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SUPPORTING INFORMATION

An efficient and sustainable catalytic reduction of carbon-carbon multiple bonds, aldehydes, and ketones using Cu nanoparticles decorated metal organic framework

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Chemicals

AR grade chemical were purchased and used without any further purification. Metal salts, trimesic acid, olefins, alkynes, aldehydes, and ketones were procured from Sigma Aldrich. Other chemicals and solvent used in this study were obtained from SpectrochemPvt. Ltd.

Synthesis of Metal organic frameworks

Synthesis of Cu-BDC-MOF

$Cu(NO_3)_2.3H_2O$ (1.06 g, 4.4 mmol) and terepthalic acid (H_2BDC; 0.73 g, 4.4 mmol) were dissolved in 50 mL of DMF at ambient condition.The reaction mixture was sealed in 100 mL Teflon lined autoclave and heated at 110 °C for 36 h. The resultant blue crystalline solid was filtered, washed with DMF, and then dried in vacuum oven at 100 °C for 12 h to obtain Cu-BDC-MOF.

Synthesis of Zr-BDC-MOF

$ZrOCl_2.8H_2O$ (0.33 g) and terepthalic acid (H_2BDC, 0.169 g) were dissolved in 50 mL of DMF. Subsequently, 0.5 mL of HCl was added drop wise to the above obtained solution. The reaction mixture was sealed in 100 mL Teflon lined autoclave and heated at 120 °C for 24 h. Autoclave was cooled to ambient temperature.The resulting solid was treated with MeOH for several times followed by drying in vacuum oven for 24 h at 100 °C.

Synthesis of Mn-BDC-MOF

$Mn(NO_3)_2.6H_2O$ (0.22 gm) was dissolved in 15 mL of EtOH. In another beaker, terepthalic acid (H_2BDC; 0.166 gm) was dissolved in 15 mL of DMF. Both the solutions were mixed and stirred for 30 minutes. The colloidal solution was transferred into a Teflon lined autoclave and heated at 180 °C for 24 h. Finally the resulting solid was filtered, washed with DMF and EtOH, and then dried in vacuum oven at 60 °C for 12 h.

Synthesis of Ni-BTC-MOF

$Ni(NO_3)_2.6H_2O$ (1.27 g) and trimesic acid (0.51 g) were dissolved in 70 mL of MeOH with stirring for 45 minute. Than the solution was transferred into a 150 mL autoclave and heated at 150 °C for 24 h. The resulting green solid product was rinsed with MeOH and then dried in vacuum at 60 °C for 12 h.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded in 2θ range of 5°-70° with a scan speed of 2°/minute on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ=0.1542 nm, 40kV, 40mA). The porosity of the catalyst was determined by surface area analysis. N_2-sorption measurements were recorded at 77 K using a Quantachrome Instrument, Autosorb-IQ volumetric adsorption analyser. Sample was degassed at 150 °C for 3 h in the degas port of the adsorption apparatus. The surface area of the catalyst was calculated from the adsorption data point obtained at P/P_0 between 0.05-0.3 using the Branauer-Emmette-Teller (BET) equation. The pore diameter was estimated using the nonlocal density functional theory (NLDFT) and Barret-Joyner-Halenda (BJH) methods. Scanning Electron Microscopy (SEM) measurement was recorded on a JEOL JSM-6610LV to understand the morphology of the catalyst. High resolution transmission electron microscopic (HR-TEM) investigations were made using FEI, Tecnai G2, F30 (300 KV) at RSIC, IIT Bombay. FT-IR spectra was recorded using Bruker Tenser 27 spectrometer. Diffused reflectance UV-visible (DR UV-vis) spectra were recorded using a Shimadzu UV-2600 spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on PHI 5000 Versa Prob II,FEI Inc. at ACMS, IIT Kanpur. Thermogramswere recorded using TGA/DSC 1 STAR^e SYSTEM from Mettler Toledo instrument with a temperature increments of10 °C /min in air stream from 27 °C to 800 °C. Metal content was determined using MP-AES 4200, Agilent technologies, USA.

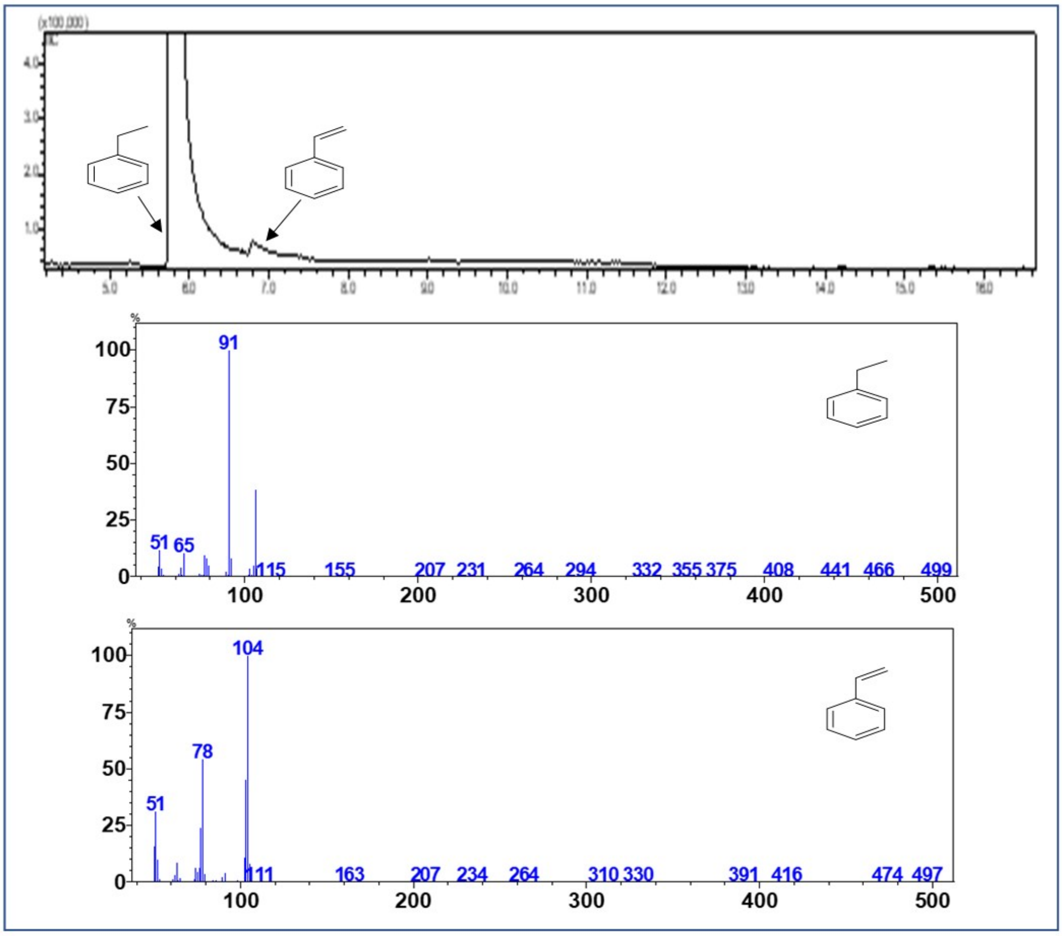

Fig. S1. GC and MS spectra of styrene and ethylbenzene obtained from the GC-MS analysis of a reaction mixture after the styrene reduction.

