Supplementary Information

Catalytically active Rh species stabilized by zirconium and hafnium on zeolites

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1. Experimental section

1.1 Reactant agents

All materials were used as received without further purification. Tetraethylorthosilicate (TEOS, 98%, Sinopharm Chemical Reagent Co., Ltd.), tetrapropylammonium hydroxide (TPAOH, 25 wt% aqueous solution, Tianjin Fuchen Chemical Reagent Factory), hafnium(IV) chloride ($HfCl_4$, 99.5%, Shanghai Aladdin Biochemical Technology Co., Ltd.), rhodium(III) chloride hydrate ($RhCl_3.xH_2O$, 99% Rh>38.5%, Innochem Science & Technology Co., Ltd.), chloroplatinic acid hexahydrate ($H_2PtCl_6.6H_2O$, Shanghai Chemical Reagent Co.), ruthenium(III) chloride hydrate ($RuCl_3.xH_2O$, 99% Ru>37%, Innochem Science & Technology Co., Ltd.), zirconium(IV) chloride ($ZrCl_4$, 98%, Shanghai Macklin Biochemical Technology Co., Ltd.), and borane-ammonia complex (NH_3BH_3, AB, 98%, Shanghai Titan Scientific Co., Ltd.). Deionized water was prepared by Millipore (Milli-Q, 18.2 MΩ/cm; Millipore, Bedford, MA).

1.2 Synthetic methods

Synthesis of silicalite-1 zeolite sample. The silicalite-1 (S-1) zeolite was synthesized by using TPAOH as the organic template with the molar composition of 1.0 SiO_2: 0.2 TPAOH: 35 H_2O under hydrothermal conditions at 170 °C for 1 day. Typically, 8.13 g TPAOH solution (25 wt% aqueous solution) was mixed with 27.2 g H_2O under stirring, Then, 10.42 g TEOS was added into the mixture and stirred continuously for 6 h. Finally, the obtained clear solution was transformed into a polytetrafluoroethylene-lined stainless-steel autoclave and crystallized in a pre-heated oven at 170 °C for 1 day. The as-prepared samples were washed thoroughly with water and dried at 80 °C in the oven. The as-synthesized S-1 zeolite sample was calcinated in air at 550 °C for 6 h to remove the organic templates.

Synthesis of Rh/S-1 sample Rh/S-1 catalyst was synthesized by an incipient wetness impregnation method. Typically, 500 mg calcinated S-1 was impregnated with 1 mL of water containing 64 mg $RhCl_3.xH_2O$ aqueous solution (10 wt%). After drastically stirred to allow the solution absorbed into the zeolite, the sample was dried at 80 °C in the oven overnight. The obtained solid (named as Rh^{3+}/S-1) was reduced in flowing hydrogen with linear heating to 400 °C for 2 h and then holding for 2 h and the obtained sample was named as Rh/S-1. The theoretical loading amount of Rh for impregnation is fixed at 0.5 wt%.

Synthesis of RhHf/S-1 sample. RhHf/S-1 sample was prepared by an incipient wetness impregnation method. Typically, 64 mg $RhCl_3.xH_2O$ aqueous solution (10 wt%) was mixed with 133 mg $HfCl_4$ aqueous solution (10 wt%), and certain amount of H_2O was added to form 1 mL solution including bimetallic ions. 500 mg calcinated S-1 was impregnated with the 1 mL of aqueous solution of $RhCl_3$ and $HfCl_4$, and then the mixture was drastically stirred to allow the solution absorbed into the zeolite. After dried in air at 80 °C overnight, the solid (named as $Rh^{3+}Hf^{4+}$/S-1) was reduced in flowing hydrogen with linear heating to 400 °C for 2 h and then holding for 2 h and the obtained sample was named as RhHf/S-1. The theoretical loading amount of Rh for impregnation is fixed at 0.5 wt%.

Synthesis of RhZr/S-1 sample. The synthesis method for RhZr/S-1 sample is similar to that of RhHf/S-1. Differently, 97 mg $ZrCl_4$ aqueous solution (10 wt%) was used instead of $HfCl_4$ solution. The obtained sample before and after the reduction in H_2 atmosphere were named as $Rh^{3+}Zr^{4+}$/S-1 and RhZr/S-1, respectively. The theoretical loading amount of Rh for impregnation is fixed at 0.5 wt%.

Synthesis of Rh/ZSM-5 and RhHf/ZSM-5 samples. Rh/ZSM-5 and RhHf/ZSM-5 samples were synthesized by an incipient wetness impregnation method similar to the preparation of Rh/S-1 and RhHf/S-1. The commercial acidic ZSM-5 zeolite with Si/Al ratio of 31 was purchased in the Alfa Aesar chemicals company.

Synthesis of Rh/SiO_2 and RhHf/SiO_2 samples. Rh/SiO_2 and RhHf/ SiO_2 samples were synthesized by an incipient wetness impregnation method similar to the preparation of

Rh/S-1 and RhHf/S-1. The commercial SiO_2 was purchased in the Alfa Aesar chemicals company. Before impregnation, 1.0 g commercial SiO_2 was treated with 10 mL of 0.1 mol/L NaOH aqueous solution at 100 °C for 2 h and washed thoroughly with deionized water.

Synthesis of Pt/S-1, PtHf/S-1, Ru/S-1, and RuHf/S-1 samples. Pt/S-1 and Ru/S-1 samples were synthesized by incipient wetness impregnation method similar to Rh/S-1. PtHf/S-1 and RuHf/S-1 samples were synthesized by incipient wetness impregnation method similar to RhHf/S-1. Differently, 68 mg $H_2PtCl_6.6H_2O$ aqueous solution (10 wt%) or 65 mg $RuCl_3.xH_2O$ aqueous solution (10 wt%) was used to replace $RhCl_3.xH_2O$ solution. After dried, the obtained samples named as $Pt^{4+}Hf^{4+}$/S-1 and $Ru^{3+}Hf^{4+}$/S-1 the sample was reduced in flowing hydrogen with linear heating to 400 °C for 2 h and then holding for 2 h; the obtained samples were named as PtHf/S-1 and RuHf/S-1, respectively. The theoretical loading amount of Pt/Ru for impregnation is fixed at 0.5 wt%.

1.3 Characterizations

Powder X-ray diffraction (XRD) tests were performed on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å, 50 KV, 200 mA). Chemical compositions were determined by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis using an iCAP 7000 SERIES. X-ray photoelectron spectroscopy (XPS) was obtained from an ESCALAB 250 X-ray photoelectron spectrometer using Al as the exciting source. Nitrogen adsorption-desorption measurements were carried out on a Micromeritics 3-flex analyser at 77 K. Degassing was performed at 300 °C under vacuum for 10 h before measurements. UV-vis diffuse reflectance spectroscopy (UV-Vis DRS) over a range of 190 to 500 nm were recorded on a SHIMADZU U-4100. Baseline correction was carried out using Al_2O_3 powder. Transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) were recorded by Tecnai F20 and JEM-2100F electron microscope operating at an acceleration voltage of 200 kV, respectively. The ^{1}H and ^{29}Si solid-state MAS NMR experiments were performed at 14.09 T on a Bruker AVANCE NEO 600WB spectrometer at resonance frequencies of 600.23 and 119.24 MHz, respectively. Single-pulse ^{1}H MAS NMR experiments were performed using a $\pi/2$ ^{1}H pulse length of 2.27 μs, a repetition time of 2 s, and 30 scans. The magic angle spinning rate for ^{1}H MAS NMR was set to 12 kHz. The ^{1}H MAS NMR signals were referenced to adamantane (1.91 ppm). Single-pulse ^{29}Si MAS NMR spectra with high power proton decoupling were recorded on a 3.2 mm probe, using a $\pi/2$ pulse of 3.6 μs, a recycle delay of 1 s and 3600 scans. The magic angle spinning rate for ^{29}Si MAS NMR was set to 10 kHz. The ^{29}Si MAS NMR spectra were referenced to kaolinite (-91.5 ppm). The data of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were collected at room temperature in the fluorescent mode with a Lytle detector at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF, China).

1.4 Thermal stability and hydrothermal stability tests

The reduction-oxidation treatments were performed to investigate the thermal stability of the RhHf/S-1 and Rh/S-1 catalysts at 600 °C. The catalyst was first calcined in flowing H_2 (30 mL/min) at 600 °C for 2 h, then calcined in the flow of air at 600 °C for 2 h. The catalyst was then retreated up to 5 consecutive cycles. The finally obtained samples were named as Rh/S-1-C5 and RhHf/S-1-C5, respectively.

To investigate the hydrothermal stability of catalysts, the RhHf/S-1 and Rh/ S-1 catalysts were loaded in a quartz reactor and heated in 10 vol% water vapor at 700 °C for 1 h. The samples after hydrothermal treatments were named as Rh/S-1-HT and RhHf/S-1-HT, respectively.

1.5 Catalytic tests

Hydrolysis reaction of borane-ammonia complex (AB). The reaction was carried out in a 25 ml double-necked round-bottomed flask connected to the gas collector at 25 °C with the stirring speed of 800 rpm. Firstly, dispersing the metal supported catalyst in 0.5 ml deionized in the flask (the molar ratio of metal/AB of all catalysts were fixed at 0.001). Then, 0.5 ml of AB solution (2 mol/L) was added to the bottle with a syringe. The amount of hydrogen generated by the reaction is recorded by reading the weight of the excurrent water on the electronic balance (Scheme S1).

