Supplementary Information

Improved Catalytic Hydrogen Release of Quasi HKUST-1 Compared to HKUST-1

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Experimental

Materials and Characterization Techniques

All reagents and materials for the synthesis and analysis were commercially available from Aldrich and Merck Company and used as received. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR spectrophotometer. Thermogravimetric analysis were measured in a PL-STA 1500 apparatus heating at a rate of 10 ºC min^{-1} in static N_2 atmosphere. Powder X-ray diffraction (PXRD) patterns were acquired using a Philips X'pert diffractometer with monochromated Cu-K$_\alpha$ radiation. Adsorption measurements were performed on a Micrometrics TriStar II 3020 surface area and a LMS BELSORP-mini II apparatuses using N_2 at 77 K. All samples were activated at 120 °C under vacuum until constant weight (about 8 h). The pore-size distributions were calculated using the BJH algorithm from the N_2 adsorption branch of the isotherms. The shape and dimensions of the powder particles were monitored with a field emission scanning electron microscope (FE-SEM) TESCAN MIRAIII (Czech Rep.). Transmission electron microscopy images were recorded at 200 kV with a Jeol microscope from lamellae obtained by FIB cutting inside the electron microscopy chamber of particles of HKUST-1 and QT-240 inside a resin matrix. EPR spectra of HKUST-1 and QH-240 were recorded by weighting 25 mg of the solids that were place in a quartz tube inserted in a Bruker EMX spectrometer operating at a frequency of 9.803 GHz with 3489.9 G of scan width and 40.95 ms of time constant and a modulation frequency 100 kHz, modulation width 1 G and 19.92 mW of irradiation power. The leaching of copper to water from QH-240 sample was calculated by inductively coupled plasma (ICP) at the end of the HGR reaction. ICP-optical emission spectrometry (ICP-OES) analysis were performed with a Varian Vista-PRO (Springvale, Australia) with a radial torch coupled to a concentric nebulizer, a Scott spray chamber and equipped with a charge-coupled detector (CCD).

Thermoprogrammed desorption (TPD) and reductions (TPR) were carried out with a TPD-TPR 2900 system equipped with a thermal conductivity detector (TCD). First, a certain known amount of the catalyst was pretreated at 150 °C in He stream at a gas rate of 20 mL min^{-1} for 1 h, then cooled down up to 40 °C, and subsequently exposed to ammonia (4 vol.% in He, 20 mL min^{-1}) for 1 h. Then, physisorbed ammonia was removed by flushing the sample with 20 mL min^{-1} of He within 30 min. Subsequently, the desorption was performed by increasing the temperature from 40 to 750 °C at a heating rate of 10 °C min^{-1} in He stream (20 mL min^{-1}). Analyses of the evolved gases present in the head space was performed by heating preactivated HKUST-1 at 150 ºC under reduced pressure for 90 min and subsequently heating at 240 ºC for 1 h in the closed round reactor flask. Aliquots of 250 μL were taken with a gas syringe and analysed with a calibrated quadrupolar Agilent mass spectrometer.

Synthesis of [Cu$_3$(BTC)$_2$(H$_2$O)$_3$]$_n$·nH$_2$OMeOH (HKUST-1)

In a typical experiment powder sample of HKUST-1 was obtained by mixing benzene-1,3,5-tricarboxylic acid (BTC, 2.1 g, 10 mmol) and Cu(OAc)$_2$. H$_2$O (3.21 g, 16 mmol) in 400 ml of a 1-to-1 mixture of H$_2$O and EtOH in a round bottom flask at 110 °C for 4 h. The resulting powder was isolated by centrifugation, washed four times with ethanol and water and dried in air for characterization. Yield: 3.185 g (91 % based on BTC). IR spectroscopic data (KBr pellet, ν/cm^{-1}): 485(w), 733(m), 756(m), 1108(w), 1374(s), 1463(s), 1557(s), 1615(s), 1656(s), 1702(m) and 3417(w-br) (Fig. S1).

Synthesis of QH-x

Deligandation of HKUST-1 was carried out by thermal treatment in air with a heating rate of 5 °C min^{-1} at temperatures of 200, 240, 260 °C for 30 min and 300 °C for 2 h to achieve Q-HKUST

which were denoted by QH-x, where "H" and "x" stand for HKUST-1 and the temperature of deligandation, respectively.

Catalytic HGR of QH-x samples

The catalytic HGR from NaBH$_4$ hydrolysis over QH-x samples was monitored through water-displacement method by measuring volume of H$_2$ gas.[1] A mixture of the desired amount of catalyst and distilled water was put in a two-necked round-bottomed flask (100 mL), which was placed in a water bath at room temperature under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to evaluate the H$_2$ volume. The reactions were started by addition of fresh aqueous NaBH$_4$ solution of a certain concentration was injected into the mixture using a syringe. The HGR occurred quickly only when NaBH$_4$ solution was in contact with QH-x catalyst (Fig. S2). The HGR efficiency was determined by measuring the volume of H$_2$ via recording the water displacement in the gas burette. The reaction was completed when no more H$_2$ gas was generated. The turnover frequency (TOF) (ml H$_2$ g$_{cat}^{-1}$ min^{-1}) for HGR was calculated as follows:

$$\text{TOF} = \text{HGR} = \frac{V_{H_2O}}{t.m_{cat}} \qquad\qquad (S1)$$

where V_{H_2O} (mL) denotes the water volume (mL) displaced by H$_2$ gas in time (t), and m$_{cat}$ refers to the catalyst weight in grams. Additionally, kinetics studies were measured in different concentrations of NaBH$_4$ and at various dosage of the optimal catalyst. The experiment was performed at different temperatures (25, 35, 40 and 45 °C) to determine the apparent activation energy as follows:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad\qquad (S2)$$

Where k in mL H_2 min^{-1} g^{-1} denotes as the constant rate, A as the pre-exponential factor, R is gas constant (8.314 J mol^{-1} K^{-1}), and T is the reaction temperature in K.

Stability of the catalyst was evaluated as soon as the last run of the HGR was completed by introducing in the reactor the same specified $NaBH_4$ amount, and measuring the released gas by the gas burette. Four HGR runs were carried out at room temperature consecutively. Upon completion of the reaction stability tests in presence of the best catalyst, the sample was separated from the reaction mixture by centrifugation and washed several times with deionized water and ethanol (1:1), then dried at 100 °C under vacuum for 10 h and finally used for PXRD and ICP analyses.