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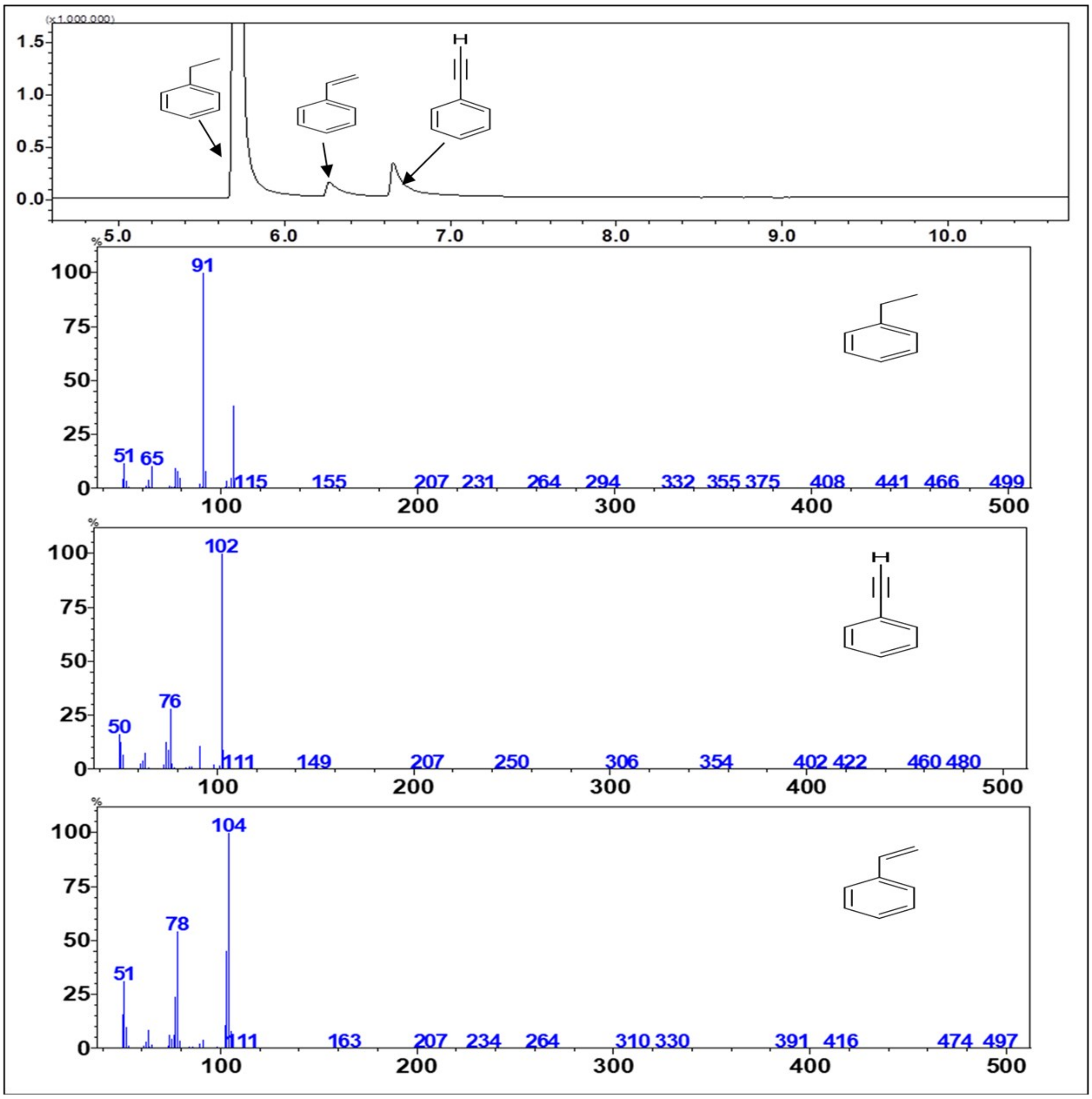

Fig. S2. GC and MS spectra of phenylacetylene, styrene, and ethylbenzene obtained from the GC-MS analysis of a reaction mixture after the phenylacetylene reduction.

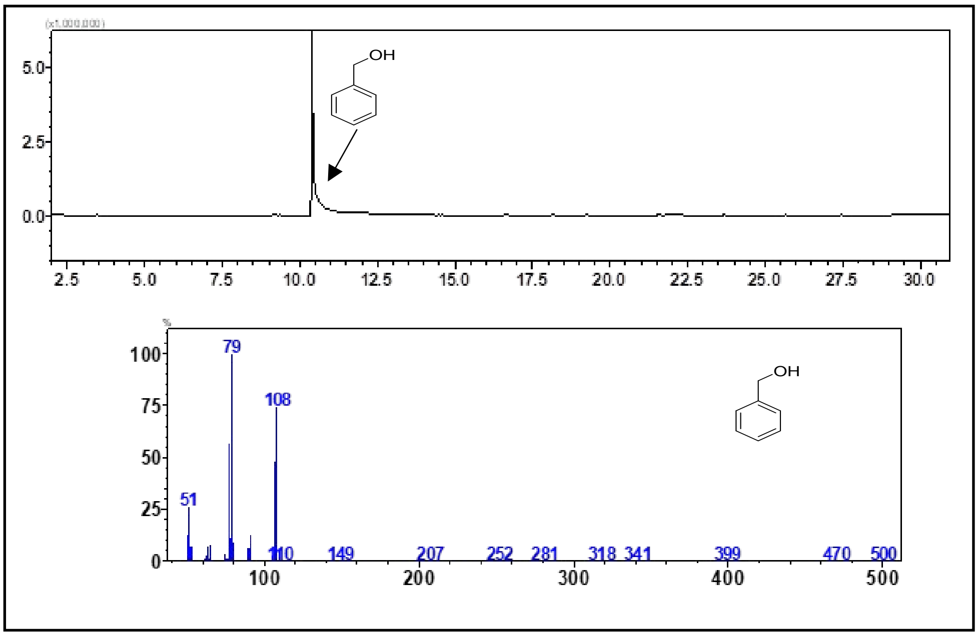

Fig. S3. GC and MS spectra of benzyl alcohol obtained from the GC-MS analysis of a reaction mixture after the complete reduction of benzaldehyde.