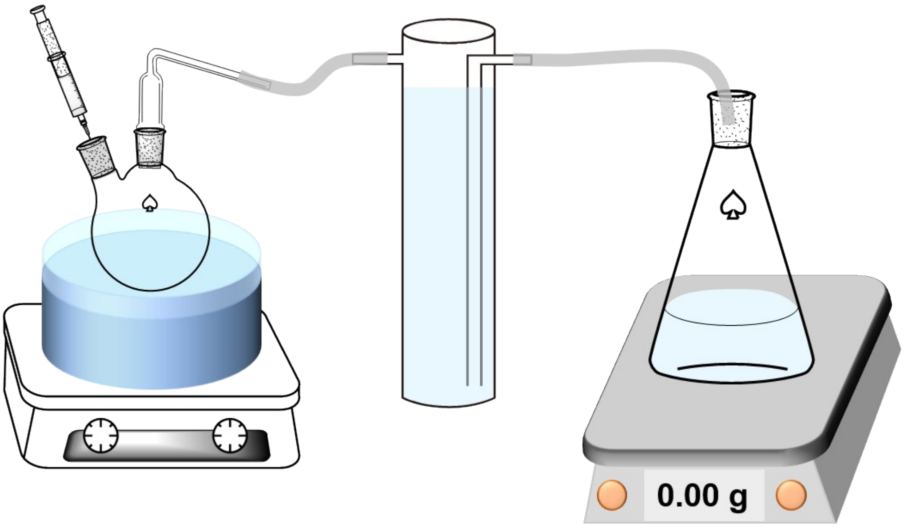
The Calculation of Turnover Frequency (TOF). The total TOF was calculated based on the number of total metal atoms in the catalysts when the conversion of AB reached up to 100%. The calculation equation is as below:

$$TOF = \frac{PV_{H_2}/RT}{n_{total\ metal}\,t}$$

Where P is the atmospheric pressure (101.325 kPa), V_{H2} is the total volume of the released gas, R is the universal gas constant (8.3145 m^3 Pa mol^{-1} K^{-1}), T is the room temperature (298 K), $n_{total\ metal}$ is the mole of total precious metal atoms in catalyst, and t is the time of completion of gas generation in minute.

Cascade hydrogenation of various nitroarenes coupling with AB hydrolysis. The cascade reactions were carried out in a 50 mL round-bottom flask at 25 °C. Typically, 0.1 mmol of nitroarene (such as nitrobenzene, 1-methyl-2-nitrobenzene, 1-methyl-4-nitrobenzene, 1,2-dimethyl-4-nitrobenzene, 1,3-dimethyl-5-nitrobenzene, 1-fluoro-4-nitrobenzene, 1-chloro-4-nitrobenzene, 1-bromo-4-nitrobenzene, and 1-nitronaphthalene) was dissolved into a mixture of 12 mL deionized water and 8 mL methanol under magnetic stirring. Then certain amount of catalysts were added in the flask (the molar ratio of metal Rh/nitroarene was fixed at 0.019). The reaction was begun with the addition of 0.5 ml AB solution (2 mol/L) into the bottle through a syringe. After extracted with ethyl acetate, the reactant and products were analyzed by Gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with a TG-5 MS column, 60 m × 320 μm × 25 μm).

2. Supplementary Figures and Tables



Scheme S1. Schematic of reaction system of H_2 generation from AB hydrolysis.

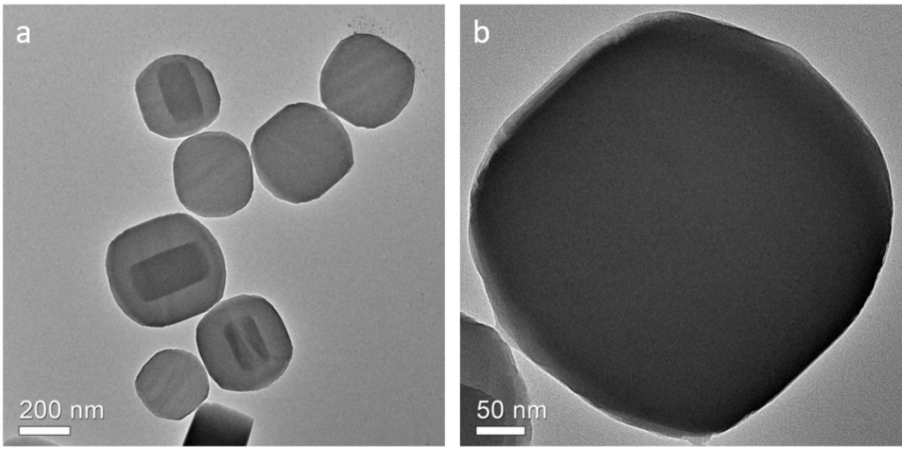


Fig. S1 TEM images of pure S-1.

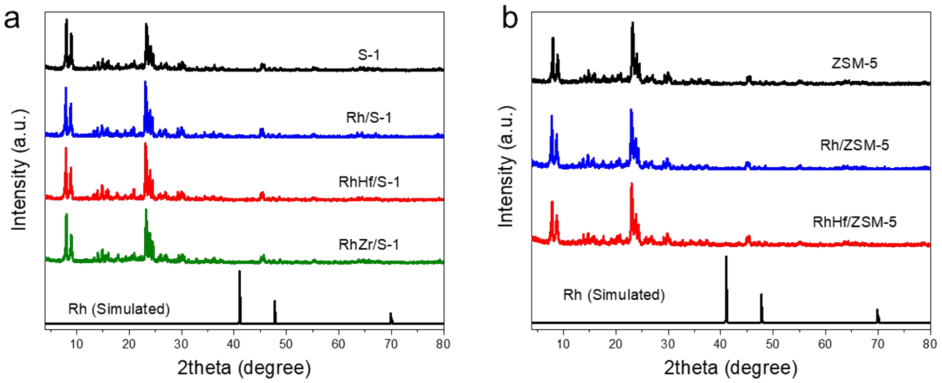


Fig. S2 The powder X-ray diffraction (XRD) patterns of (a) S-1, Rh/S-1, RhHf/S-1, RhZr/S-1, (b) ZSM-5, Rh/ZSM-5, RhHf/ZSM-5, and metal Rh (simulated).

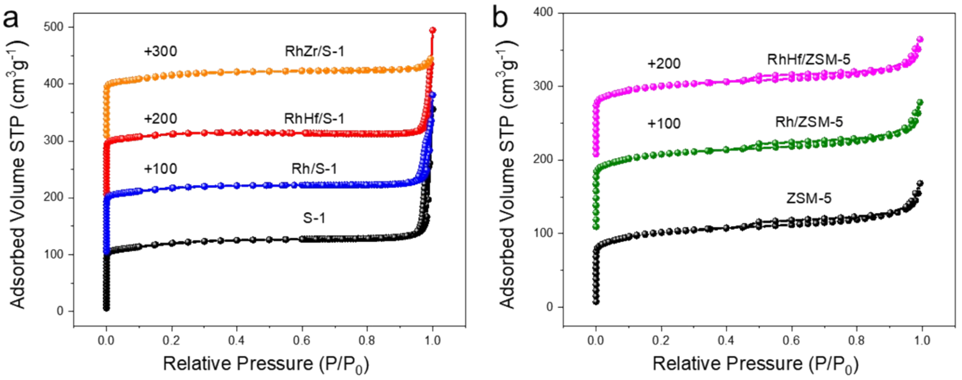


Fig. S3 N_2 adsorption-desorption isotherms of (a) S-1, Rh/S-1, RhHf/S-1, RhZr/S-1, (b) ZSM-5, Rh/ZSM-5, and RhHf/ZSM-5.

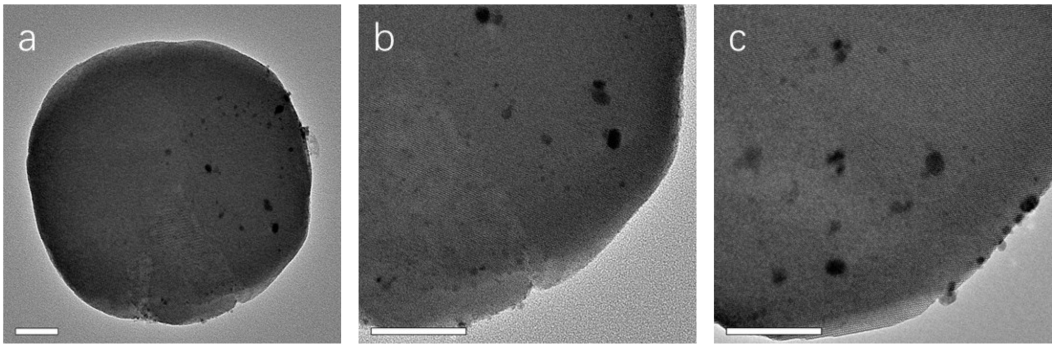


Fig. S4 TEM images of Rh/S-1 zeolite samples after reduction by H_2 at 400 °C. Scale bars, 50 nm.

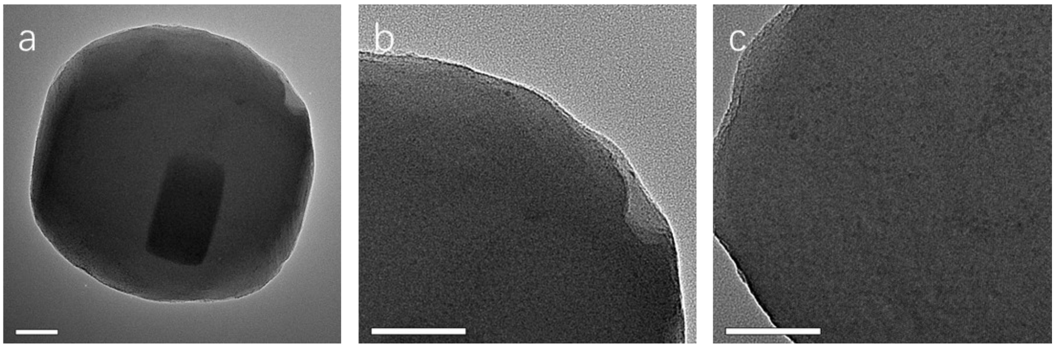


Fig. S5 TEM images of RhHf/S-1 zeolite samples after reduction by H_2 at 400 °C. Scale bars, 50 nm.

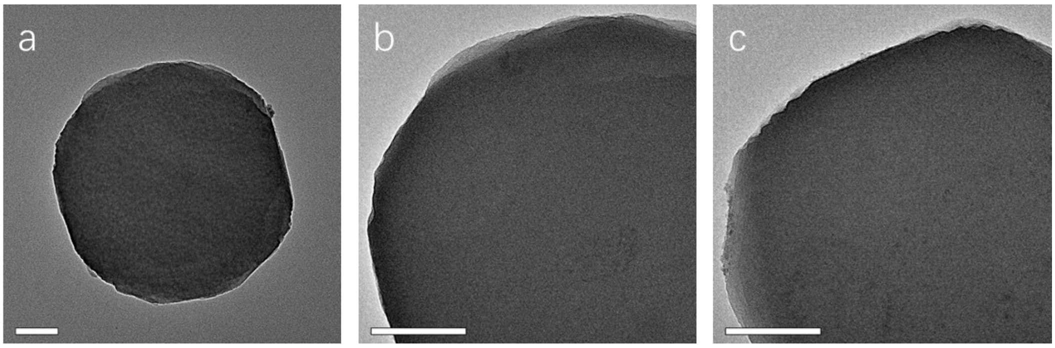


Fig. S6 TEM images of RhZr/S-1 zeolite samples after reduction by H_2 at 400 °C. Scale bars, 50 nm.

