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Electronic Supplementary Information

Ru–B nanoparticles on metal-organic framework as excellent catalyst for benzene hydrogenation to cyclohexane under mild reaction conditions

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1. Preparation

(1) Materials

Analytical grade aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$), chromic nitrate ($Cr(NO_3)_3{\cdot}9H_2O$), sodium borohydride (KBH_4), 1,4-benzenedicarboxylic acid (H_2BDC), toluene, *p*-xylene, and mesitylene were purchased from Sinopharm. Ethanol (CH_3CH_2OH) was purchased from Shanghai Zhenxing. N,N-dimethylformamide (DMF) was purchased from Chinasun. Hydrofluoric acid (HF, 40%) was purchased from Jiangsu Shengtong. Ruthenium trichloride ($RuCl_3{\cdot}3H_2O$) was purchased from Shanghai Aoke. Benzene was purchased from Shanghai Baosteel. *o*-Xylene and *m*-xylene were purchased from Adamas-Beta.

(2) Synthesis of the MIL-53(Al), MIL-53(Cr), and MIL-53(AlCr) MOFs

MIL-53(Al): MIL-53(Al) was synthesized following the method reported by Loiseau *et al.*[1] under hydrothermal condition using $Al(NO_3)_3{\cdot}9H_2O$ and H_2BDC as the starting materials. The molar composition of the starting gels was 1 Al (20.8 g):0.5 H_2BDC (4.61 g):80 H_2O. The synthesis was carried out in a 100 ml Teflon-lined stainless steel autoclave at 220°C under autogenous pressure for three days. After filtering and washing with deionized water, the white product was collected and denoted as MIL-53(Al)$_{as}$ (subscript "*as*" stands for as-synthesized). The free acid in the pores of MIL-53(Al)$_{as}$ was removed by the solvothermal method in DMF at 150°C for 15 h.[2] Typically, 1.0 g of MIL-53(Al)$_{as}$ was dispersed in 25 ml of DMF for this purpose. The product was cooled down, filtered off, and calcined in air at 280°C for 12 h at a heating rate of 5°C min^{-1}, which was labelled as MIL-53(Al).

MIL-53(Cr): MIL-53(Cr) was synthesized following the method reported by Serre *et al.* under hydrothermal condition using $Cr(NO_3)_3·9H_2O$, H_2BDC, and HF as the starting materials.[3] The synthesis was carried out in a 150 ml Teflon-lined stainless steel autoclave at 220°C under autogenous pressure for three days. The molar composition of the starting gels was 1 Cr (10.0 g):1 H_2BDC (4.15 g):1 HF (0.50 g):280 H_2O. After filtering and washing with deionized water, the green product was collected and denoted as MIL-53(Cr)$_{as}$. The free acid in the pores of MIL-53(Cr)$_{as}$ was removed by the solvothermal method in DMF at 150°C for 15 h.[2] Typically, 1.0 g of MIL-53(Cr)$_{as}$ was dispersed in 25 ml of DMF for this purpose. The product was cooled down, filtered off, and calcined in air at 200°C for 12 h at a heating rate of 5°C min^{-1}, which was labelled as MIL-53(Cr).

MIL-53(AlCr): MIL-53(AlCr) was synthesized using $Al(NO_3)_3·9H_2O$, $Cr(NO_3)_3·9H_2O$, H_2BDC, and HF as the starting materials with some modifications in the synthesis protocols for MIL-53(Al) and MIL-53(Cr). The synthesis was carried out in a 150 ml Teflon-lined stainless steel autoclave at 220°C under autogenous pressure for three days. The molar composition of the starting gels was 1 Al (5.63 g):1 Cr (6.0 g):1.5 H_2BDC (3.74 g):1 HF (0.30 g):360 H_2O. After filtering and washing with deionized water, the green product was collected and denoted as MIL-53(AlCr)$_{as}$. The free acid in the pores of MIL-53(AlCr)$_{as}$ was removed by the solvothermal method in DMF at 150°C for 15 h.[2] Typically, 1.0 g of MIL-53(AlCr)$_{as}$ was dispersed in 25 ml of DMF for this purpose. The product was cooled down, filtered off, and calcined in air at 150°C for 12 h at a heating rate of 5°C min^{-1}, which was labelled as MIL-53(AlCr).

(3) Preparation of the Ru–B/MIL-53 Catalysts

The Ru–B/MIL-53 catalysts were prepared by the wetness impregnation-chemical reduction method. Specifically, 100 mg of the MIL-53 powder (MIL-53(Al), MIL-53(Cr), and MIL-53(AlCr)) was suspended in 0.40 ml of water and 0.20 ml of aqueous $RuCl_3$ solution (0.40 M) under ultrasonication for 30 min. Then, the suspension was reduced by adding dropwise 1.0 M KBH_4 aqueous solution with gentle stirring in an ice bath. The molar ratio of B/Ru was 4/1 to ensure that all the Ru^{3+} ions were completely reduced. The resulting Ru–B/MIL-53 catalyst was washed three times with distilled water and two times with ethanol. Prior to the activity test, no further activation of the catalysts was required, as they had already been in the reduced state.