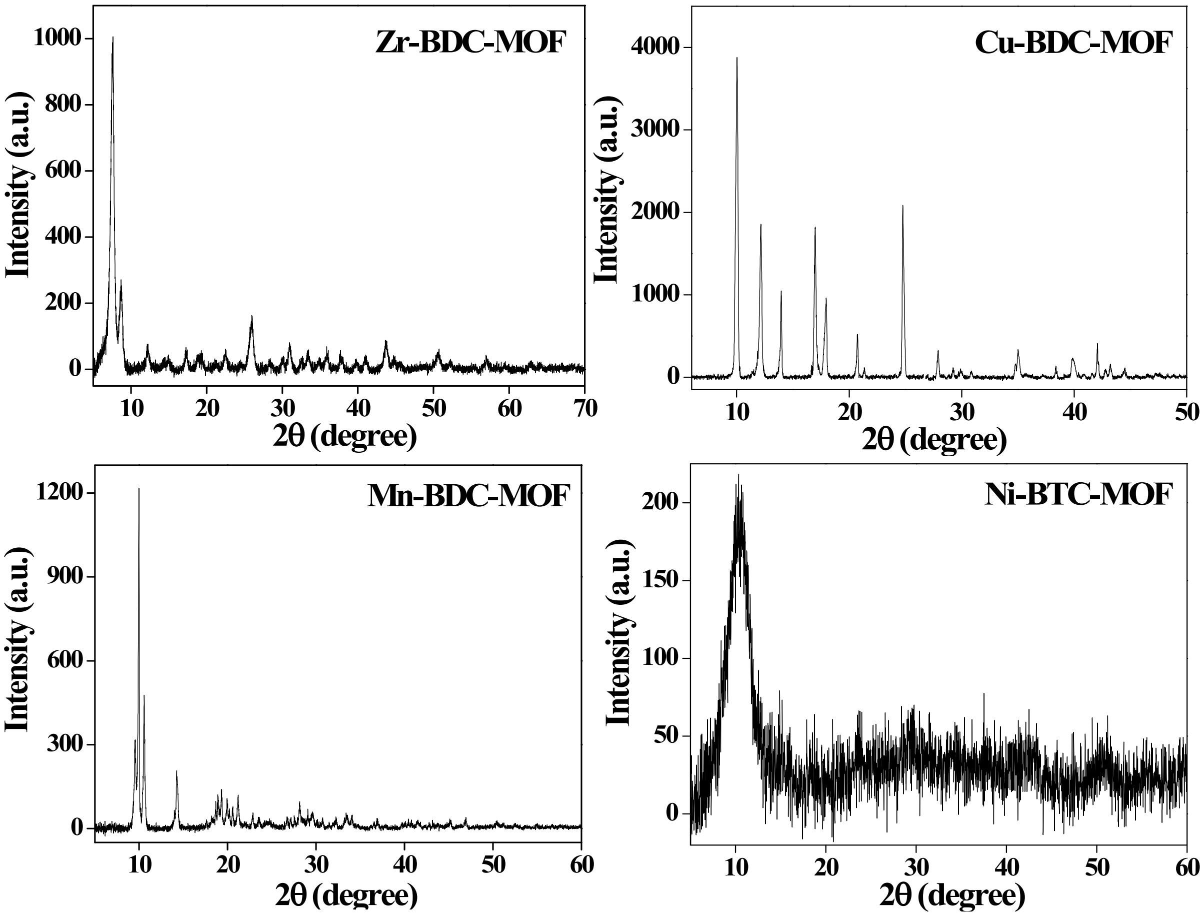

Fig. S4. Powder XRD patterns of Cu-BDC-MOF, Mn-BDC-MOF, Ni-BTC-MOF, and Zr-BDC-MOF.

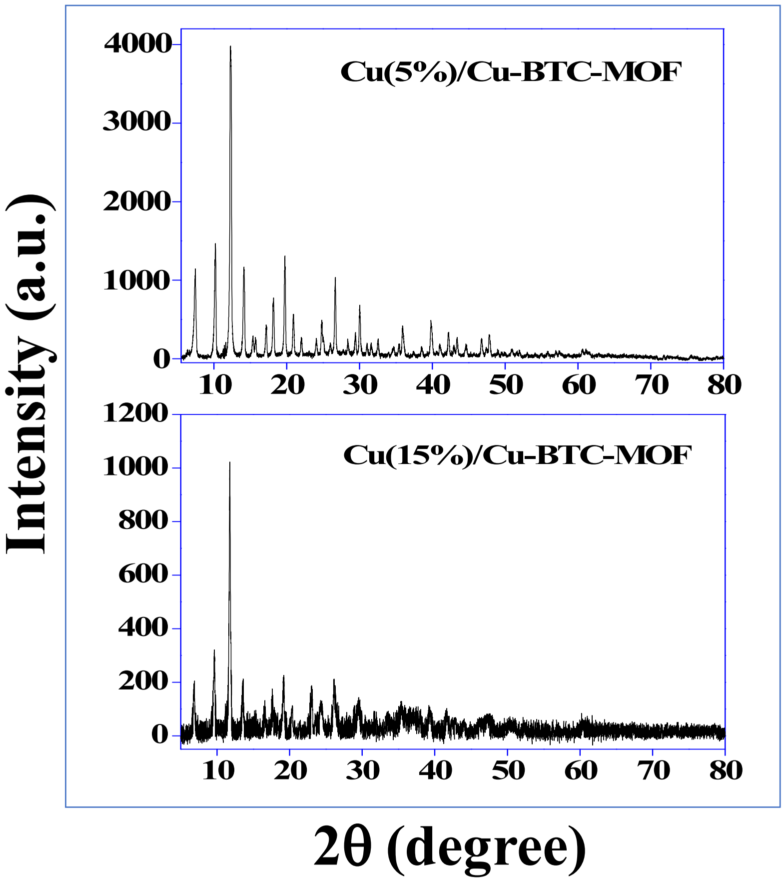

Fig. S5. Powder XRD patterns of Cu(5%)/Cu-BTC-MOF and Cu(15%)/Cu-BTC-MOF.

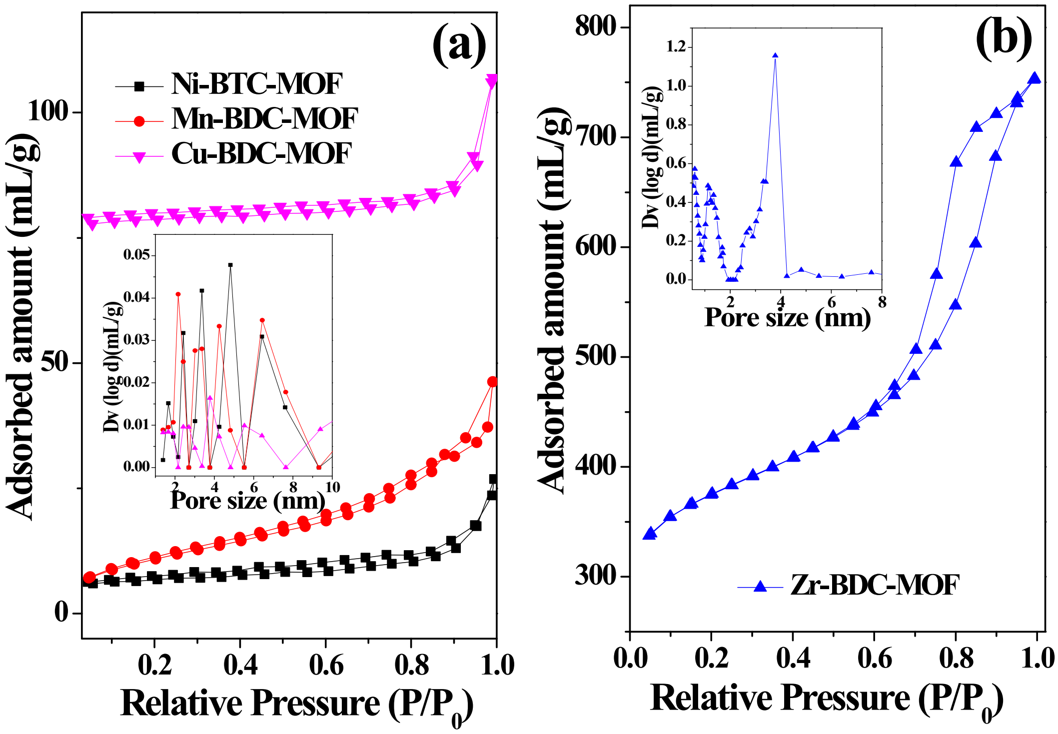

Fig. S6. N_2-adsorption desorption isotherms of (a) Cu-BDC-MOF, Mn-BDC-MOF, and Ni-BTC-MOF, (b) Zr-BDC-MOF. Inset shows BJH pore size distribution.

