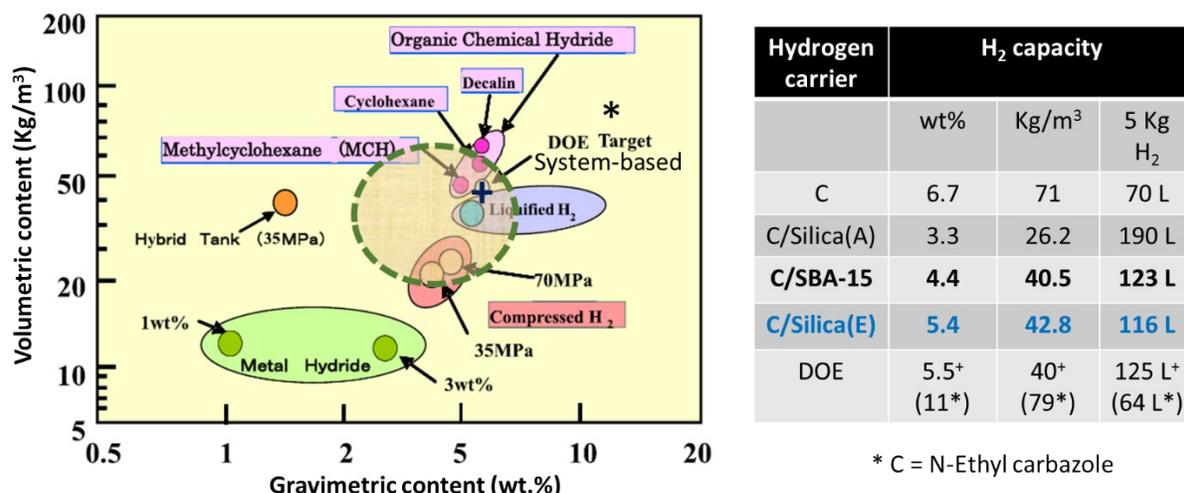


Figure S5. (left) State-of-the-art hydrogen storage systems and their volumetric and gravimetric H₂ capacities. (right) H₂ capacities for N-ethyl carbazole impregnated on different fluidized mesoporous silicas (C/Silica) compared to pure N-ethyl carbazole (C).

Synthesis of Solid Organic Hydrogen Carriers (SOHCs)

Solid Organic Hydrogen Carriers (SOHCs) were prepared by adapting reported procedure [3]. 5 gr of KOH was added to a stirred solution of 7.5 grams of carbazole (C) in 250 mL of acetone at RT. 1.57 mL of dibromomethane (or 2.4 mL of 1,3-dibromopropane) were added to this solution and refluxed for 2 h to obtain bis(carbazol-9-yl)methane (C₂Me) (or 1,3-bis(carbazole-9-yl)propane (C₂Pr)). The resulting mixture was poured onto crushed ice, filtered and washed with water. The final product was crystallized by dissolving in hot mixtures of H₂O/acetone. The composition and purity of the resulting compounds were confirmed by NMR in chloroform (Figure S6 and S7).