Calculation of The activation parameters

The activation parameters including activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) were also estimated by the Eyring equation:

$$\ln(\frac{k_{app}}{T}) = -\frac{\Delta H^{\#}}{RT} + \ln(\frac{k_B}{h}) + \frac{\Delta S^{\#}}{R} \qquad (S3)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (S4)$$

where $\Delta H°$ and $\Delta S°$ are the changes in the enthalpy (J/mol) and the entropy (J/mol K) respectively. The k_B and h are Boltzmann (1.380649×10^{-23} J.K^{-1}) and Planck (6.6×10^{-34} J.s) constants, respectively.
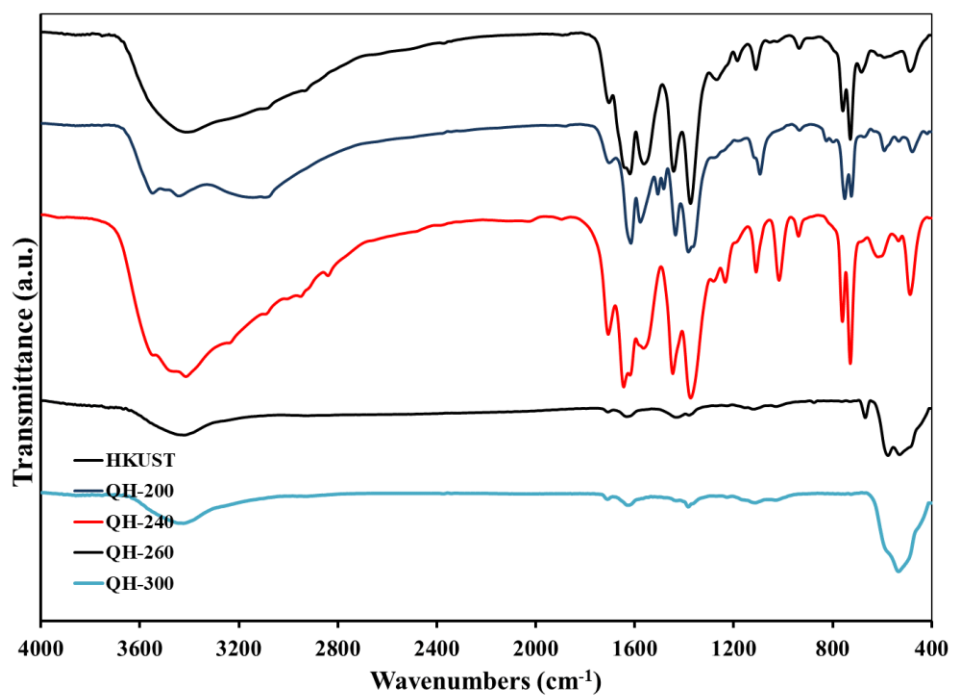
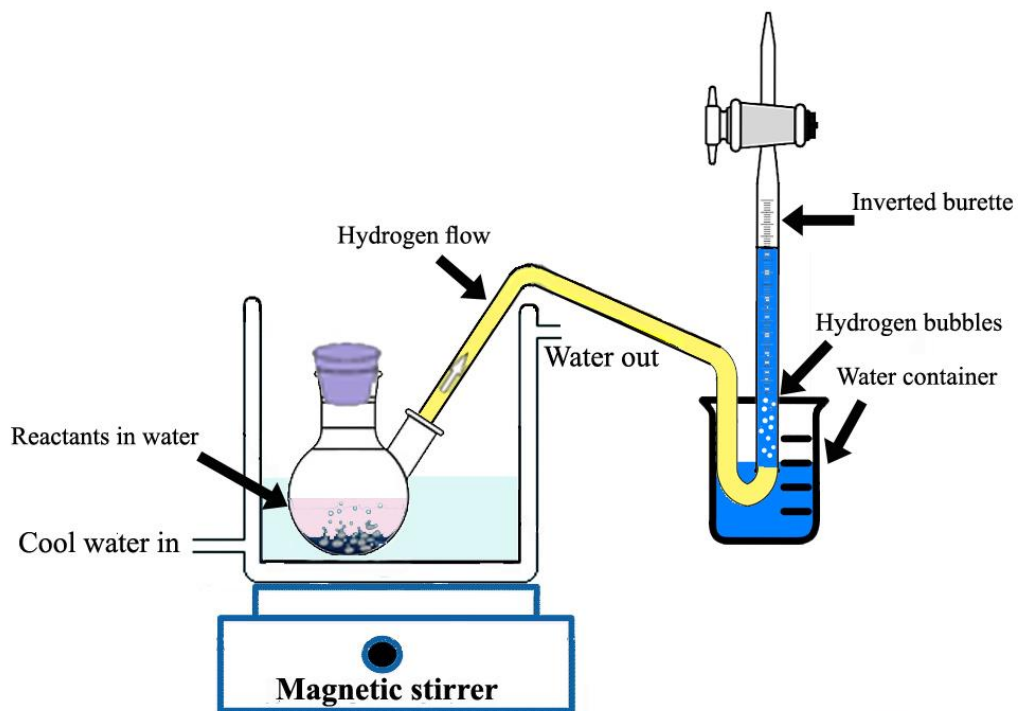**Fig. S1.** IR spectra of HKUST and QH-x samples.

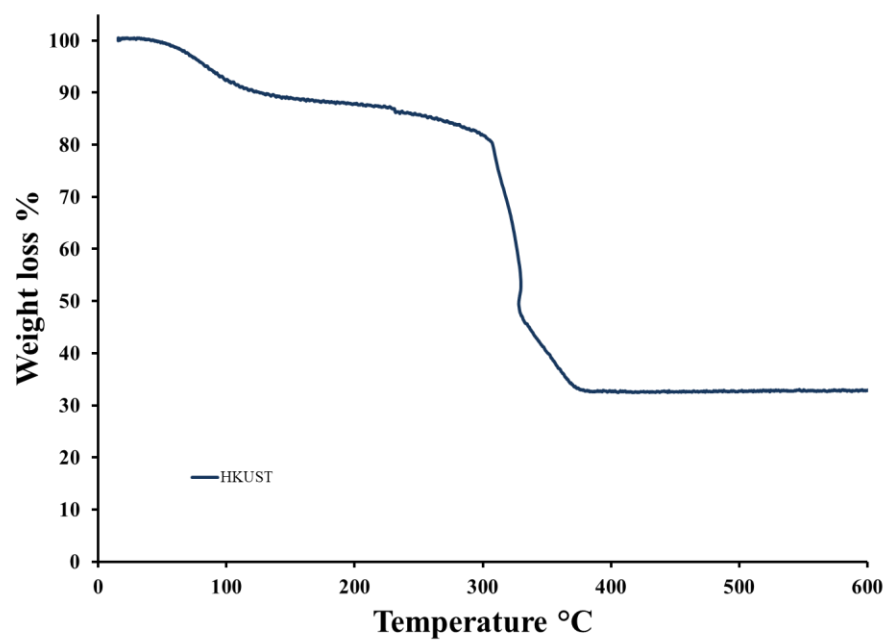**Fig. S2.** Schematic representation of hydrogen generation reaction setup**.**