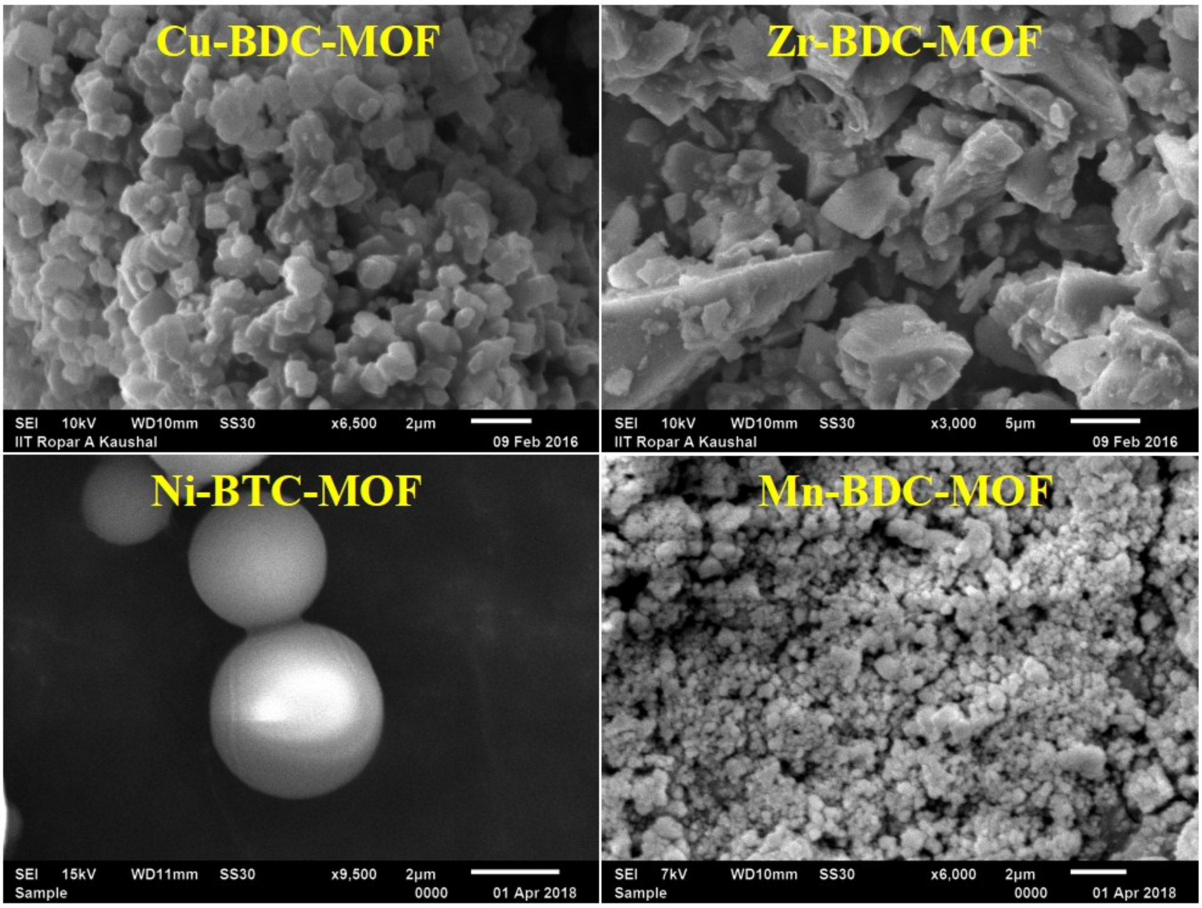

Fig. S7. SEM micrographs of Cu-BDC-MOF, Zr-BDC-MOF, Mn-BDC-MOF, and Ni-BTC-MOF.

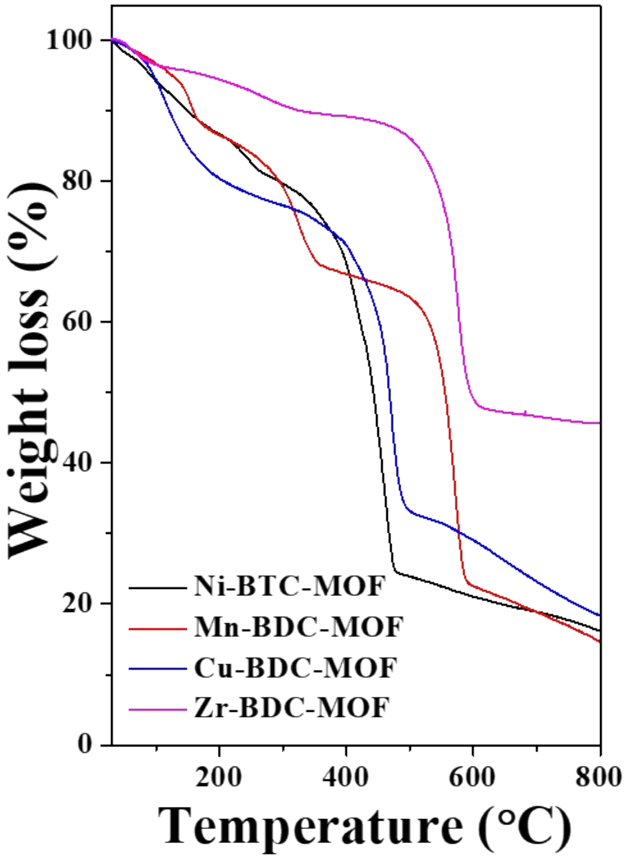

Fig. S8. Thermograms of Cu-BDC-MOF, Zr-BDC-MOF, Mn-BDC-MOF, and Ni-BTC-MOF.

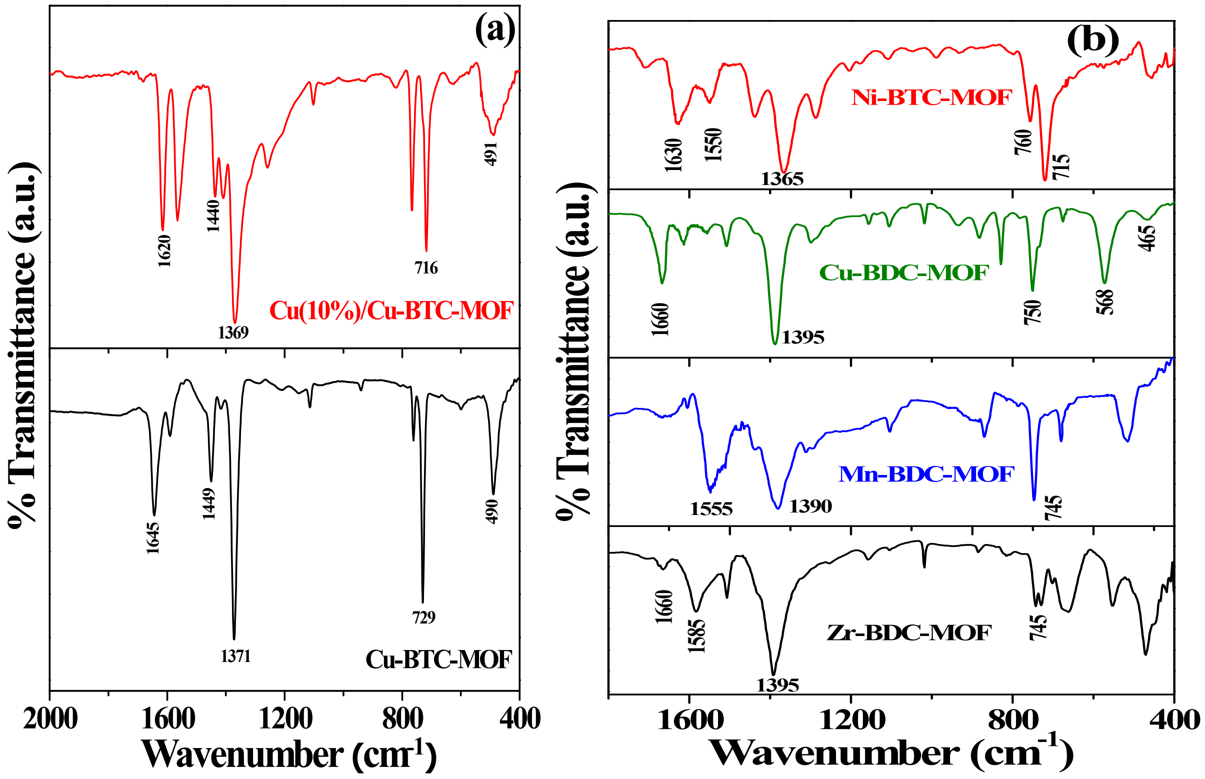

Fig. S9. FT-IR spectra of (a) Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF, (b) Ni-BTC-MOF, Cu-BDC-MOF, Mn-BDC-MOF, and Zr-BDC-MOF synthesized in this study.