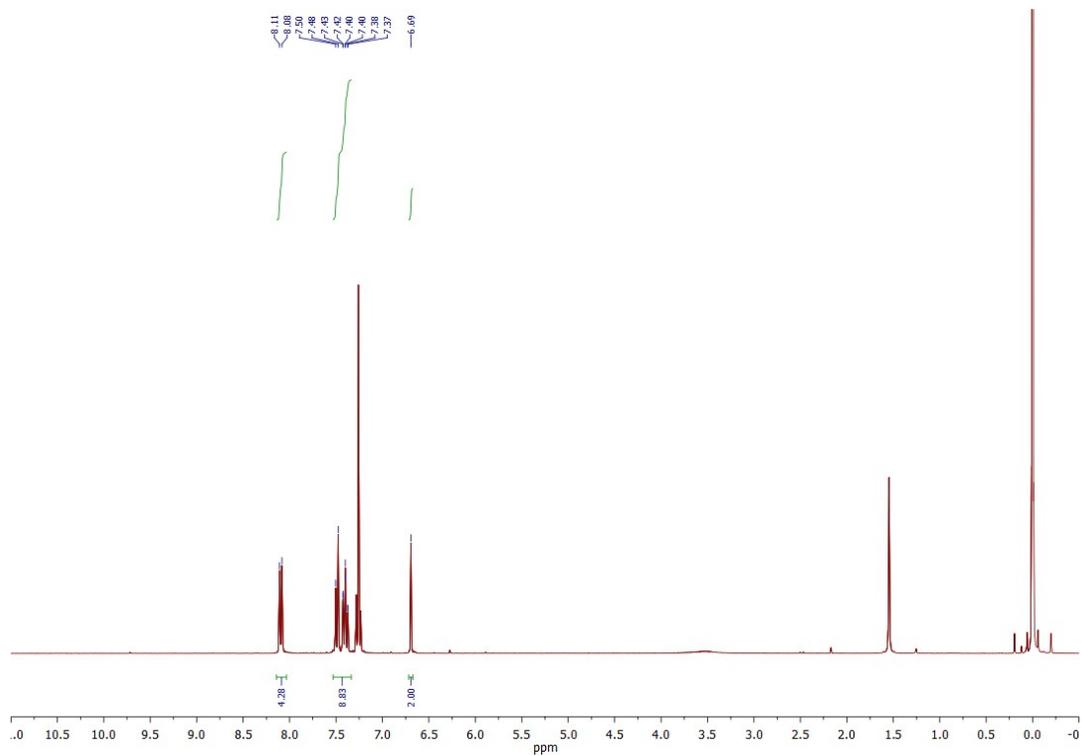


Figure S6. NMR for C_2Me .

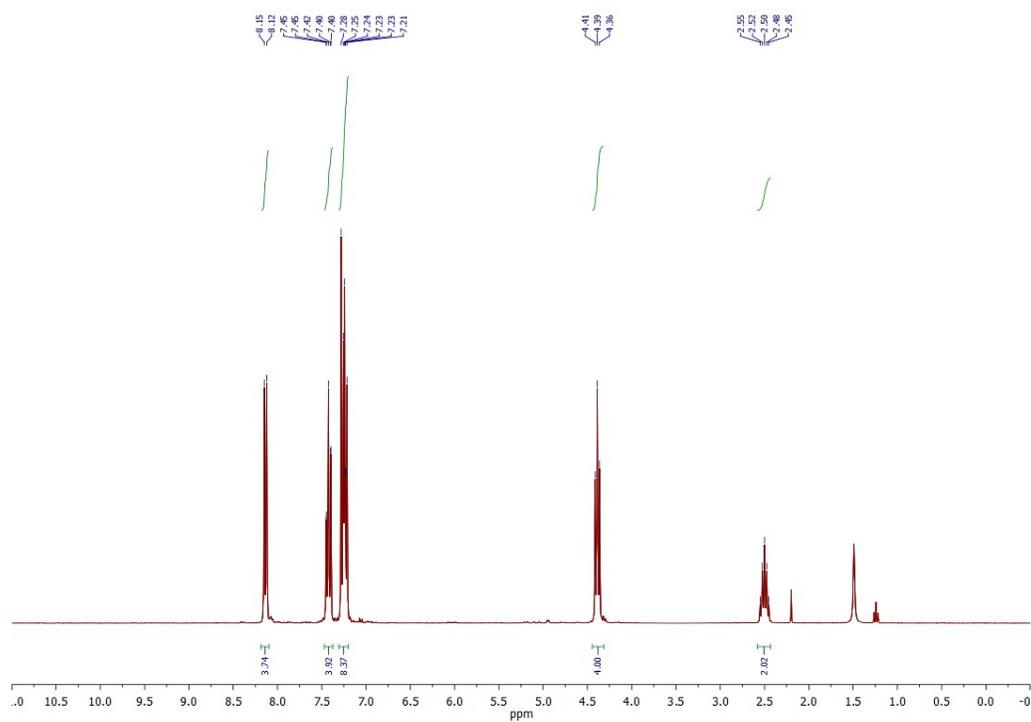


Figure S7. NMR for C_2Pr .