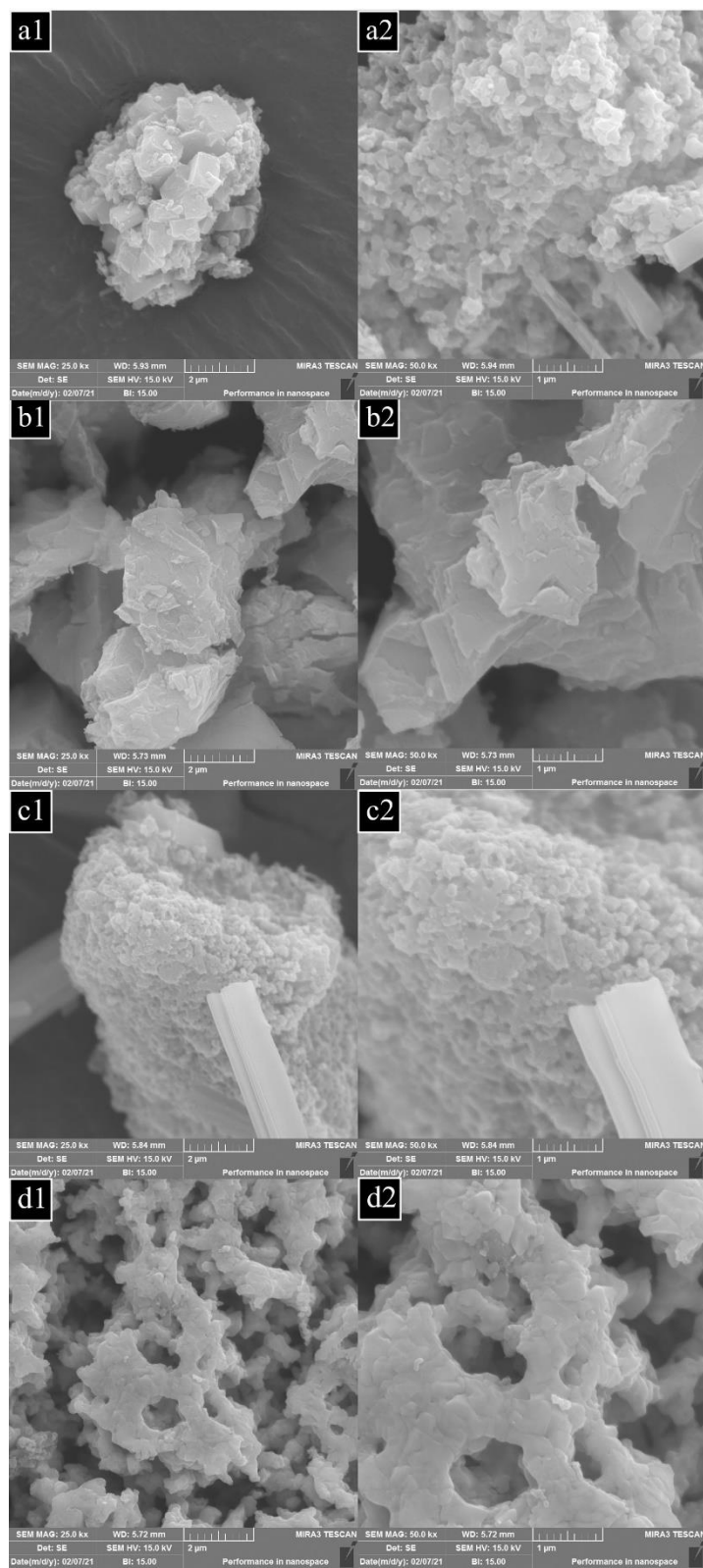**Fig. S3.** Thermogravimetric profiles of HKUST.