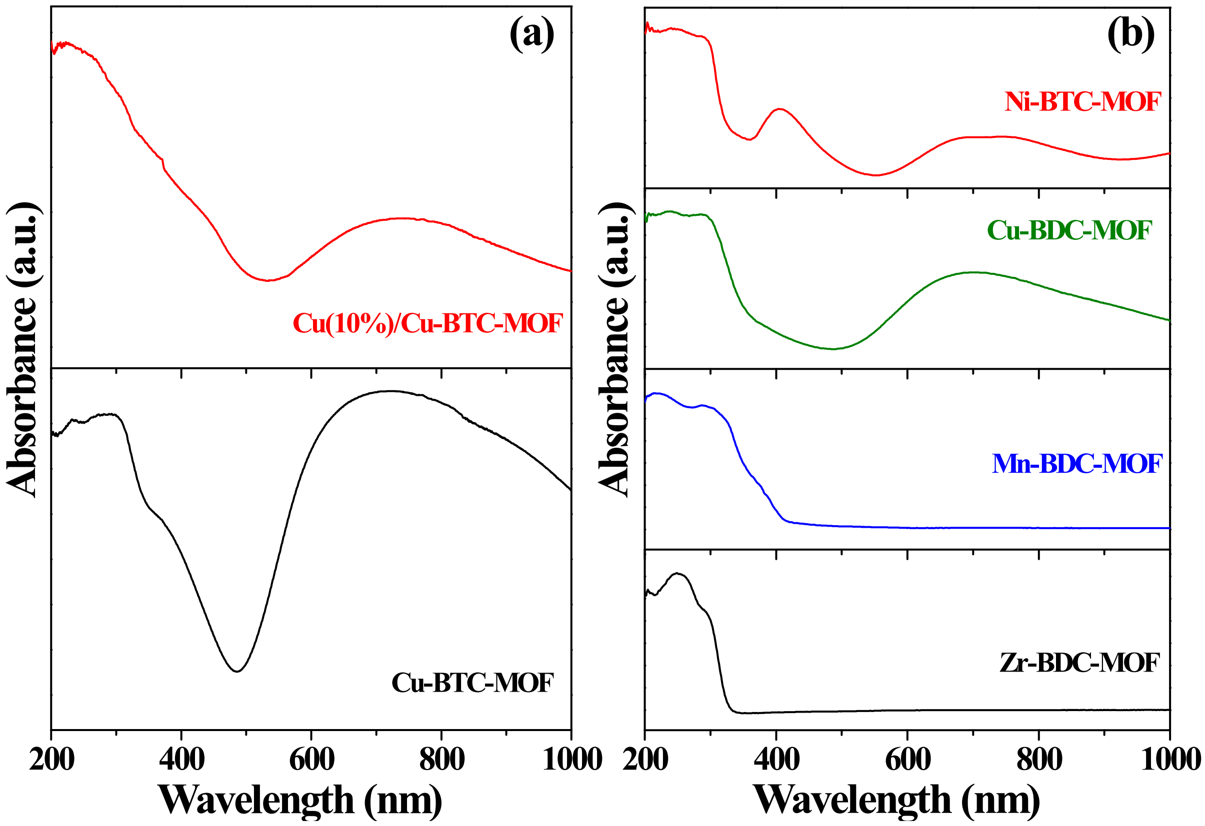

Fig. S10. DRUV-visible spectra of (a) Cu-BTC-MOF and Cu(10%)/Cu-BTC-MOF and (b) (b) Ni-BTC-MOF, Cu-BDC-MOF, Mn-BDC-MOF, and Zr-BDC-MOF synthesized in this study.

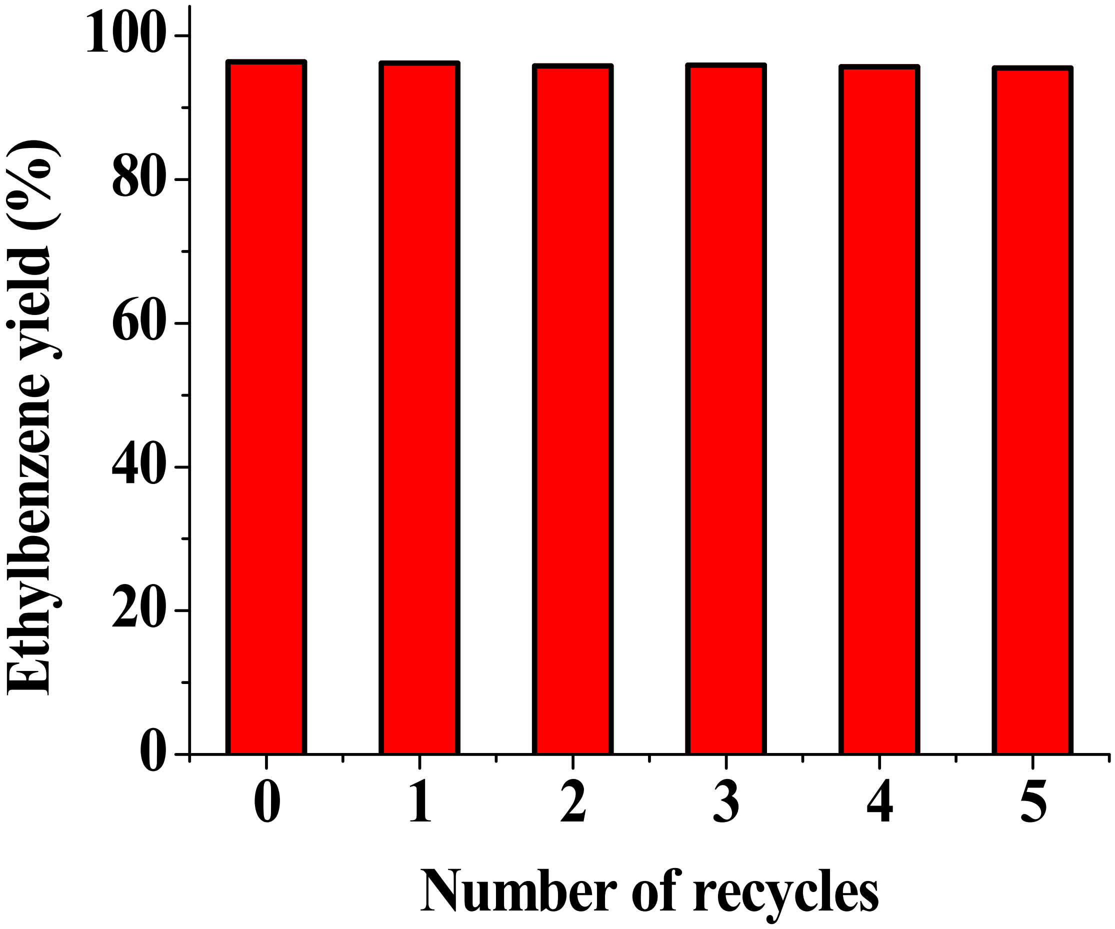

Fig. S11. Recyclability studies during the reduction of styrene in the presence of hydrazine hydrate using Cu(10%)/Cu-BTC-MOF.