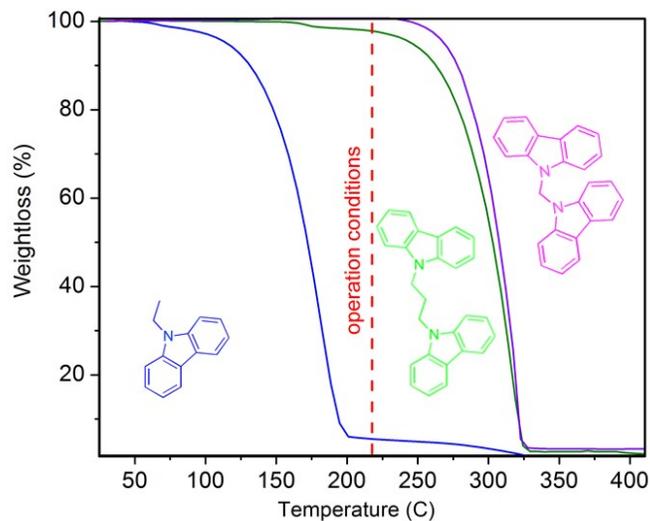


Figure S8. TGA under N₂ for two solid OHCs (used for our novel FNHCs): C₂Me (violet) and C₂Pr (green) compared to C (blue).

FNHCs preparation: SOHCs infiltration within the Fluidized Nanoreactors (FNs)

1 gram of SOHC and 2 grams of Fluidized Nanoreactor (1.7 wt.% Pd/ZrO₂/Silica(A) prepared via pyrolysis under N₂ at 650 °C) were placed into a glass ampule and evacuated under vacuum at 100 °C for 30 minutes. The glass ampule was sealed under vacuum and heated at 260 °C for melting the solid OHC, which is absorbed within the mesoporous FN. The resulting Fluidized Nanoreactor Hydrogen Carriers (FNHCs) contain 33 wt.% of SOHC. Silica (A) is used for preparing FNHCs due to its excellent fluidizability, as demonstrated in our recent work [4].

Hydrogenation-dehydrogenation performance testing of FNHCs

1 gram of FNHC was placed in a Parr bomb reactor equipped with a pressure transducer. The reactor was filled with 800 (or 30) psig of H₂ for the hydrogenation (or dehydrogenation) reaction. The reactor was heated at 220 °C and held until the pressure was stabilized (1-2 hours), which determines the end of the reaction, and the reactor was cooled down. H₂ consumption and release was monitored by the pressure, as shown in Figure S9. Hydro-/dehydrogenated SOHCs were analyzed by GC of samples extracted with CHCl₃ from solid aliquots of FNHCs after reaction.

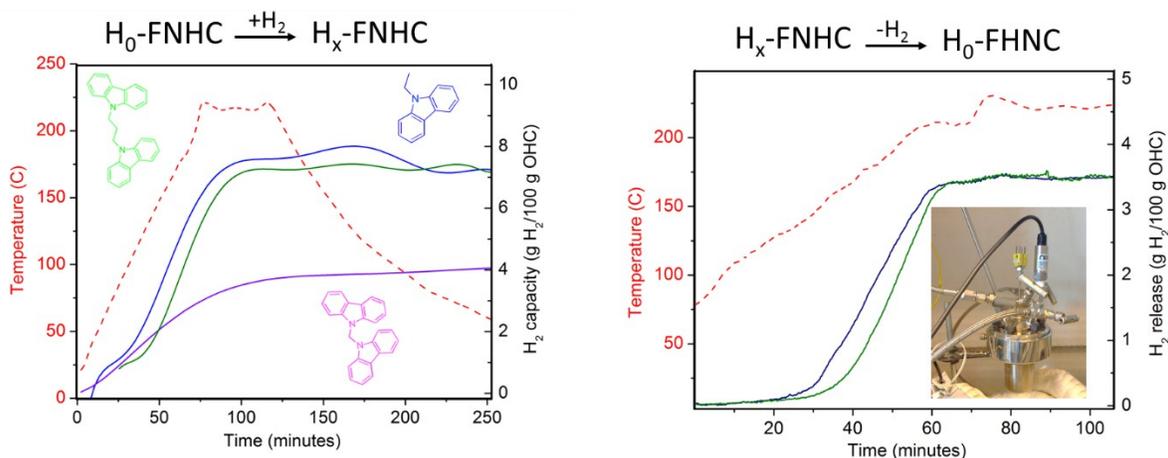


Figure S9. Hydrogenation (left) and dehydrogenation (right) kinetics of FNHCs containing N-ethylcarbazole (blue), bis(9-carbazolyl)methane (violet) or 1,3-bis(9-carbazolyl)propane (green). H_2 evolution profiles were calculated from P and T in the reactor and fitted to a polynomial line of order 9.