Fig. S4. FE-SEM images of the (a) HKUST-1, (b) QH-200, (c) QH-240 and (d) QH-260 samples.
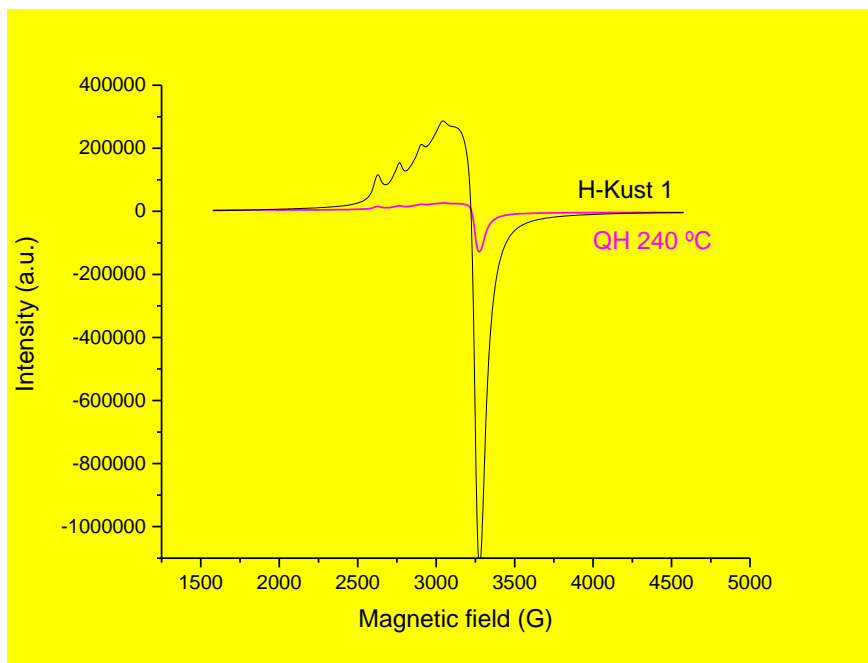
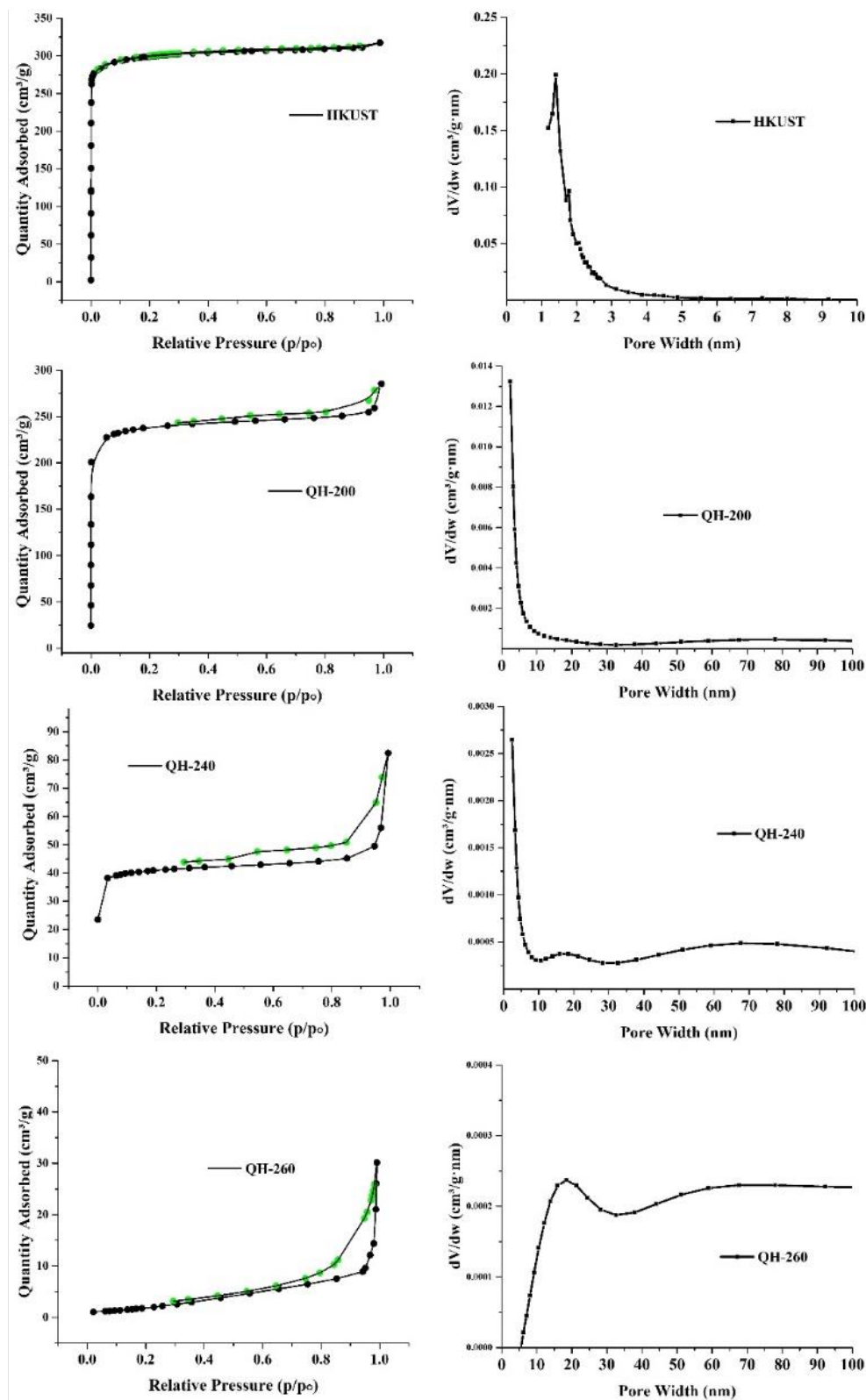**Fig. S5.** Comparison of EPR spectra of HKUST-1 and QH 240 samples.

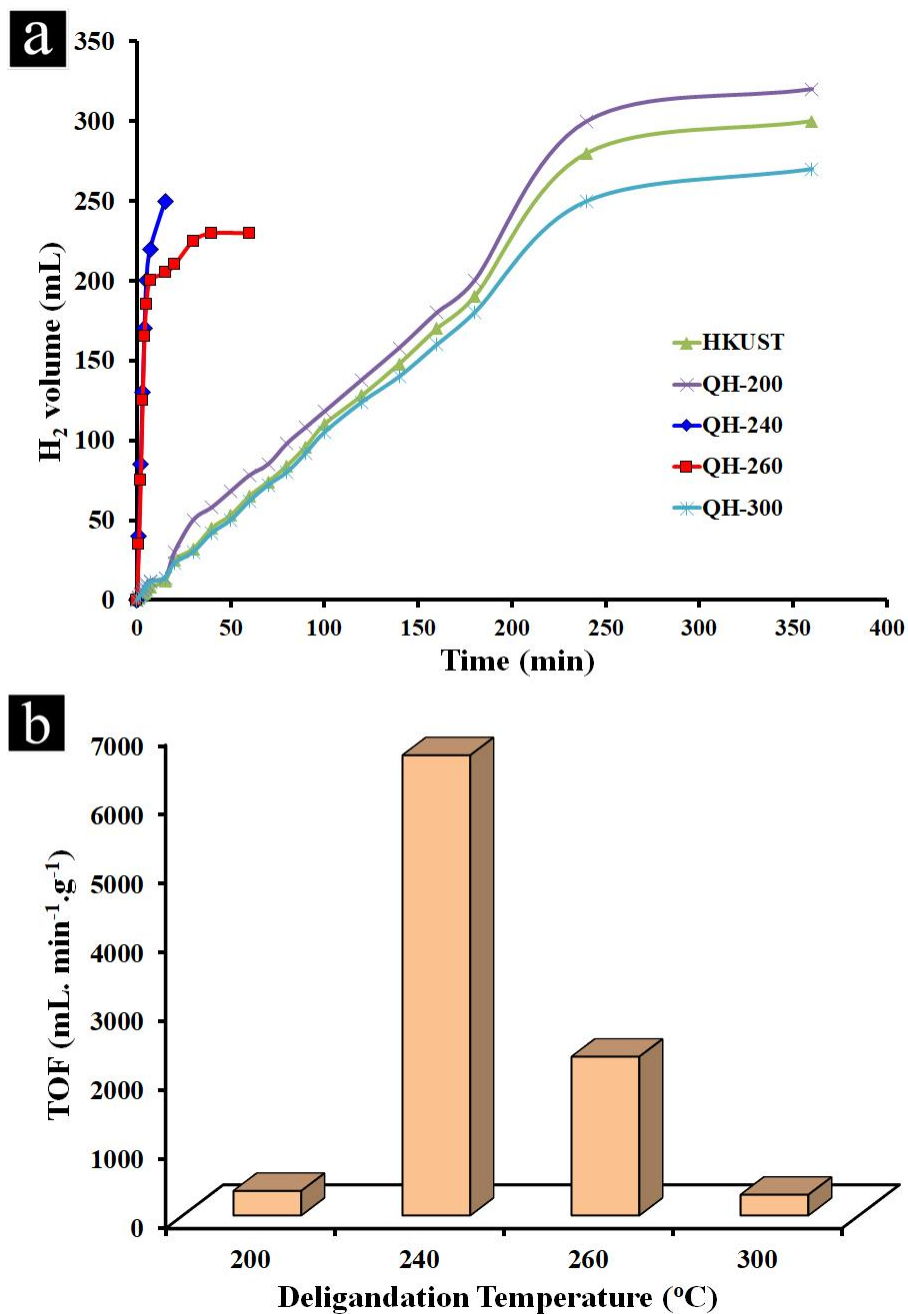**Fig. S6.** N_2 adsorption-desorption at 77 K and 1 bar and pore size distribution for HKUST-1 and QH-x.