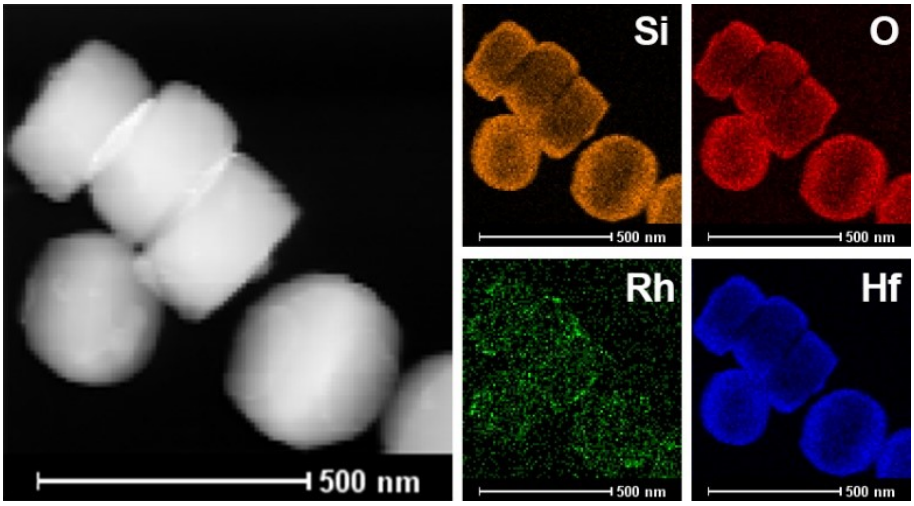


Fig. S7 High-angle annular dark field scanning transmission electron microscopy (HAADF STEM) image and elemental mappings for Si, O, Rh and Hf elements of RhHf/S-1 sample.

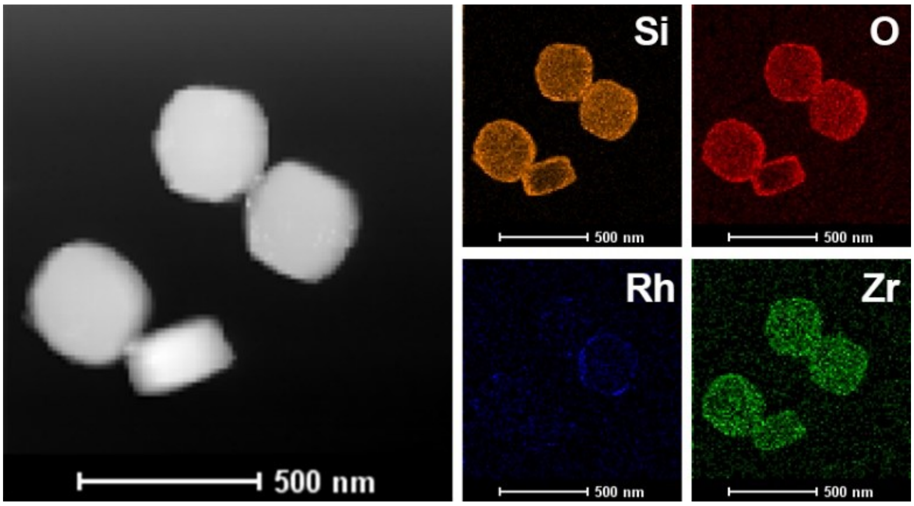


Fig. S8 High-angle annular dark field scanning transmission electron microscopy (HAADF STEM) image and elemental mappings for Si, O, Rh and Zr elements of RhZr/S-1 sample.

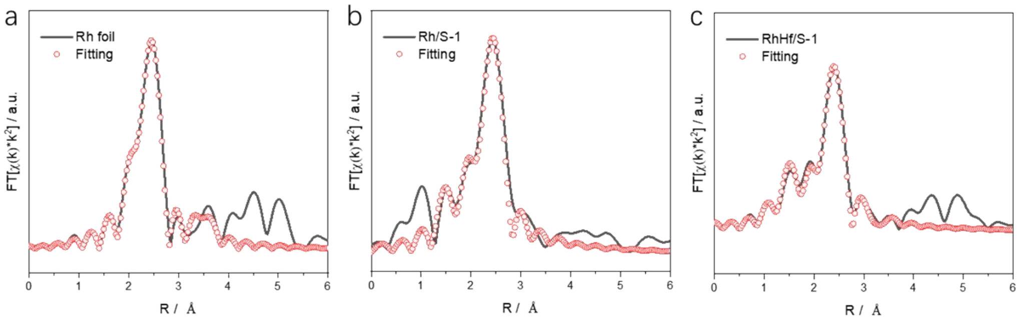


Fig. S9 Fourier transform of k^2-weighted EXAFS spectra of (a) Rh foil, (b) Rh/S-1 and (c) RhHf/S-1 at Rh K-edge.

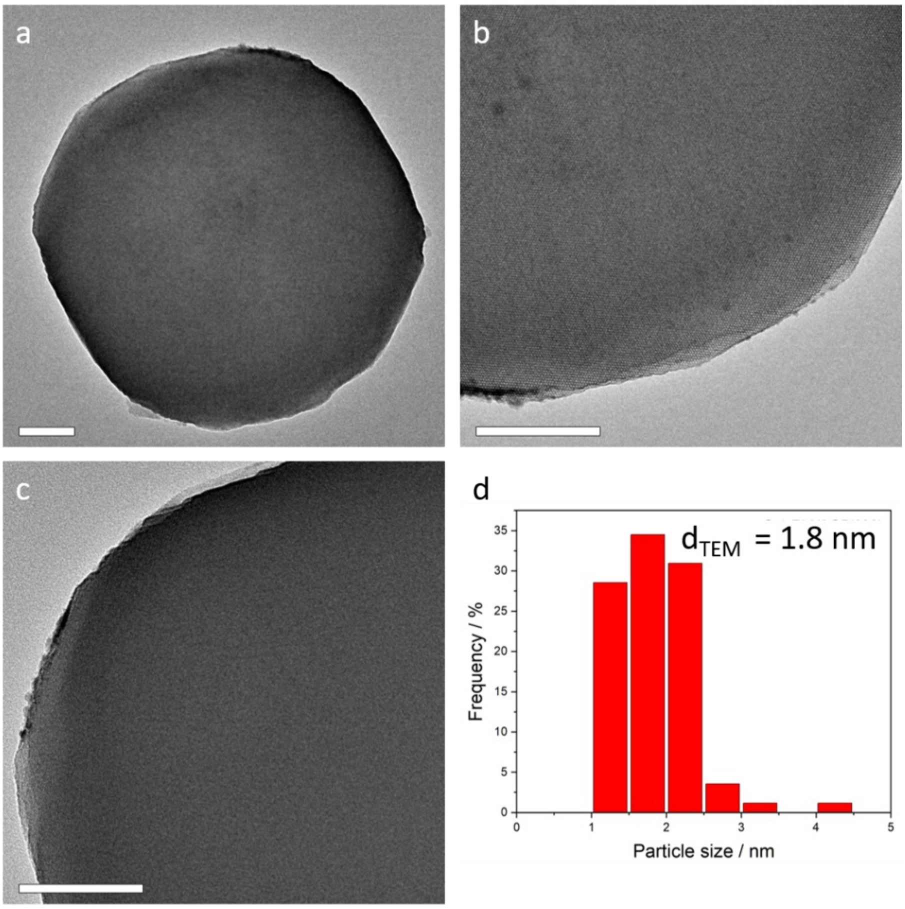


Fig. S10 TEM images and the corresponding particle size distribution of RhHf/S-1 sample after 5 cycles of H_2-O_2 treatment at 600 °C (RhHf/S-1-C5), Scale bars, 50 nm.

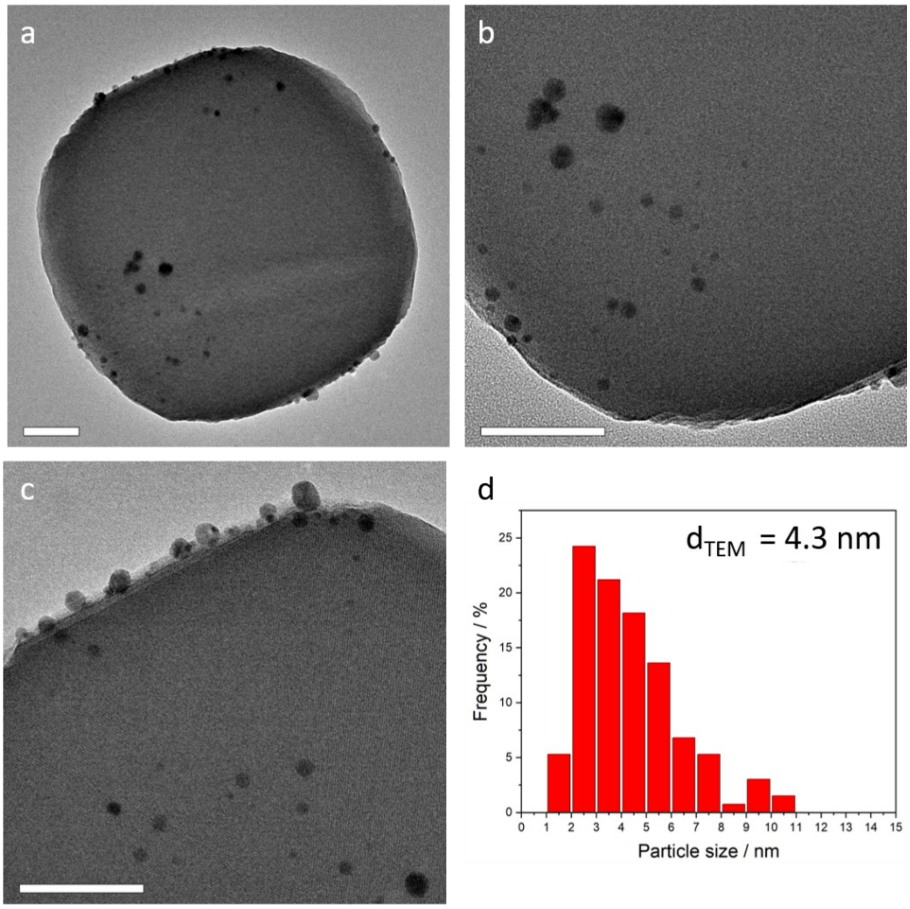


Fig. S11 TEM images and the corresponding particle size distribution of Rh/S-1 sample after 5 cycles of H_2-O_2 treatment at 600 °C (Rh/S-1-C5), Scale bars, 50 nm.