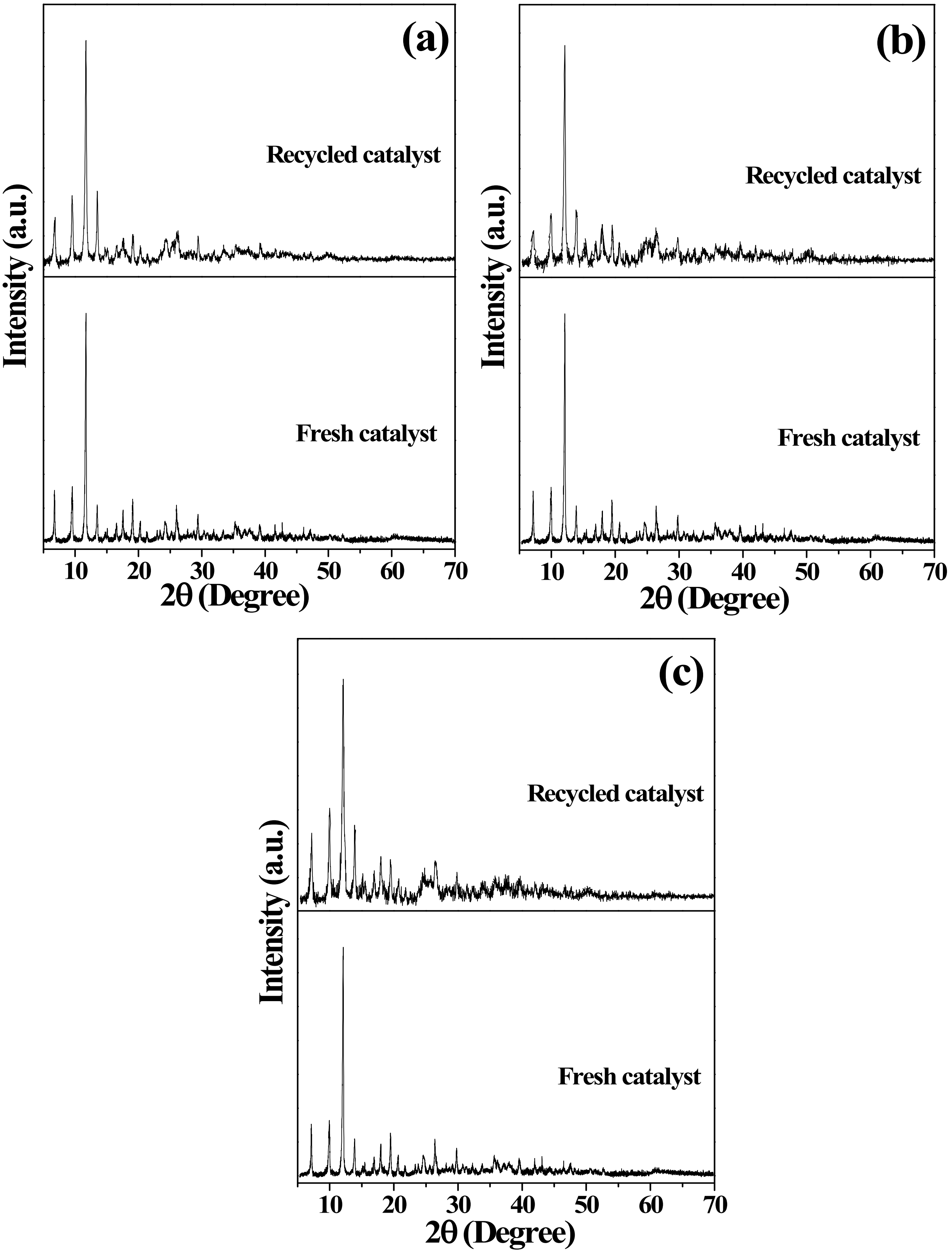

Fig. S12. Powder XRD patterns of fresh and recycled catalyst after (a) styrene reduction, (b) phenylacetylene reduction and (c) benzaldehyde reduction using Cu(10%)/Cu-BTC-MOF.

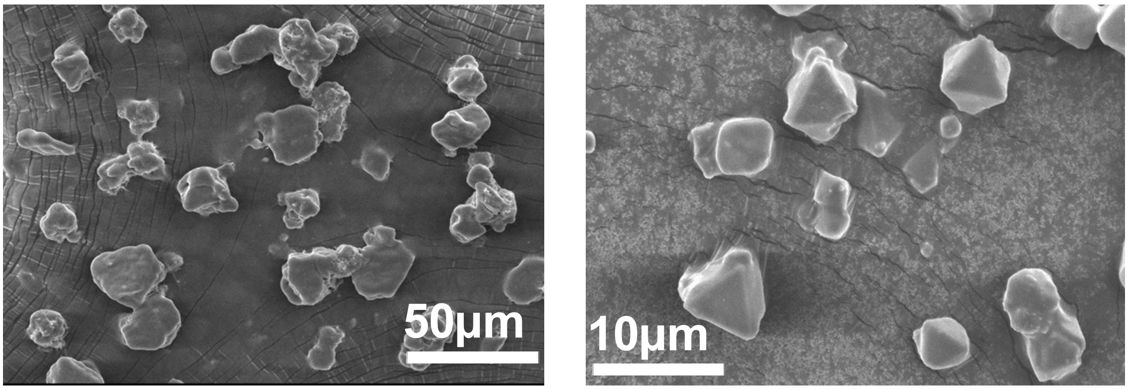

Fig. S13. SEM images of recovered Cu(10%)/Cu-BTC-MOF obtained after styrene reduction.