Fig. S7. The effect of deligandation temperatures on H_2 release and TOF over various QH-x catalysts.
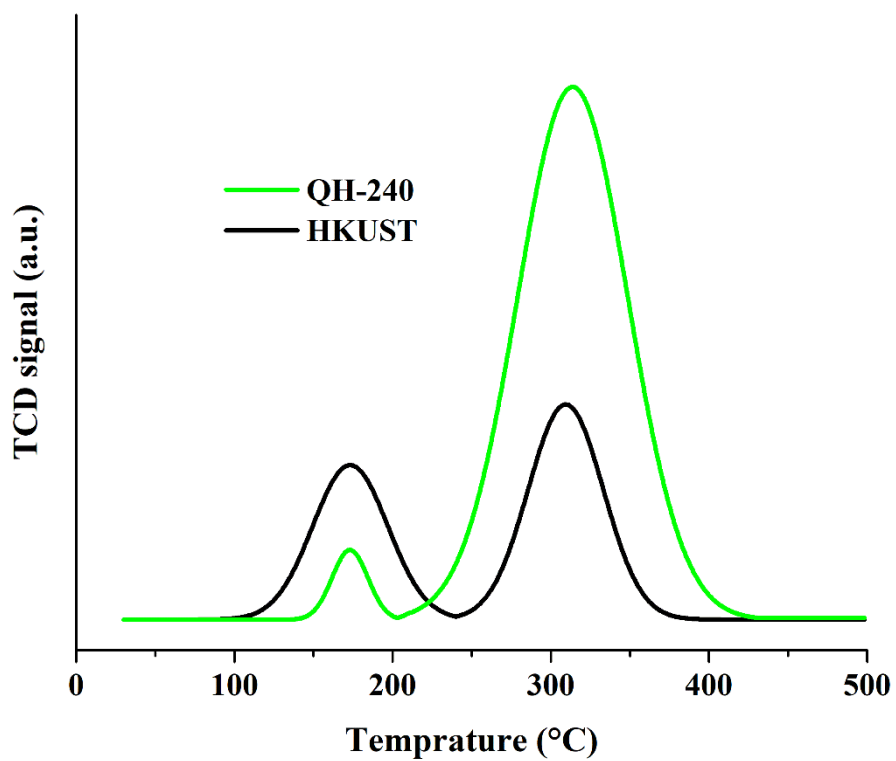
Fig. S8. Temperature-programmed NH_3 desorption for HKUST and QH-240 catalysts.
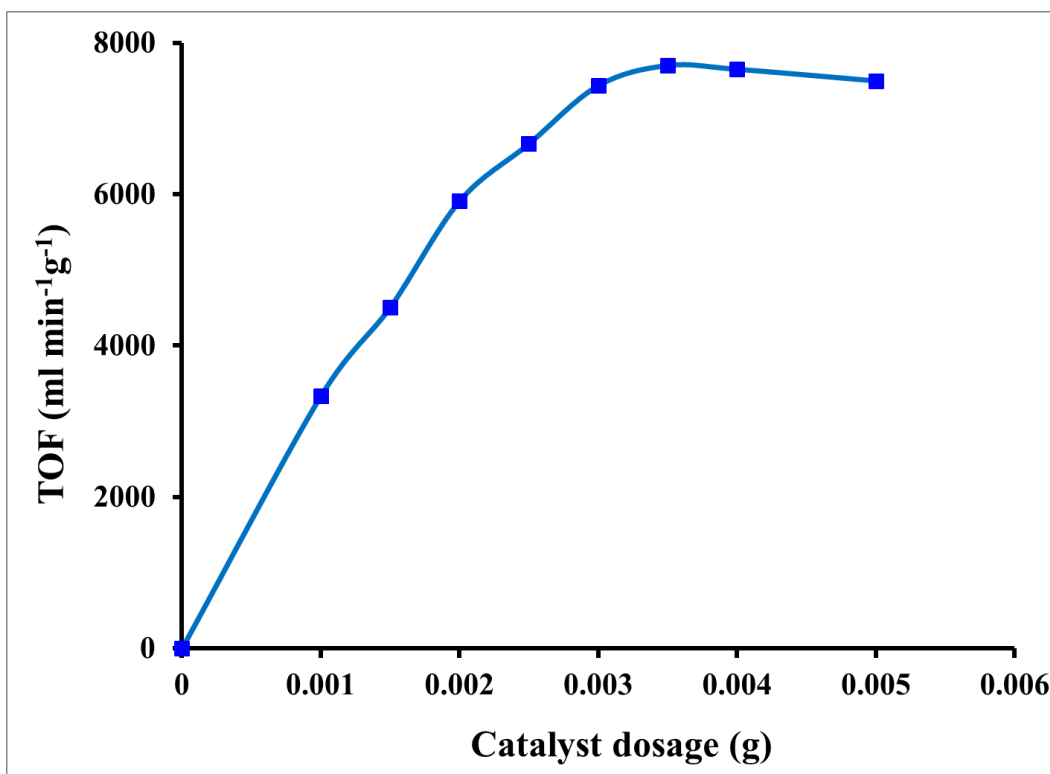
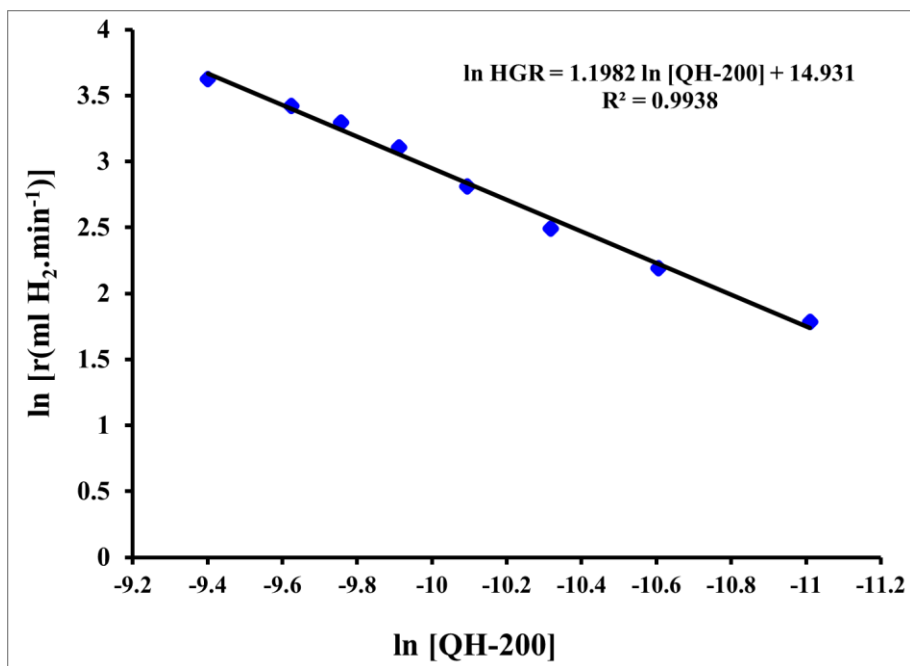**Fig. S9.** TOF values in presence of various amount of QH-240 catalyst.