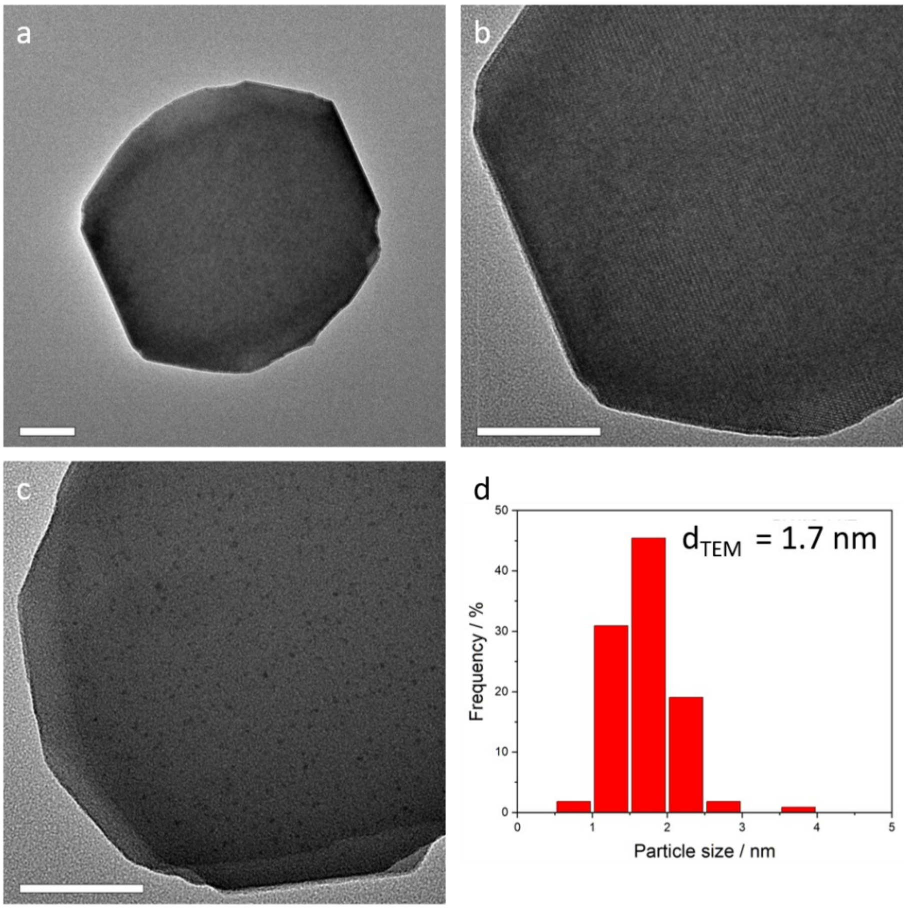


Fig. S12 TEM images and the corresponding particle size distribution of RhHf/S-1 sample after hydrothermal treatment at 700 °C for 1 hour (RhHf/S-1-HT), Scale bars, 50 nm.

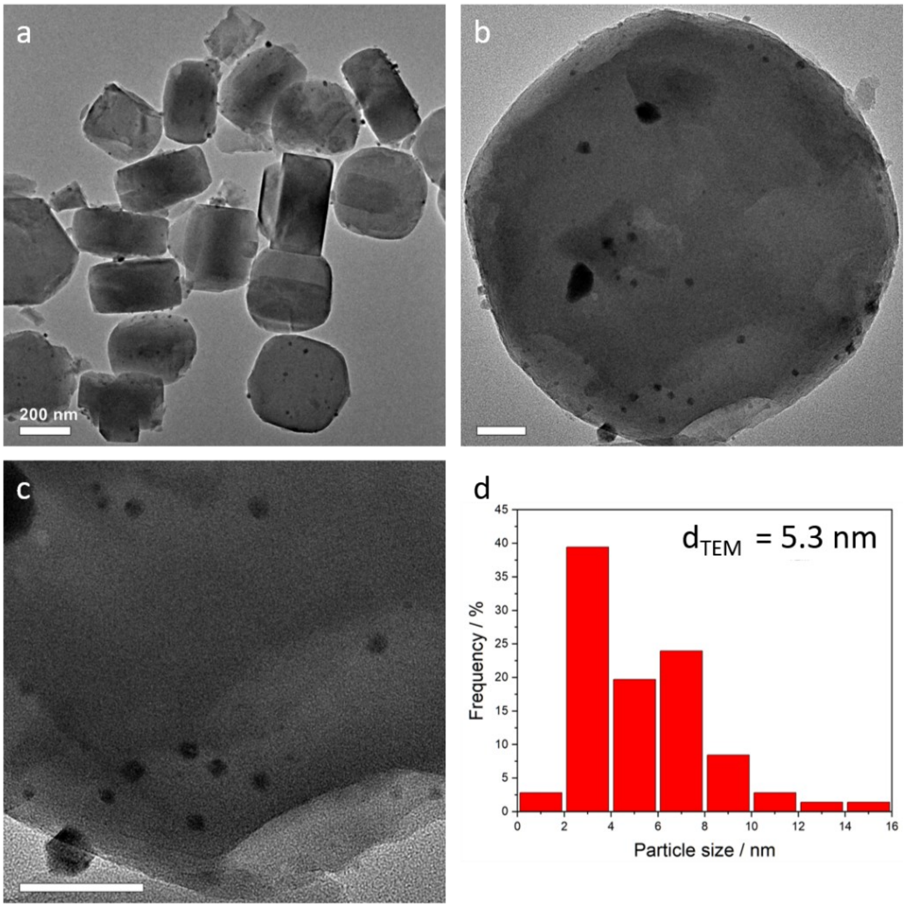


Fig. S13 TEM images and the corresponding particle size distribution of Rh/S-1 sample after hydrothermal treatment at 700 °C for 1 hour (Rh/S-1-HT), Scale bars, (a) 200 nm, (b-c) 50 nm.

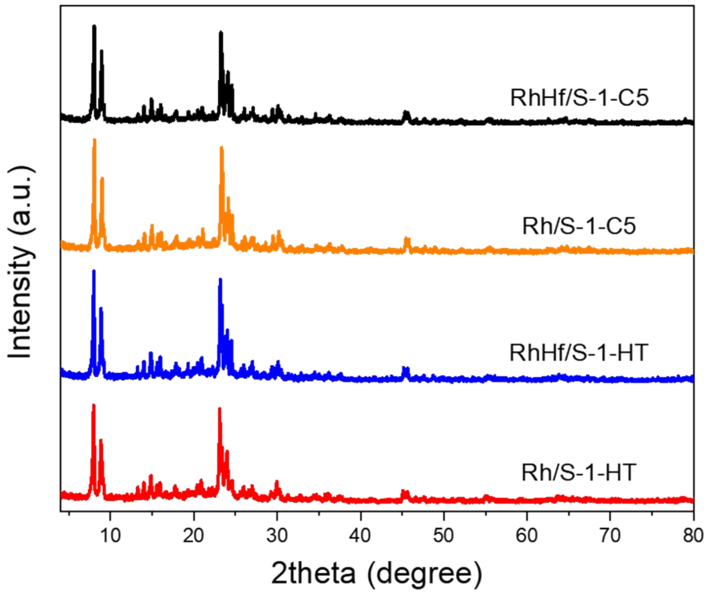


Fig. S14 XRD patterns of samples after 5 cycles of H_2-O_2 treatment (RhHf/S-1-C5 and Rh/S-1-C5) and the samples after water vapor treatment (RhHf/S-1-HT and Rh/S-1-HT).

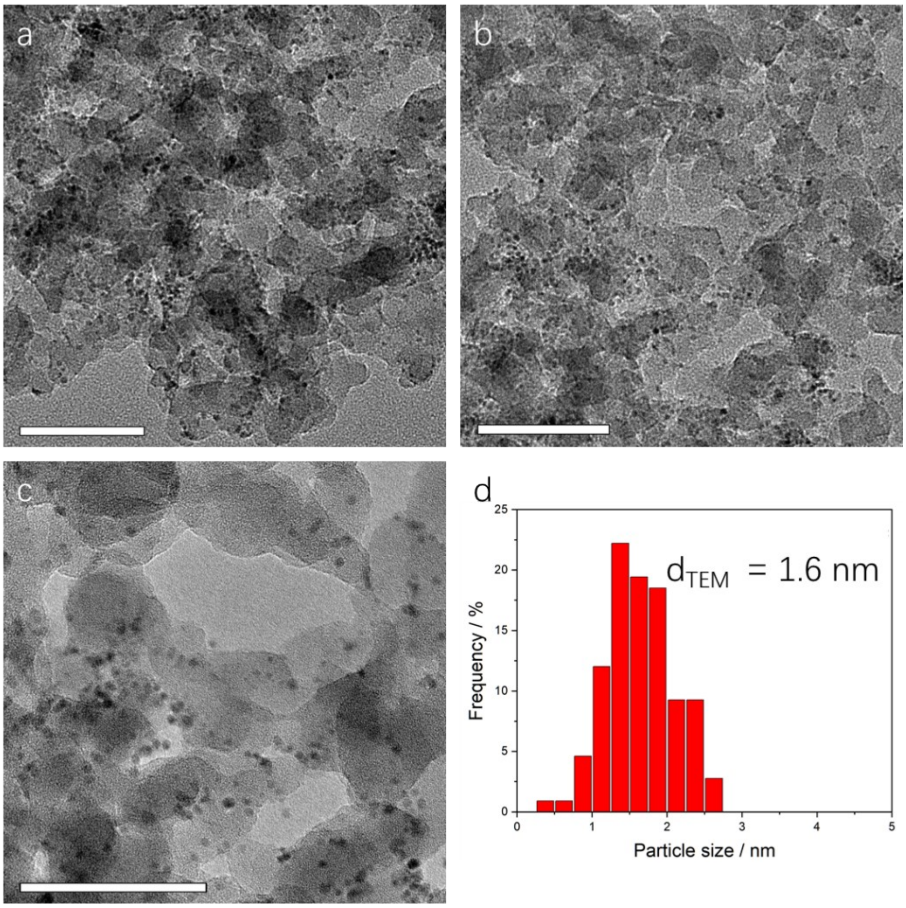


Fig. S15 TEM images and the corresponding particle size distribution of RhHf/SiO_2 sample, Scale bars, 50 nm.