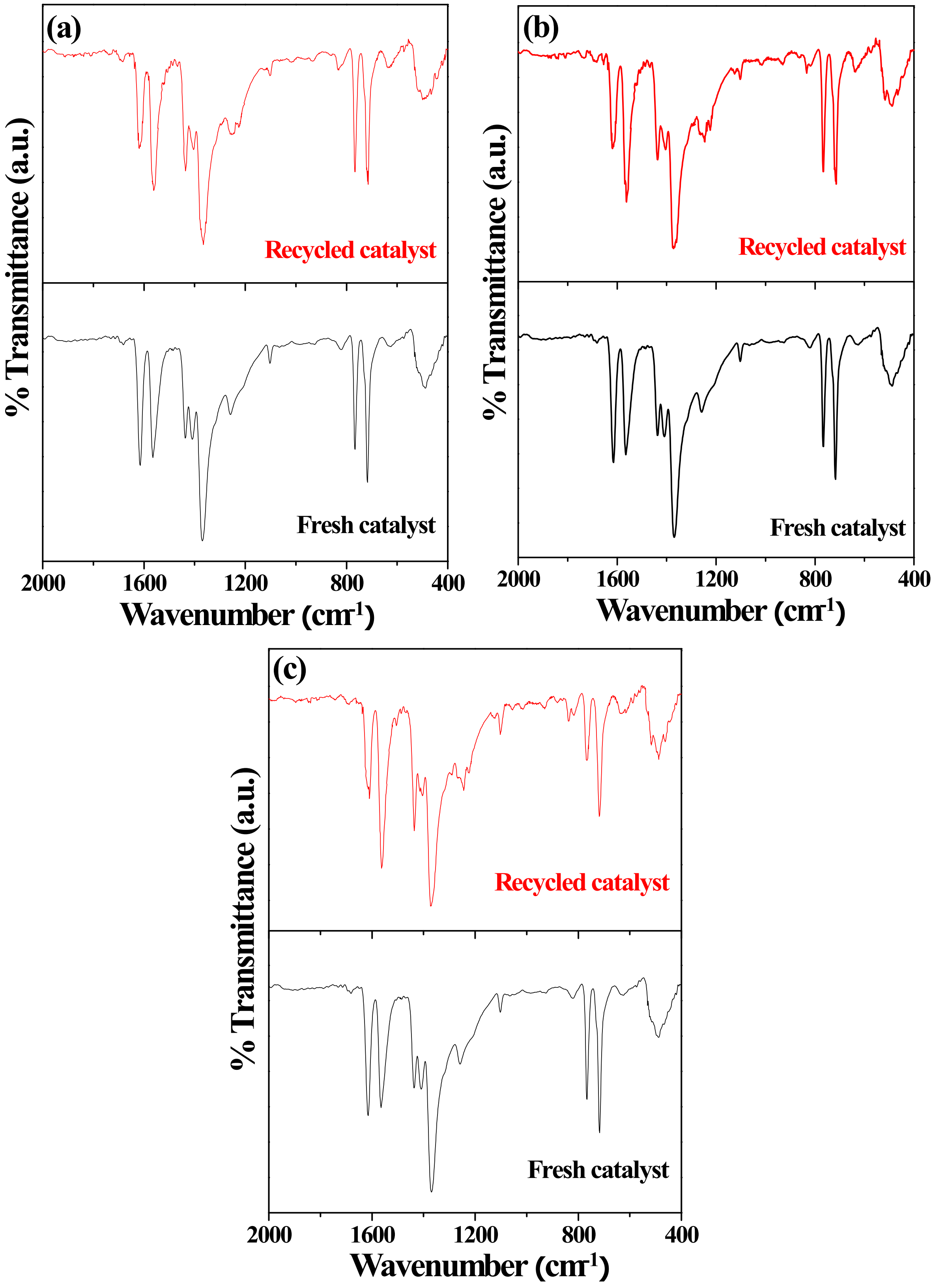

Fig S14. FT-IR spectra of fresh and recycled catalyst after (a) styrene reduction, (b) phenylacetylene reduction and (c) benzaldehyde reduction.

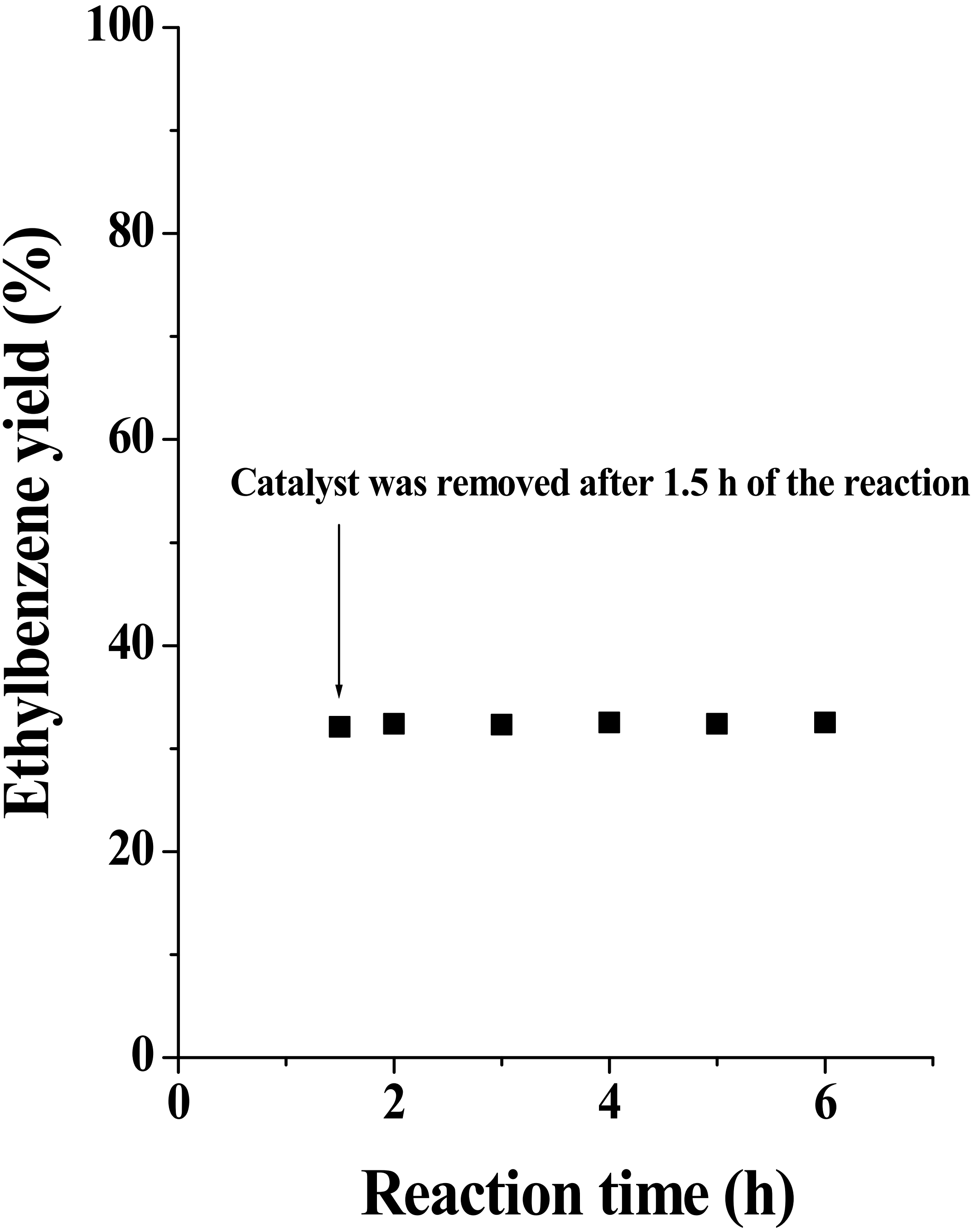

Fig. S15. Influence of catalyst leaching on the ethylbenzene yield after the removal of catalyst after 1.5 h of the reduction reaction of styrene.

Table S1. Physico-chemical properties of various catalysts investigated in this study.

Catalyst	**S_{BET} (m^2/g)**	**S_{EA} (m^2/g)**	**V_{Total} (cc/g)**
Zr-BDC-MOF	808	335	0.55
Mn-BDC-MOF	71	12	0.05
Ni-BTC-MOF	13	07	0.03
Cu-BDC-MOF	213	163	0.42

S_{BET} = Total surface area, S_{EA} = External surface area, V_{Total} = Total pore volume.

Table S2. Influence of catalyst amount, various solvents and reducing agents investigated in the reduction of styrene to ethylbenzene investigated in this study.