Fig. S10. Plot of HGR versus the concentration of QH-240 catalyst both in natural logarithmic scales.
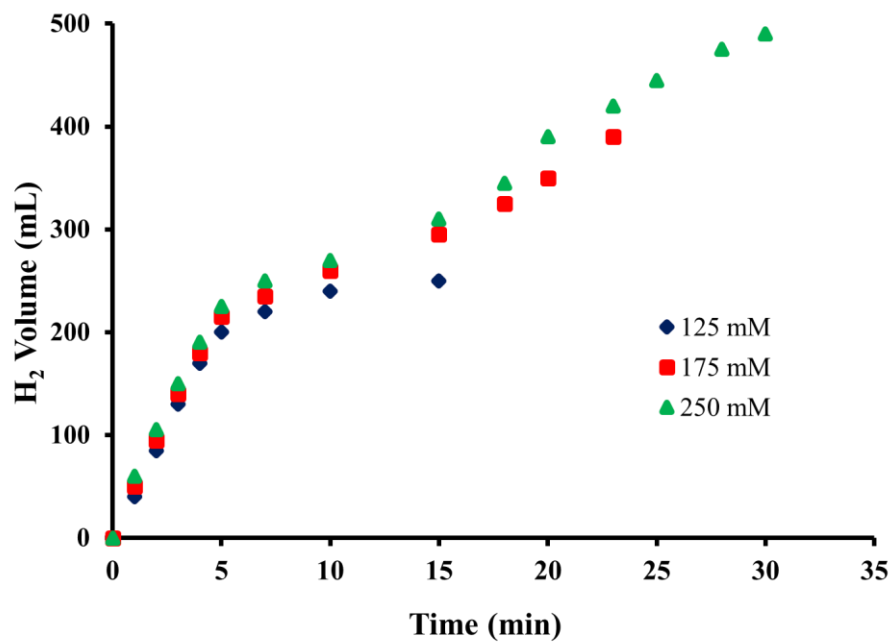
Fig. S11. The effect of $NaBH_4$ concentrations on H_2 release over QH-240 catalyst.
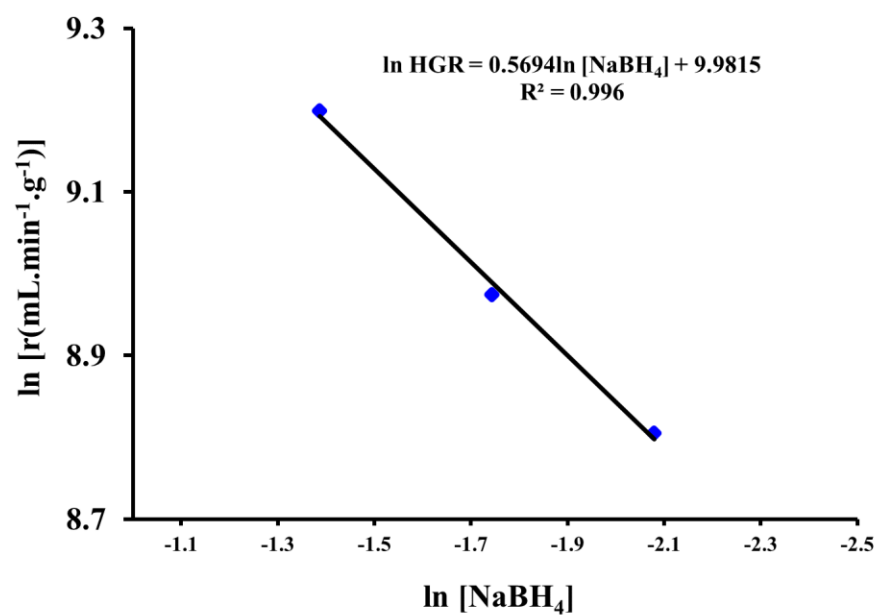
Fig. S12. Plot of HGR versus the concentration of $NaBH_4$ (both in natural logarithmic scales) over QH-240 catalyst at 25 °C.
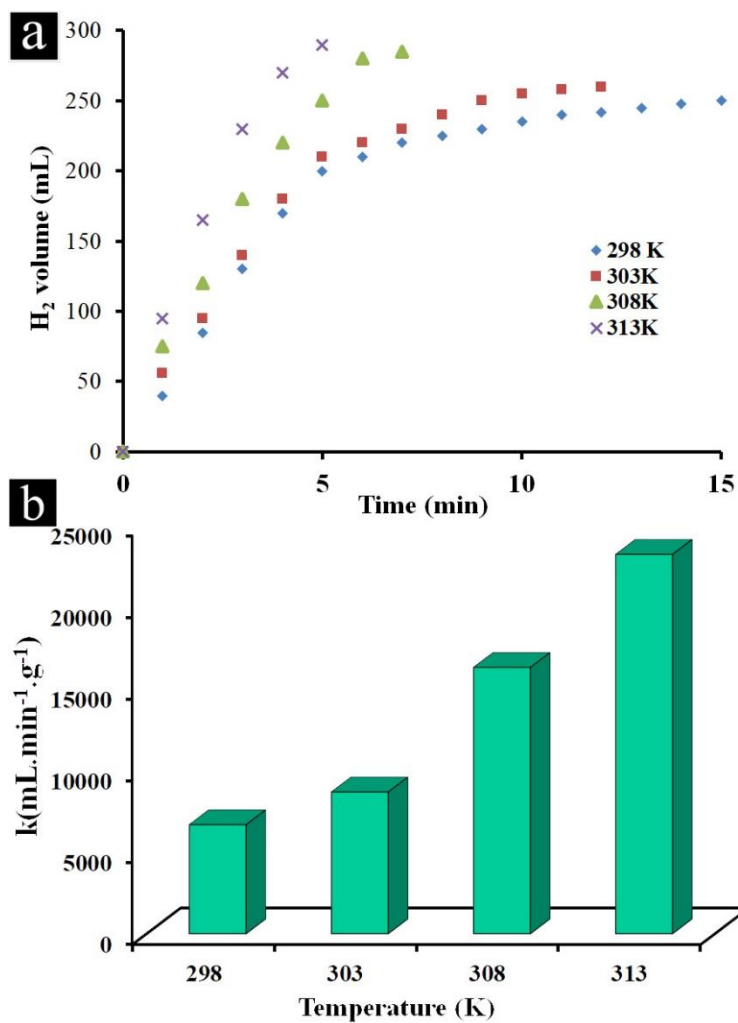
Fig. S13. (a) Catalytic H_2 release upon hydrolysis of $NaBH_4$ over QH-240 as catalyst at various temperatures as indicated in the plot and (b) Temperature dependence of rate constant for HGR over QH-240 catalyst. Reaction conditions: QH-240 mass = 2.5 mg and $[NaBH_4]$ = 125 mM.
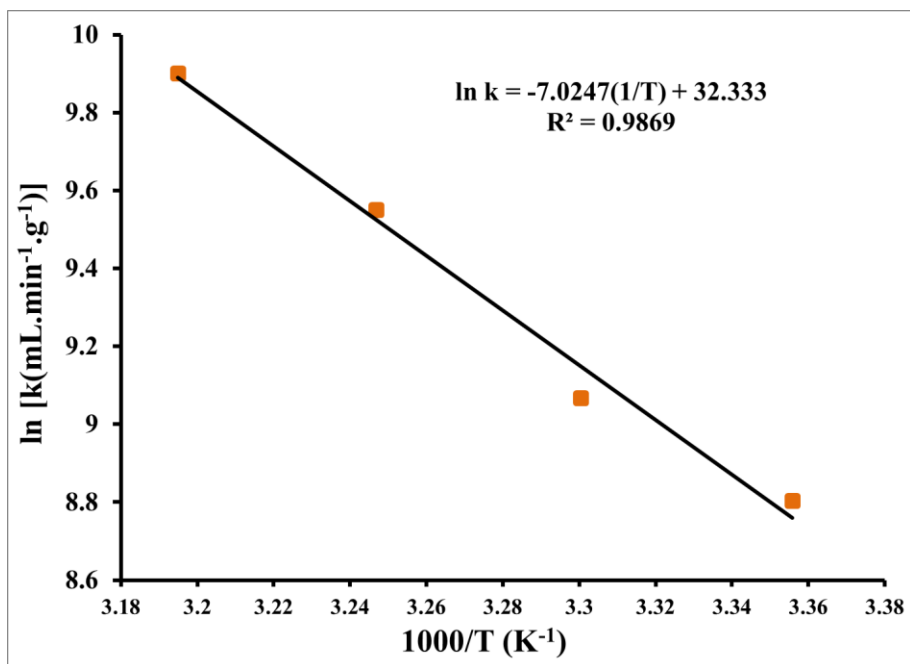
Fig. S14. Catalytic HGR over QH-240 and its related Arrhenius plot.