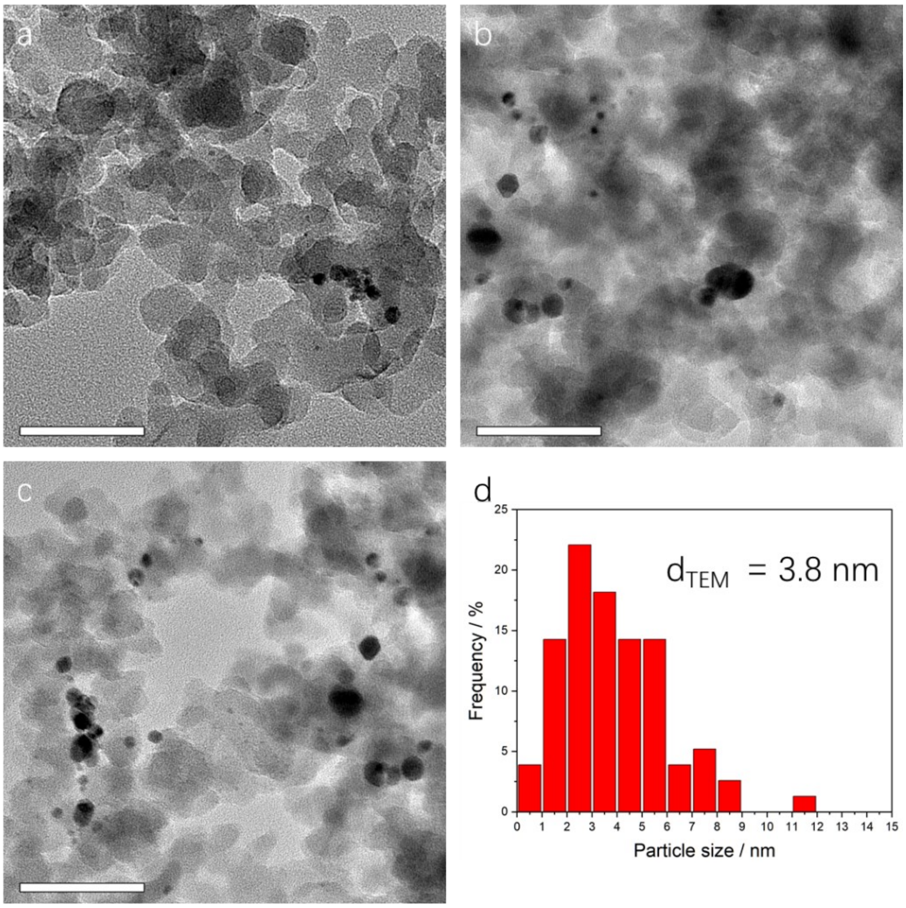


Fig. S16 TEM images and the corresponding particle size distribution of Rh/SiO_2 sample, Scale bars, 50 nm.

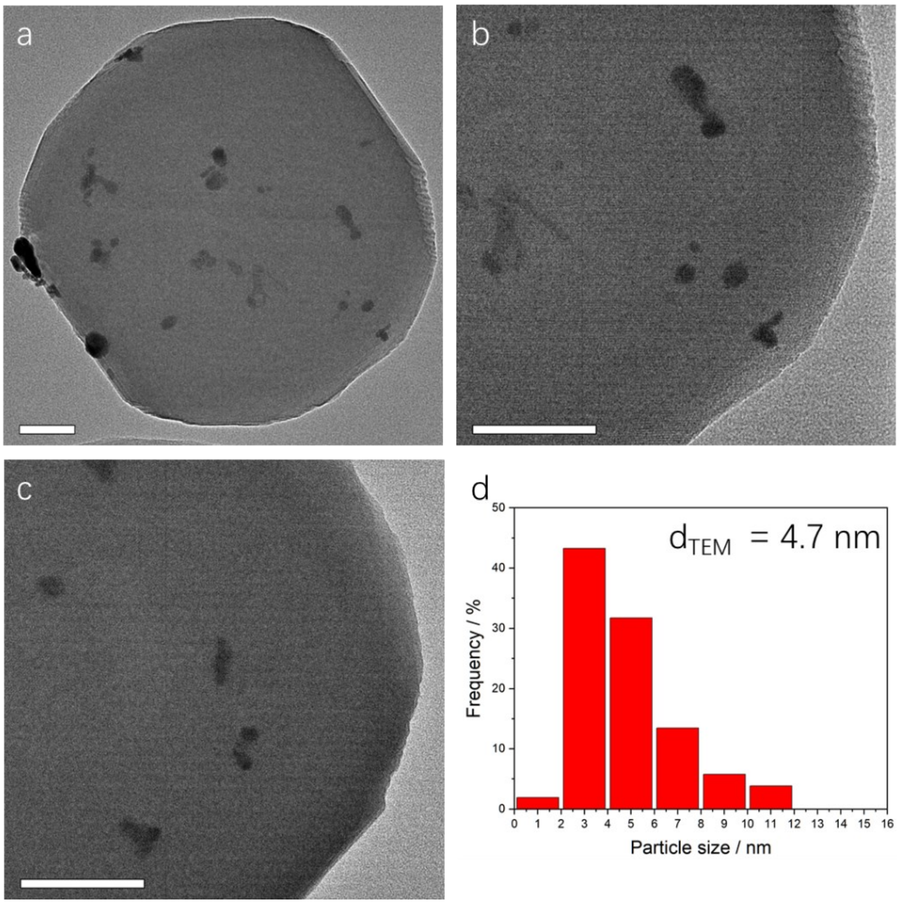


Fig. S17 TEM images and the corresponding particle size distribution of Pt/S-1 sample, Scale bars, 50 nm.

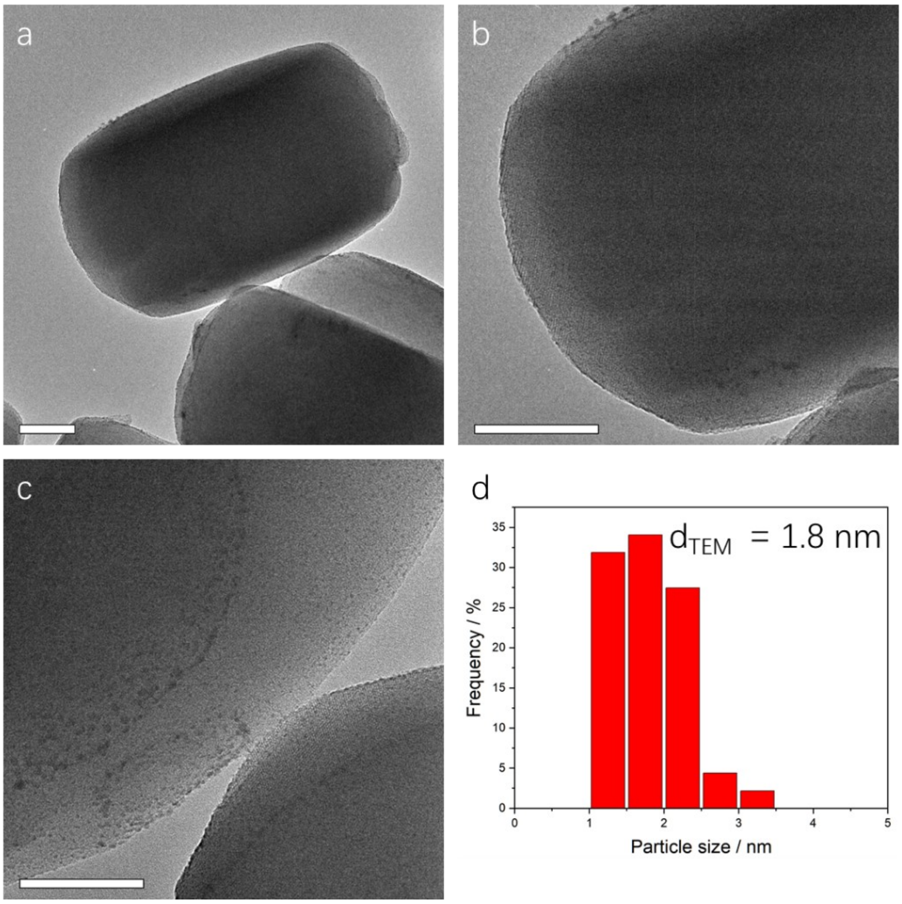


Fig. S18 TEM images and the corresponding particle size distribution of PtHf/S-1 sample, Scale bars, 50 nm.

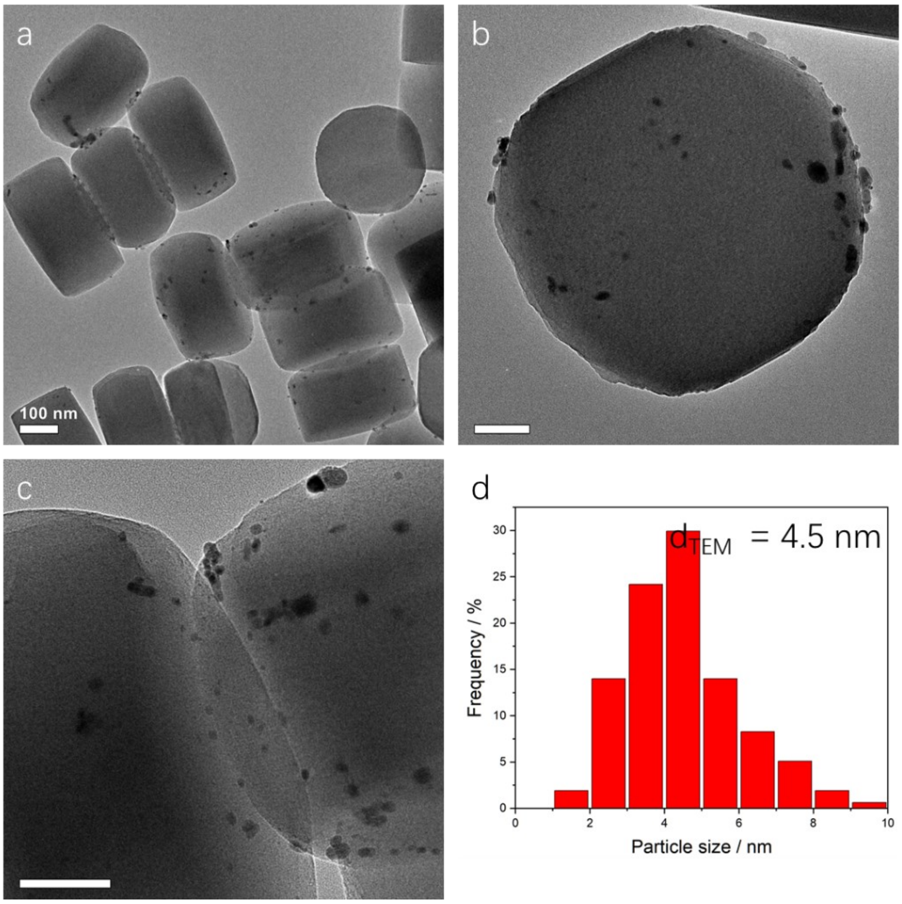


Fig. S19 TEM images and the corresponding particle size distribution of Ru/S-1 sample Scale bars, (a) 100 nm, (b-c) 50 nm.