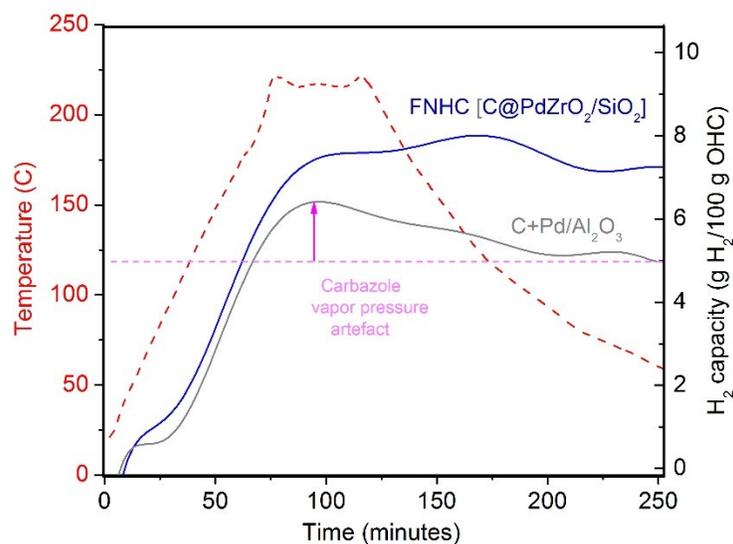


Figure S10. Commercial Pd/Al_2O_3 showing lower capacity compared to FNHCs (at same loading of Pd) due to the bad contact between Pd active sites and N-ethylcarbazole (in gas-phase). Dehydrogenation reaction of highly volatile 9-ethyl-perhydrocarbazole with Pd/Al_2O_3 showed almost no activity compared to FNHCs (see Figure S9).

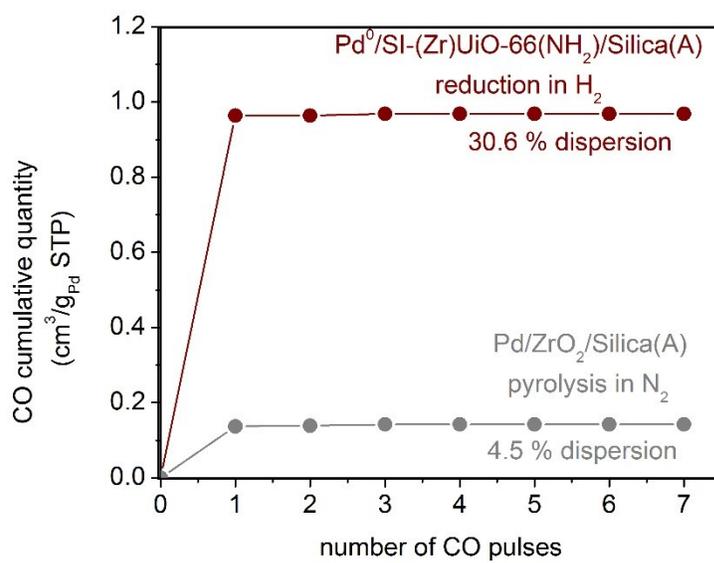


Figure S11. CO pulse chemisorption experiments for determining the Pd active surface (dispersion) of catalysts obtained from 1.5 wt.% PdCl-SI-(Zr)UiO-66(NH₂)/Silica(A) by reduction in H₂ (wine line) and pyrolysis in N₂ (grey line).

References

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- [2] I. Luz, M. Soukri and M. Lail, *Chemistry of Materials*, 2017, **29**, 9628-9638.
- [3] E. Asker and F. Filiz, *Journal of Molecular Structure*, 2013, **1040**, 65-74.
- [4] I. Luz, M. Soukri and M. Lail, *Chemical Science*, 2018, **9**, 4589-4599.