Fig. S15. The Eyring plot on HGR catalyzed by QH-240.

Fig. S16. Comparison of the temporal profiles of H_2 evolution by $NaBH_4$ hydrolysis in two systems of H_2O and D_2O over 2.5 mg of QH-240 catalyst at 25 °C.

Fig. S17. (a) The reusability of the QH-240 catalyst on NaBH4 hydrolysis at 25 °C for four catalytic cycles and (b) the XRD pattern of the QH-240 catalyst after four catalytic runs.

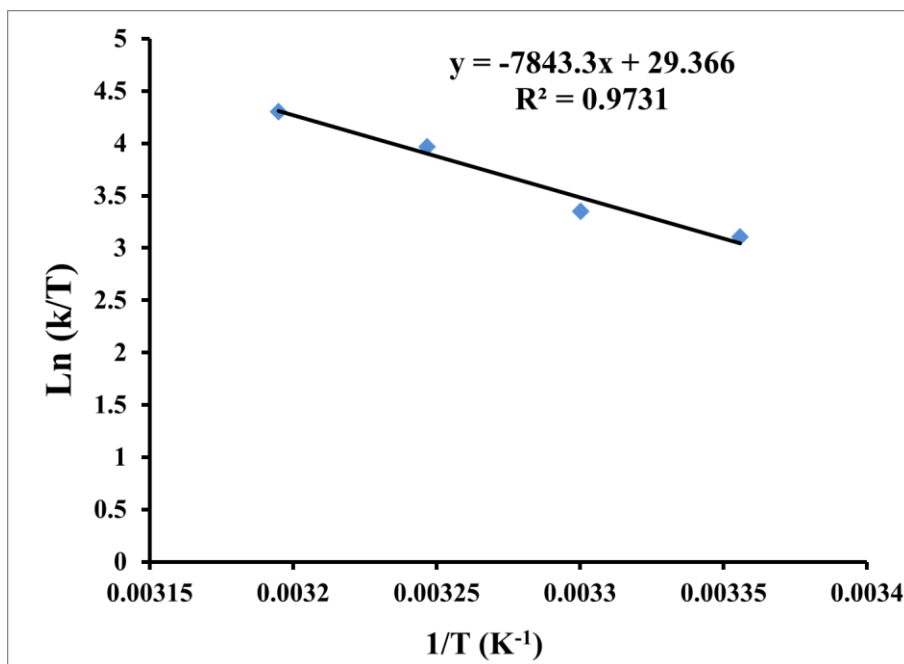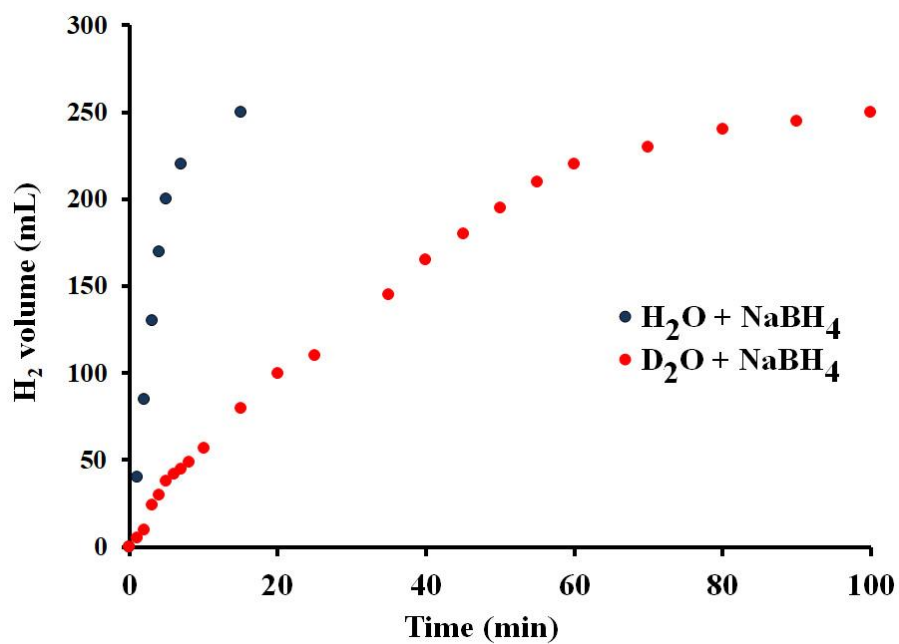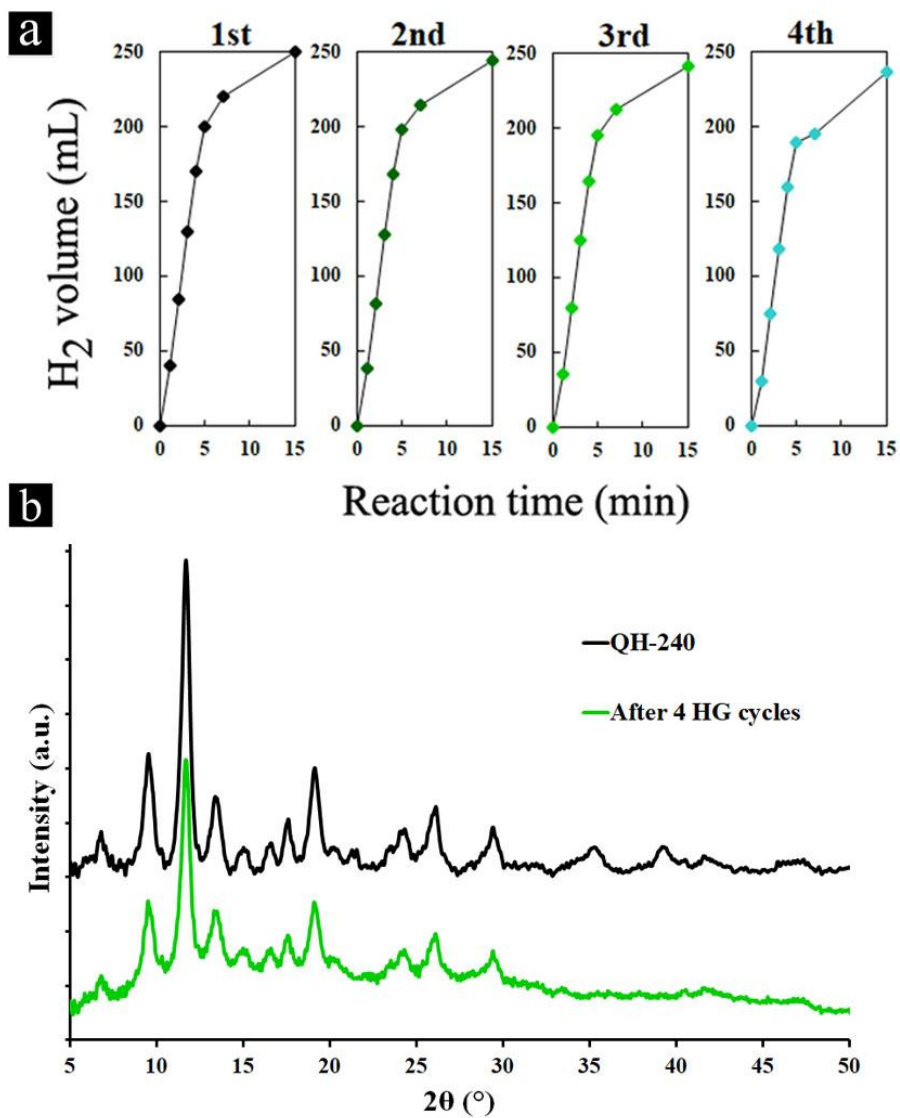**Table S1**. BET surface area, total pore volume, micro- and mesopore volume of the synthesized MOFs.

Sample	S_{BET} (m^{2}g^{-1})	V_t (cm^{3}g^{-1})	V_{micro} (cm^{3}g^{-1})	V_{meso} (cm^{3}g^{-1})
HKUST	1182	0.489	0.462	0.027
QH-200	913	0.436	0.369	0.067
QH-240	160	0.122	0.06	0.062
QH-260	5.6	0.046	0.002	0.044

Table S2. Amount of acid sites in HKUST-1 and QH-240 according to NH_3-TPD measurements.

| Catalyst | weak acid | | Strong acid | | Total active acid sites |
	Peak position (°C)	Value (mmolg^{-1})	Peak position (°C)	Value (mmolg^{-1})	(mmolg^{-1})
HKUST	170	9.1	309	12.6	21.7
QH-240	172	1.7	313	46.8	48.5

Table S3. Effect of QH-240 dosage used as catalyst on TOF for NaBH$_4$ hydrolysis.

Entry	Catalyst dosage (mg)	TOF (ml min^{-1}g^{-1})	Time (min)
1	0	--	60