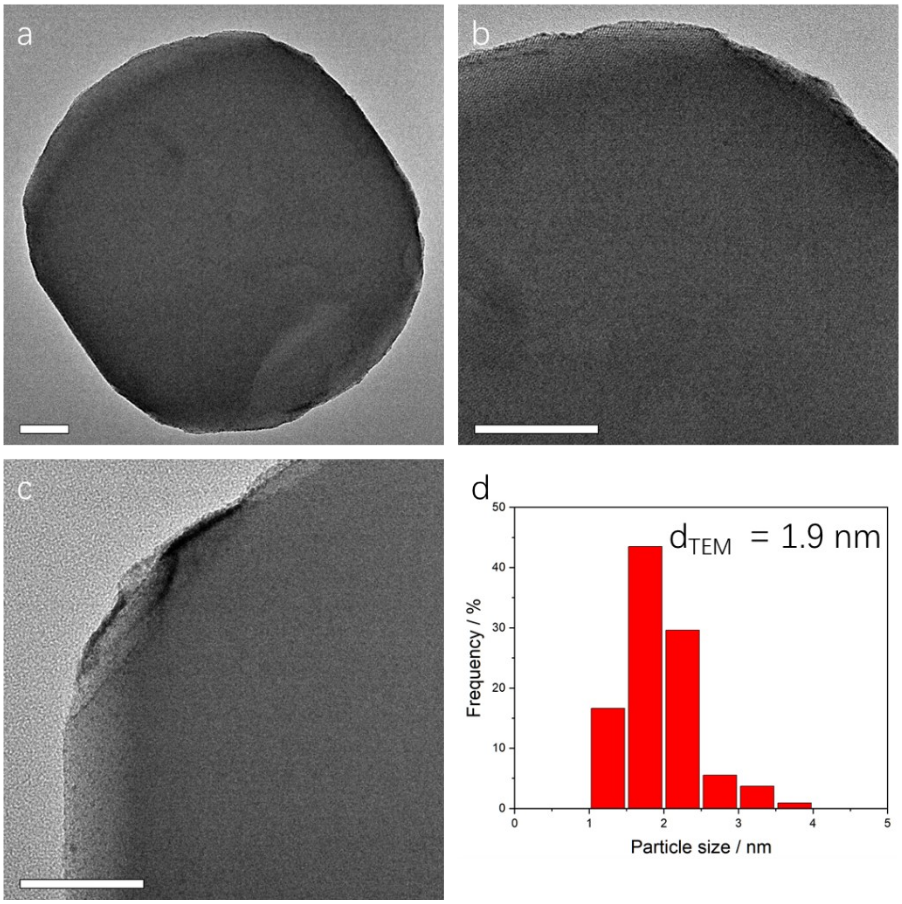


Fig. S20 TEM images and the corresponding particle size distribution of RuHf/S-1 sample, Scale bars, 50 nm.

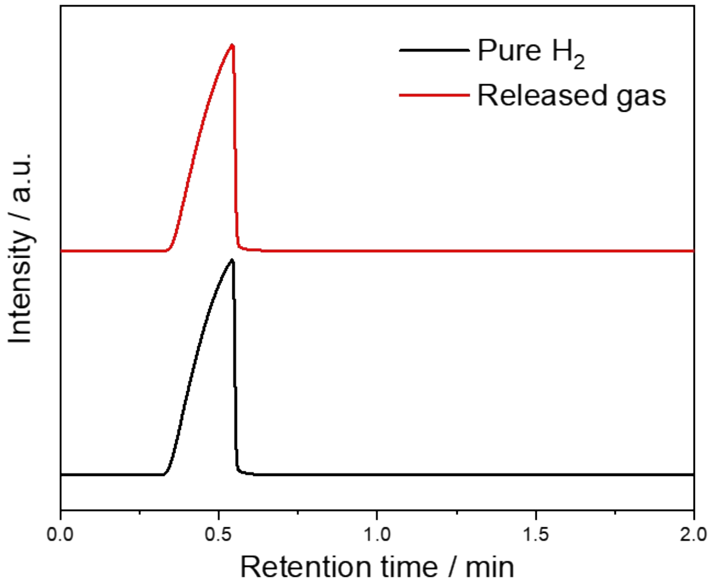


Fig. S21 GC spectra for the released gas from AB hydrolysis over RhHf/S-1 and pure H_2.

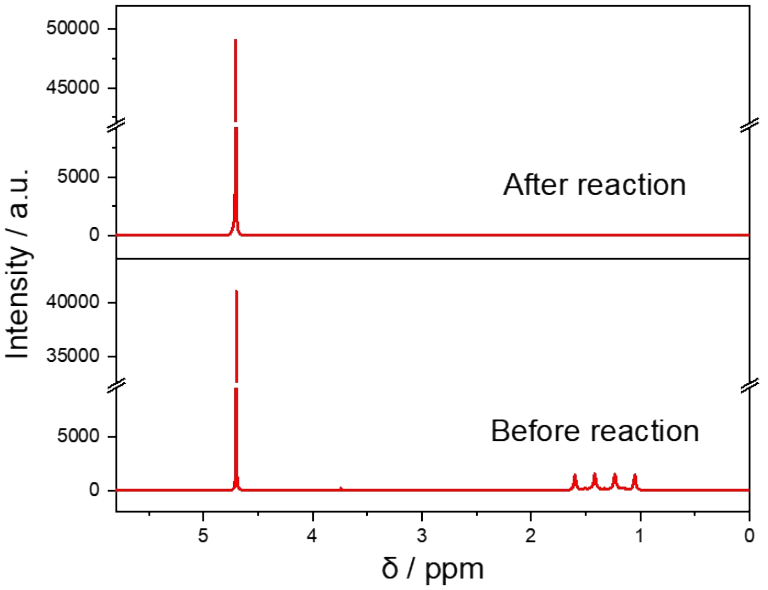


Fig. S22 ^{1}H NMR spectra of the NH_3BH_3 solution in D_2O before and after reactions.

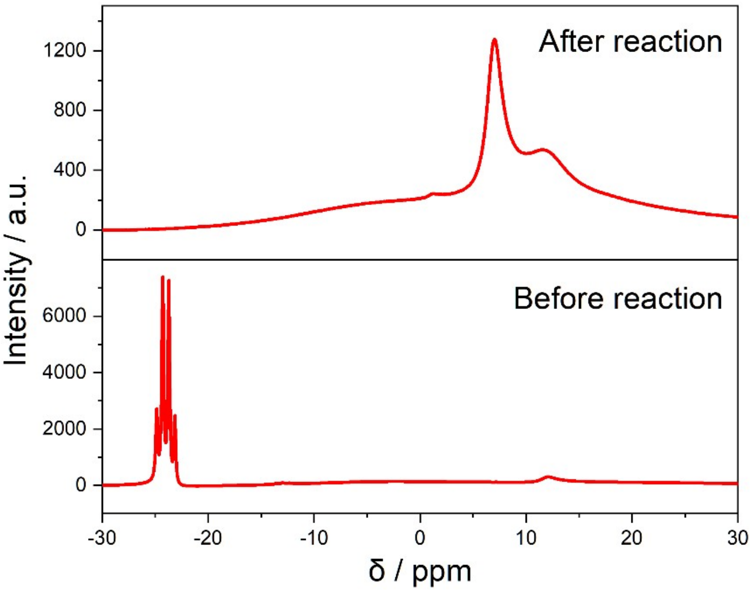


Fig. S23 ^{11}B NMR spectra of the NH_3BH_3 solution in D_2O before and after reactions.

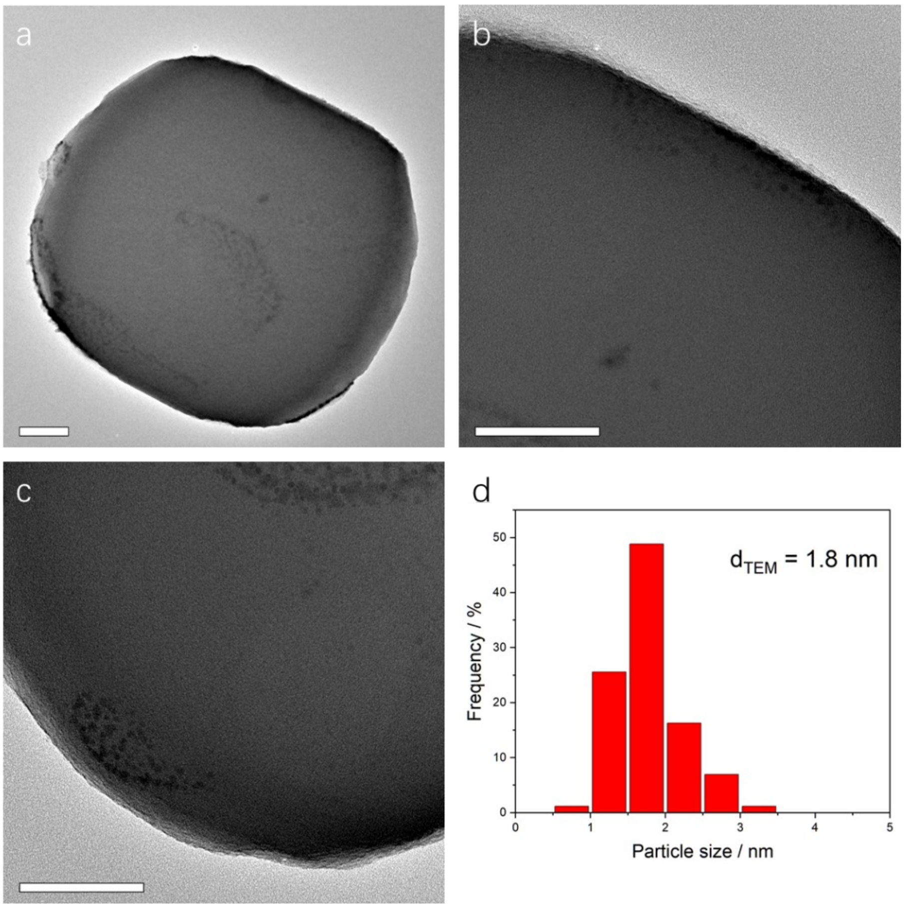


Fig. S24 TEM images and the corresponding particle size distribution of RhHf/S-1(800°C) sample, Scale bars, 50 nm.