2. Characterization

The chemical composition was analysed by inductively coupled plasma-atomic emission spectroscopy (ICP–AES; Thermo Elemental IRIS Intrepid). The Brunauer–Emmet–Teller (BET) surface area and pore volume were determined by N_2 physisorption at –196°C on a Micromeritics TriStar 3000 apparatus.

The active surface (S_{Ru}) was measured by pulsed CO adsorption on a Micromeritics 2750 chemisorption system at 30°C. The dispersion of Ru was calculated based on CO uptake with the assumptions of the CO:Ru stoichiometry of 0.6:1[4] and the Ru surface atomic density of 1.63×10^{19} atoms m^{-2}.[5]

X-ray diffraction (XRD) was executed on a Bruker AXS D8 Advance X-ray diffractometer employing Ni-filtered Cu Ka radiation (λ = 0.15418 nm). The tube voltage was 40 kV, and the current was 40 mA. The morphology, particle size, and selected-area electron diffraction (SAED) pattern were observed by transmission electron microscopy (TEM; JEOL JEM2011) operated at 200 kV.

Fourier transformed infrared (FTIR) spectra were recorded on a Nicolet Nexus 470 infrared spectrometer in the range of 4000–400 cm^{-1}, with the catalyst powders mixed with KBr being pressed into a self-supporting wafer. The spectral resolution was 4 cm^{-1}, and 32 scans were recorded for each spectrum.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Series thermal analysis system with a heating rate of 5°C min^{-1} and an air flow rate of 20 ml min^{-1}. The chemical state of Ru was determined by X-ray photoelectron spectroscopy (XPS) on a Perkin Elmer PHI 5000C ESCA system in the Ru 3p region, since the C 1s peak overlaps with the most intensive Ru $3d_{3/2}$ peak. The Mg Kα line ($h\nu$= 1253.6

eV) was used as the excitation source.

3. Activity Testing

The liquid-phase hydrogenation of benzene to cyclohexane or methyl-substituted benzene derivatives to saturated cycloparaffins was carried out in a 50 ml Hastelloy autoclave with a magnetically coupled propeller stirrer. Typically, 108 mg of the as-prepared catalyst, 5.0 ml of benzene, and 15 ml of ethanol as the solvent were introduced. Since the saturation of the phenyl ring is highly exothermic, ethanol was employed to facilitate heat dissipation so as to avoid local overheating of the catalyst that would result in disguised activity. Then the autoclave was sealed and purged with H_2 for more than ten times to expel air. If unspecified, the typical reaction conditions were 30^{o}C, 1.0 MPa of H_2, and stirring rate of 1200 rpm to exclude the diffusion effect. The reaction process was monitored by taking a small amount of the reaction mixture at intervals, followed by analysis on a GC122 gas chromatograph fitted with a PEG-20 M packed column and a thermal conductivity detector (TCD). To compare the intrinsic catalytic performance, the activity was expressed as the turnover frequency (TOF) of benzene. In order to calculate the TOF, the weight-specific activity (r_0), that is, mmol of benzene converted per minute per gram of the catalyst at zero reaction time, was obtained by fitting the experimental benzene content–reaction time (t) curve with a polynomial equation, which was then differentiated, and the r_0 was acquired by substituting zero for t. Then, the TOF value in unit of s^{-1} was calculated as TOF = $7.7r_0/S_{Ru}$, where S_{Ru} is the active surface area of Ru per gram Ru in unit of $m^2\ g_{Ru}^{-1}$.

4. Control Experiments

(1) Leaching Test

The leaching test was performed in the same way as described in **Section 3** on the Ru–B/MIL-53(AlCr) catalyst as a representative. After 70 min of reaction, the catalyst was removed by centrifugation, and the content of Ru in the filtrate was detected by ICP–AES with the detection limit of ~50 ppb. In another catalytic run, after 30 min of reaction, the catalyst was removed by centrifugation from the liquid phase, and then the autoclave containing the filtrate was sealed and pressurized with H_2 again. The reaction was recommenced and continued for another 4.5 h.

(2) Blanket Test

The catalytic activity of the MIL-53(AlCr) support (100 mg) was checked in the hydrogenation of 5.0 ml benzene in 15 ml ethanol, which was performed in the same way as described in **Section 3**, while the reaction time was prolonged to 5.0 h.