Entry	**Solvent**	**Catalyst amount (mg)**	**Reducing agent**	**Ethylbenzene yield (%)**
1.	Toluene	20	Hydrazine hydrate	23.9
2.	Dichloromethane	20	Hydrazine hydrate	33.8
3.	Diethyl ether	20	Hydrazine hydrate	57.4
4.	THF	20	Hydrazine hydrate	24.4
5.	Acetonitrile	20	Hydrazine hydrate	42.7
6.	Ethanol	20	Hydrazine hydrate	96.4
7.	Neat	20	Hydrazine hydrate	26.1
8	Ethanol	5	Hydrazine hydrate	28.9
9	Ethanol	10	Hydrazine hydrate	50.6
10	Ethanol	25	Hydrazine hydrate	99.1
8.	Ethanol	20	Isopropanol	0
9.	Ethanol	20	Aq. Formaldehyde(37%)	0
10.	Ethanol	20	Formic acid	0
11.	Ethanol	20	NH_3 (30%)	0

Reaction condition: Styrene (0.6 mmol), reducing agent (1.2 mmol), solvent (2.0 mL), temperature (25-27° C), time (6 h).

Table S3.Comparative catalytic activity data reported in literature for the reduction of styrene to ethylbenzene over various reported heterogeneous catalyst using hydrazine hydrate as a reducing agent.

S.N	Catalyst	Reaction condition	$Y_{Ethylbenzene}$ (%)	References
1	Ni–K10	Substrate (0.9 mmol), hydrazine hydrate (0.4 mL), ethanol (3 mL), catalyst (100 mg), 8 h, 343 K.	82	59
2	$Al_2(BDC)_3$	Styrene (0.05 mL), catalyst (84 mol%), acetonitrile (5 mL), 0.04 mL of 25% aqueous ammonia, 298 K, 24 h, 36 μL hydrazine hydrate.	66	27
3	CuNPs/Diamond NPs	Styrene (1 mmol), catalyst (20 mg), $N_2H_4.H_2O$ (0.1 mL), aq. NH_3 (0.025 mL), ethanol (4 mL), 60^0C.	99	60
4	Fe(BTC)	Styrene (0.05 mL), catalyst (150 mg), acetonitrile (5 mL), 0.04 mL of 25% aqueous ammonia, 298 K, 24 h, 36 μL hydrazine hydrate.	51.5	27
5	$Cu_3(BTC)_2$	Styrene (0.05 mL), catalyst (150), acetonitrile (5 mL), 0.04 mL of 25% aqueous ammonia, 298 K, 24 h, 36 μL hydrazine hydrate.	59.4	27
6	Zn-MOF	Styrene (0.05 mL), catalyst (150), acetonitrile (5 mL), 0.04 mL of 25% aqueous ammonia, 298 K, 24 h, 36 μL hydrazine hydrate.	13.9	27
7	HKUST-1(Hydrotalchite)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).	16	27
8	Cu(bdc)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).	8	61
9	Cu-AlPO-5	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (5 mol%).	32	61
10	$Cu(OH)x@Al_2O$	styrene (0.2 mmol), acetonitrile	16	61

		(5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (6 mol%).		
11	CuCl$_2$(diamine)meso	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (6 mol%).	58	61
12	CuMgAl HT (9.9% Cu)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).	58	61
13	CuAl HT (52% Cu)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).	48	61
14	MIL-100 (Fe)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (100 mol%).	44	61
15	Basolite F300	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).	19	61
16	Fe–AlPO-5	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (5 mol%).	30	61
17	FeMgAl HT (2.2% Fe)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (5 mol%).	44	61
18	Basolite A100	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (75 mol%).	20	61
19	MIL-53 (Al)	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (75 mol%).	38	61
20	AlPO-5	Styrene (0.2 mmol), acetonitrile	31	61

		(5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (76 mol%).		
21	Zeolite β	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (25 mol%).	13	61
22	Sn–zeolite β	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (1mol%).	15	61
23	Ti–zeolite β	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (0.5 mol%).	14	61
24	Zr–zeolite β	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (1mol%).	13	61
25	MCM-41	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (0.5 mol%).	2	61
26	Zr-MCM-41	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (0.5 mol%).	3	61
27	Cu(10%)/Cu-BTC-MOF	Styrene (0.6 mmol), hydrazine hydrate (1.2 mmol), catalyst (20 mg), reaction time (6 h), ethanol (2 mL), temp (RT).	96.4	This study

Table S4. Comparative catalytic activity data reported in literature for the reduction of phenylacetylene to ethyl benzene over various reported catalyst.

S.N	Catalyst	Reaction condition	$Y_{Ethylbenzene}$ (%)	References
1	G1-HMDI-Pd	Phenylacetylene (1 mL), catalyst (4 mg), H_2 (10atm), reaction time(1 h), temp (80^{0}C).	67	12
2	SGR/PANI-Ni	Phenylacetylene (1 mmol), MeOH (10 mL), catalyst (50 mg), H_2 (100 psi), reaction time (24 h), temp (25 ^{0}C).	60	13
3	Nano ferrite-Ni	Phenylacetylene (1 mmol), MeOH (2 mL), catalyst (50 mg), H_2 (100 psi), reaction time (24 h), temp (25 ^{0}C).	97	11
4	Au@Ni	Phenylacetylene (5 mL), MeOH (50 mL), catalyst (5 mg), H_2 (50 psi), reaction time (4 h), temp (80^{0}C).	100	14
5	CuNPs/Y-zeolite	Phenylacetylene (1 mmol), 2-propanol (2 mL), catalyst (30 mg), reaction time (1 h), temp (70 °C).	78	21
6	Cu(10%)/Cu-BTC-MOF	Phenylacetylene (0.6mmol), hydrazine hydrate (2.4 mmol), catalyst (20 mg), reaction time (6 h), ethanol (2 mL), temp (80 ^{0}C).	96.8	Present study

Table S5. Comparative catalytic activity data reported in literature for the reduction of benzaldehyde to benzyl alcohol over various reported catalyst.

S.N	Catalyst	Reaction condition	$Y_{Benzylalcohol}$ (%)	References
1	Ag−Fe_3O_4@CMC	Benzaldehyde (0.33 mmol), H_2O (9 mL), H_2(40 bar), catalyst (6.5 mol %), reaction time (24 h), temp (100°C).	95	17
2	Au/TiO_2	Benzaldehyde (1 mmol), 2-propanol (10 mL), Au (0.78 mol %), 0.3 equiv. KOH, reaction time (4 h), temp (82 °C) in N_2 atm.	99	15
3	nanoFe@SiO_2Ru	Benzaldehyde (1 mmol), 2-propanol (5 mL), catalyst (100 mg), K_2CO_3 (0.2 mmol), reaction time (45 min), temp (100°C) under M.W irradiation.	85	18
4	Co@Pt	Benzaldehyde (0.25 mmol), Toluene (0.1 mL), H_2 (1 atm), catalyst (2 mol %), reaction time (16 h), temp (100 °C).	100	19
5	$Zr_{0.8}Ni_{0.2}O_2$	Benzaldehyde (8 mmol), 2-propanol (15 mL), KOH (8 mmol), catalyst (10 % m/m), reaction time (6 h), temp (82 °C).	87	20
6	CuNPs/Y-zeolite	Benzaldehyde (1 mmol), 2-propanol (2 mL), catalyst (30 mg), reaction time (1 h), temp (70 °C).	78	21
7	NiMCM-41	Benzaldehyde (20 mmol), 2-propanol (20 mL), KOH (20 mmol), catalyst (100 mg), reaction time (2.5 h), temp (82°C).	94	22
8	Pt/CMK-3	Benzaldehyde (21 mmol), H_2 (4.0 MPa), H_2O+MeOH (18 mL+ 2 mL), catalyst (100 mg), reaction time (1 h), temp (400 °C) at 12000 rpm.	99	23
9	Cu(10%)/Cu-BTC-MOF	Benzaldehyde (0.6 mmol), hydrazine hydrate (1.2 mmol), catalyst (20 mg), reaction time (6 h), ethanol (2 mL), temp (25 °C).	100	Present study