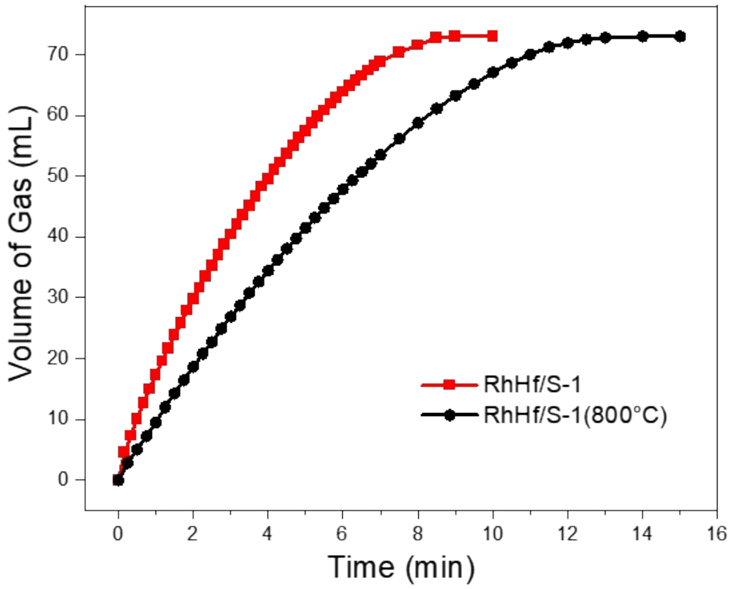


Fig. S25 The volume of the H_2 produced from AB hydrolysis versus time over RhHf/S-1 and RhHf/S-1(800°C) catalysts, reaction conditions: 25 °C, 1 mol/L of AB, $n_{Rh}/n_{AB} = 0.001$.

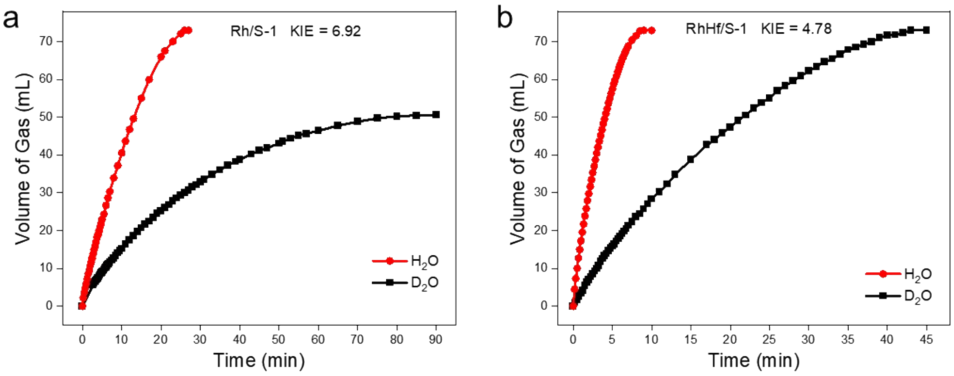


Fig. S26 Kinetic isotope measurements and catalytic activity of H_2 generation from AB hydrolysis over various zeolite catalysts. The volume of the H_2 produced from AB hydrolysis using H_2O and D_2O versus time over (a) Rh/S-1 and (b) RhHf/S-1. Reaction conditions: 25 °C, 1 mol/L of AB, $n_{Rh}/n_{AB} = 0.001$.

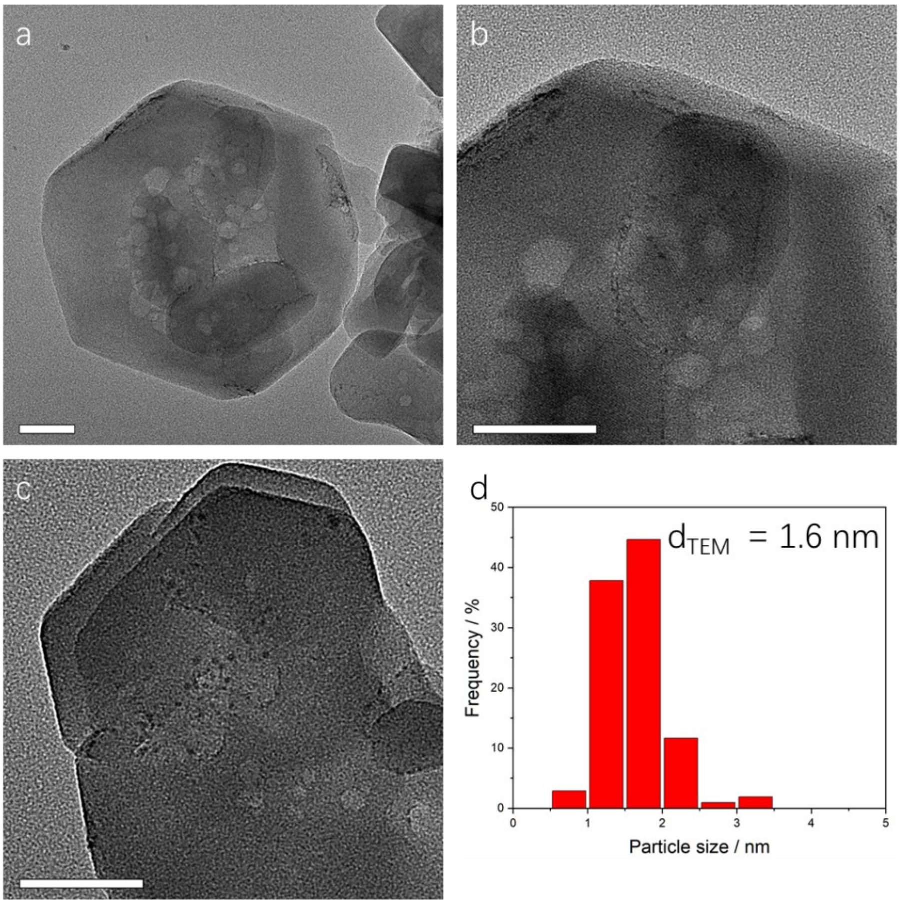


Fig. S27 TEM images and the corresponding particle size distribution of RhHf/ZSM-5 sample, Scale bars, 50 nm.

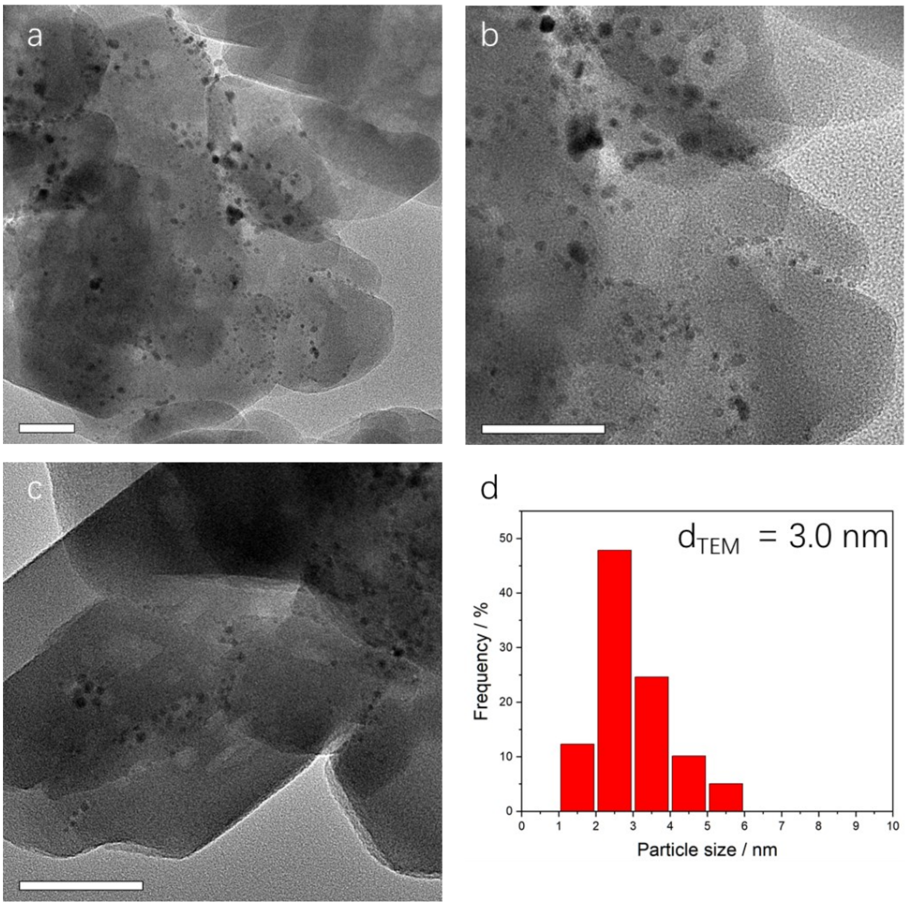


Fig. S28 TEM images and the corresponding particle size distribution of Rh/ZSM-5 sample, Scale bars, 50 nm.

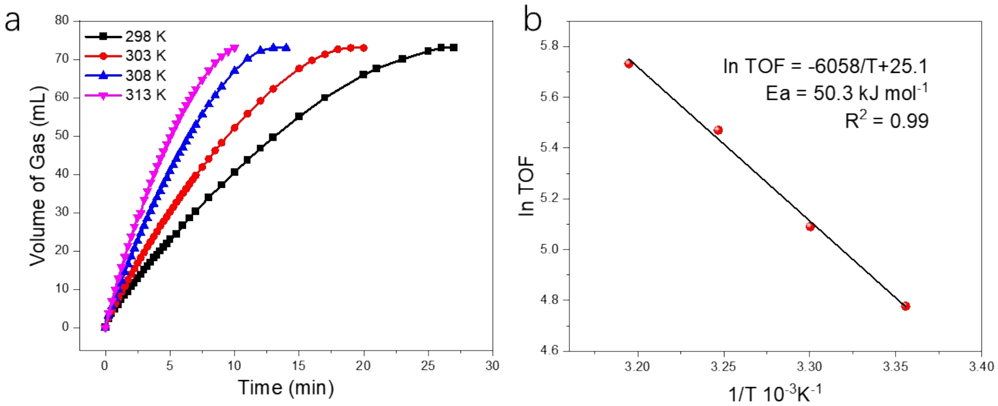


Fig. S29 (a) Volume of the H_2 generated from AB (1 M) hydrolysis versus time at various temperatures over Rh/S-1 catalyst, (b) Arrhenius plot (ln TOF versus 1/T).