(3) Reusability

The reusability of the Ru–B/MIL-53(AlCr) catalyst was examined in the same way as described in **Section 3**. After one catalytic run for 1.0 h, the catalyst was separated by centrifugation, washed three times by ethanol, redispersed in the mixture of benzene and ethanol, and reused in another catalytic run under identical reaction conditions.

Table S1 Summary of the catalytic activities expressed as TOF in the hydrogenation of benzene to cyclohexane under mild reaction conditions over the literature catalysts

Catalyst	T (°C)	P_{H2} (MPa)	TOF (s^{-1})	Ref.
Rh/HEA-C16	20	0.1	0.025	S6
Raney Ni–P	100	1	0.024	S7
Ir NPs	20	4	0.10	S8
Ru/SBA-15	20	1	0.024	S9
Ru0	20	0.1	0.007	S10
0.7 wt%Rh(cod)-9.86 wt%Pd/SiO_2	40	3	0.34	S11
1.4%Ru(0)-Zeolite-Y	22	0.28	0.29	S12
6.3 wt%Pd-6.9 wt%Rh/CNT	20	1	0.16	S13
11.2 wt%Rh/MWNTs	20	1	0.29	S14
0.27%Ru/NFS	25	0.29	1.5	S15
Pt–Rh/MWNTs	20	1	0.54	S16
$Rh_{0.5}Ni_{0.5}$	25	4	0.081	S17
Ru/γ-Al_2O_3	80	2	0.39	S18
2 mol.%Perfluoro-tagged Ru	60	0.1	0.008	S19
Ir NPs@zeolite	25	0.3	0.89	S20
Ru/CNTs	80	4	1.9	S21

Table S2 Physicochemical properties of the MIL-53 supports and the Ru−B/MIL-53 catalysts

Sample	Ru loading (wt%)	Composition (atomic ratio)	S_{BET} ($m^2\ g^{-1}$)	V_p ($cm^3\ g^{-1}$)	d_p (nm)	S_{Ru} ($m^2\ g_{\mathrm{Ru}}^{-1}$)
MIL-53(Cr)	-	-	1113	0.52	1.0	-
Ru–B/MIL-53(Cr)	7.98	$Ru_{62.22}B_{37.78}$	977	0.42	1.0	15
MIL-53(Al_1Cr_1)	-	-	853	0.54	1.1	-
Ru–B/MIL-53(Al_1Cr_1)	7.97	$Ru_{57.47}B_{42.53}$	817	0.51	1.1	17
MIL-53(Al)	-	-	1037	0.54	1.1	-
Ru–B/MIL-53(Al)	7.98	$Ru_{66.91}B_{33.09}$	806	0.41	1.1	10

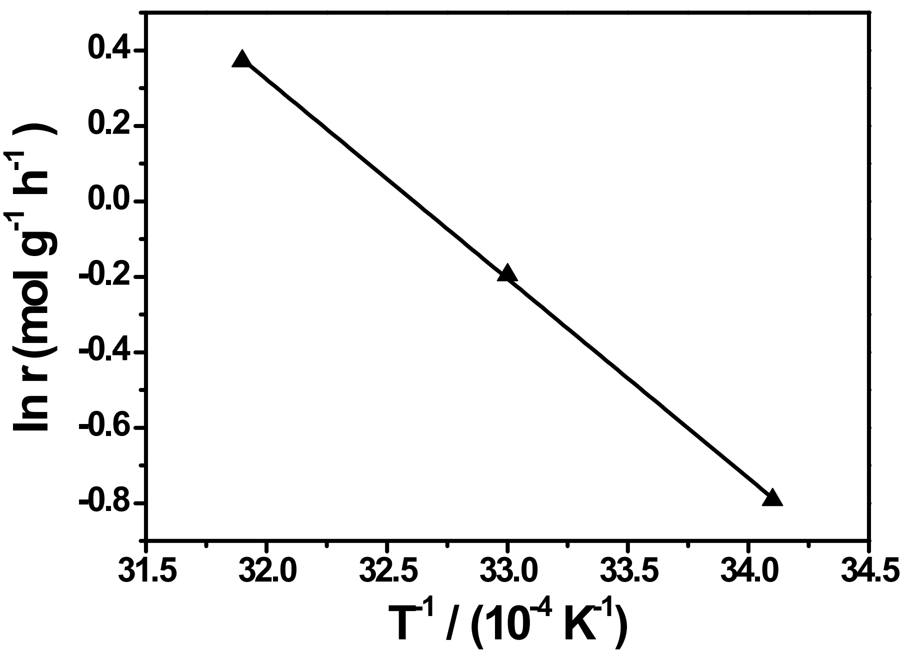

Fig. S1 The Arrhenius plot of the catalytic hydrogenation of benzene over the Ru−B/MIL-53(AlCr) catalyst.

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