2	1	3333	60
3	1.5	4505	38
4	2	5909	22
5	2.5	6667	15
6	3	7436	13
7	3.5	7702	12
7	4	7653	10
8	5	7500	8

Reaction conditions: [NaBH$_4$] = 125 mM, T= 25 °C.

Table S4. Comparison of TOF and activation energies (E_a) of HGR from NaBH$_4$ hydrolysis by various catalysts.

Catalyst	TOF (mL.min^{-1}.g^{-1})	E_a (kJ/mol)	Temperature range (°C)	Ref.
CoB/ZIF-8	506	57.7	35	[2]
Co-Cu-B	2120	49.6	20	[3]
Co(II)-Cu(II) 40:60	254.5[a]	-	30	[4]
Co-ZIF-9	3642	-	40	[5]
Quasi HKUST-1 (QH-240)	6667 23200	58.4	25 40	This study

[a] The TOF(s) was calculated from Fig. 7 in Ref. [4].

Table S5. Thermodynamic parameters of HGR on QH-240 at various temperatures.

Catalyst	T (K)	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	R^2
QH-200	298	-72.7	65.21	244.15	0.973
	303	-73.9			
	308	-75.1			
	313	-76.4			

1.   C. Xing, Y. Liu, Y. Su, Y. Chen, S. Hao, X. Wu, X. Wang, H. Cao and B. Li, *ACS Appl. Mater. Interfaces*, 2016, **8 24**, 15430-15438.
2.   Q. Li, W. Yang, F. Li, A. Cui and J. Hong, *Int. J. Hydrogen Energy*, 2018, **43**, 271-282.
3.   X.-L. Ding, X. Yuan, C. Jia and Z.-F. Ma, *Int. J. Hydrogen Energy*, 2010, **35**, 11077-11084.
4.   D. Kılınç, C. Saka and Ö. Şahin, *J. Power Sources*, 2012, **217**, 256-261.
5.   Q. Li and H. Kim, *Fuel Process. Technol.*, 2012, **100**, 43-48.