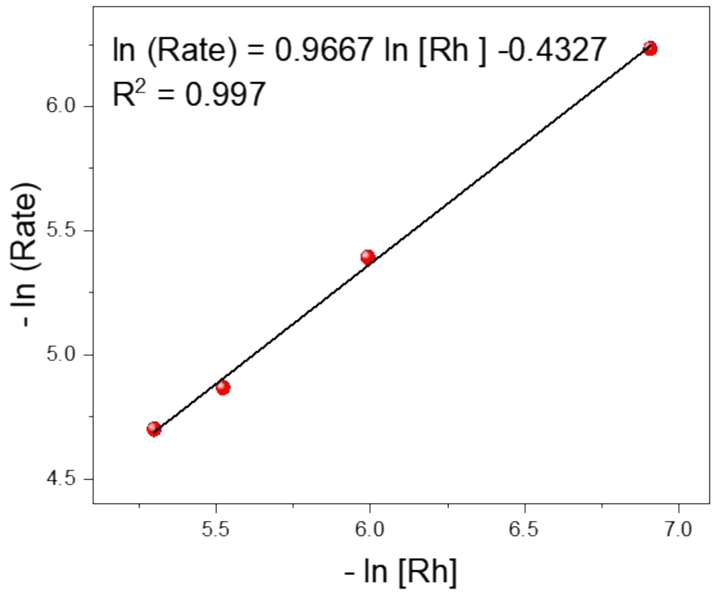


Fig. S30 The logarithmic plots of hydrogen generation rate versus concentration at 25 °C catalyzed over RhHf/S-1 catalyst.

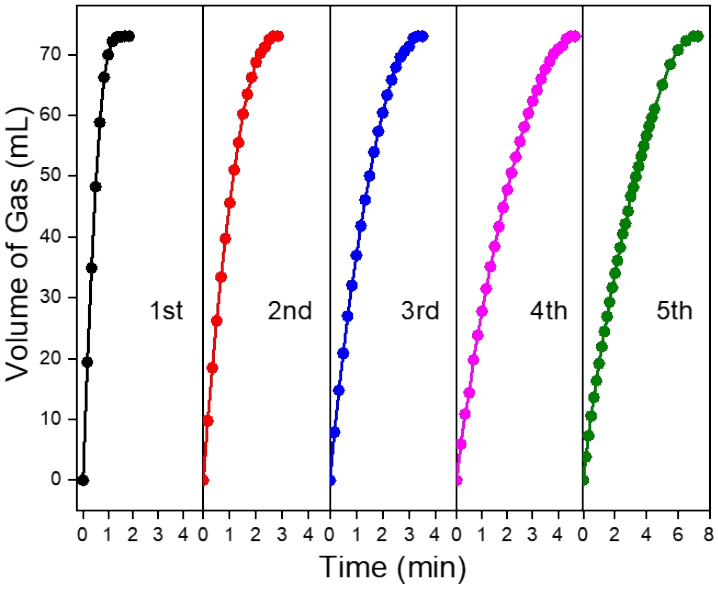


Fig. S31 The recycling tests of AB hydrolysis over RhHf/S-1 catalyst, reaction conditions: 25 °C, 1 mol/L of AB, $n_{Rh}/n_{AB} = 0.005$.

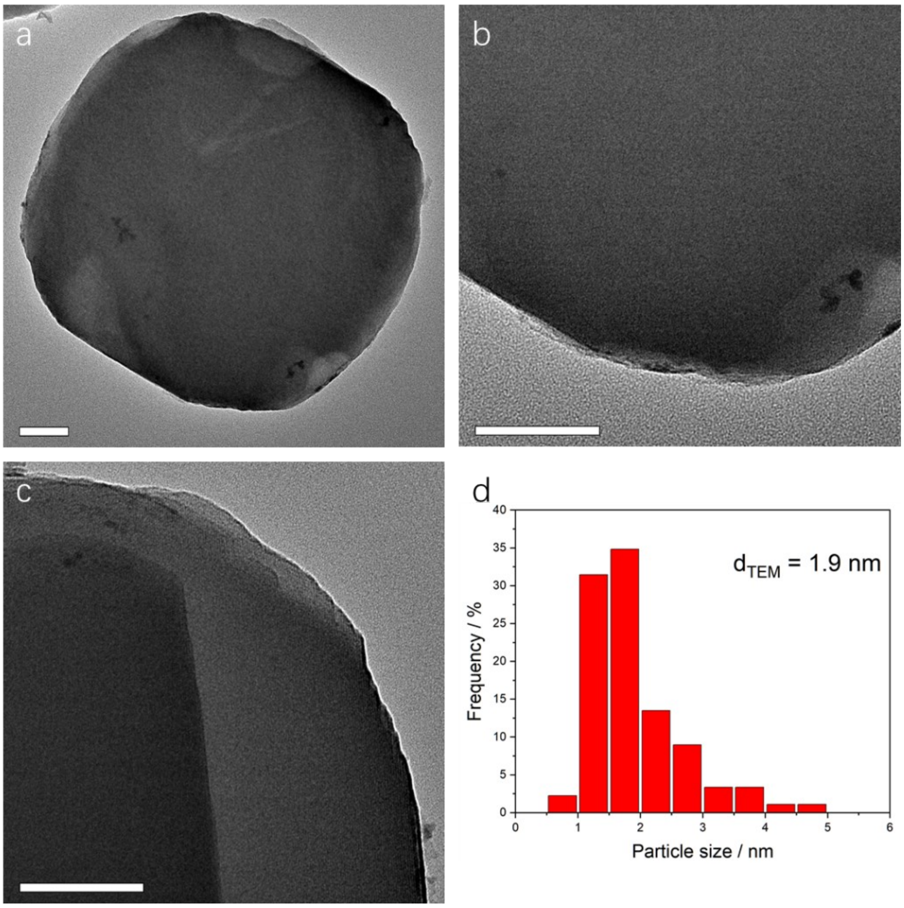


Fig. S32 TEM images and the corresponding particle size distribution of used RhHf/S-1 catalyst after five recycling tests of AB hydrolysis, Scale bars, 50 nm.

Table S1. Metal loading and porosity of various zeolite samples.

Sample	Metal loading[a] (wt%)					S_{BET}[b] (m^2/g)	S_{micro}[c] (m^2/g)	S_{ext}[c] (m^2/g)	V_{total}[d] (cm^3/g)	V_{micro}[c] (cm^3/g)
	Rh	Hf	Zr	Al	Si/Al					
silicalite-1	-	-		-	-	460	328	132	0.45	0.13
Rh/S-1	0.12	-		-	-	452	333	119	0.35	0.13
RhHf/S-1	0.32	1.43		-	-	434	328	106	0.35	0.13
RhZr/S-1	0.45	-	0.68	-	-	437	289	148	0.22	0.11
Rh/ZSM-5	0.27	-		1.43	31	403	261	142	0.28	0.11
RhHf/ZSM-5	0.43	1.43		1.42	31	374	233	141	0.25	0.09

[a] Measured by determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). [b] Specific surface area calculated from the nitrogen adsorption isotherm using the BET method. [c] S_{micro} (micropore area), S_{ext} (external surface area), and V_{micro} (micropore volume) calculated using the t-plot method. [d] Total pore volume at $P/P_0 = 0.99$.

Table S2. The binding energy of Rh($3d_{5/2}$), Hf^{4+} ($4f_{5/2}$) and Hf^{4+} ($4f_{7/2}$) calculated from XPS data for the reduced samples.

Sample	$Rh^{\delta+}$ (eV)	Rh^0 (eV)	Rh^0 (%)	$Hf^{4+}4_{f5/2}$ (eV)	$Hf^{4+}4f_{7/2}$ (eV)
Rh/S-1	-	307.5	100	-	-
RhHf/S-1	310.1	307.9	84	18.5	16.8
Hf/S-1	-	-	-	18.7	17.0
HfO_2	-	-	-	18.8	17.1

Table S3. Structure parameters of Rh/S-1 and RhHf/S-1 as well as Rh foil extracted from the EXAFS fitting.

	Shell	C.N.[a]	R (Å)[b]	σ^2 (Å^2)[c]	ΔE_0 (eV)[d]
Rh/S-1	Rh-O	1.7±0.4	2.04±0.01	0.003±0.001	-1.6±1.4
	Rh-Rh	6.3±1.0	2.69±0.05		
RhHf/S-1	Rh-O	1.5±0.4	2.02±0.02	0.004±0.001	-4.7±1.3
	Rh-Rh	4.4±0.7	2.67±0.01		
	Rh-Hf	1.6±0.3	3.54±0.05		
Rh foil	Rh-Rh	12	2.69±0.003	0.003±0.0005	3.3±0.6

[a] C.N.: coordination number; [b] R: the distance between absorber and backscatter atoms. [c] σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); [d] ΔE_0 is an edge-energy shift (the difference between the zero-kinetic energy value of the sample and that of the theoretical model).

Table S4. The summary of TOF values of various catalysts for the AB hydrolysis.

Catalysts	n_{Rh}/n_{AB}	Temperature /K	TOF [a] /mol_{H2} mol_{metal}^{-1} min^{-1}	TOF [b] /mol_{H2} mol_{metal}^{-1} min^{-1}
RhHf/S-1	0.001	298	363	801
Rh/S-1	0.001	298	119	211
Rh/ZSM-5	0.001	298	281	530
RhHf/ZSM-5	0.001	298	412	960
RhHf/S-1	0.001	303	488	1015
RhHf/S-1	0.001	308	661	1277
RhHf/S-1	0.001	313	841	1579
Rh/S-1	0.001	303	162	293
Rh/S-1	0.001	308	238	414
Rh/S-1	0.001	313	309	543

[a] The TOF values were calculated with a conversion of AB of 100%. [b] The TOF values were calculated with a conversion of AB of less than 20%.