Supporting information

An efficient halometallate ionic liquid functionalized mesoporous ZSM-5 for the reduction of carbon-carbon multiple bonds

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Table S1. Comparative catalytic activity data reported in literature for the reduction of styrene to ethylbenzene over various reported heterogeneous catalyst using hydrazine hydrate as reducing agent.

Materials

Tetraethylorthosilicate (TEOS, Aldrich, 99%), tetrapropyl ammonium hydroxide (TPAOH, 40% aqueous solution, Aldrich), sodium aluminate (53 % Al_2O_3, 43% Na_2O, National Chemicals, Gujrat), n-propyltriethoxy silane (Aldrich, 99%), 1-methylimidazole (Spectrochem Pvt. Ltd., India, 99%), 1-chloro butane (Alfa-aesar, 99%), metal salts (MCl_2, M= Mn, Fe, Cu, Loba Chemie Pvt. Ltd., India) were used as received without further purification. Reactants used in the catalytic reactions were obtained from Aldrich. Solvents were purchased from Merck India Pvt. Ltd.

Catalysts characterizations

Powder X-ray diffraction (PXRD) patterns were recorded in the 2θ range of 5–80° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA). Nitrogen adsorption measurements were carried out at 73 K using Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was degassed at 423 K for 3 h in the degas port. The specific surface area of the material was calculated using the Brunauer-Emmett-Teller (BET) equation and the data points obtained at P/P_0 between 0.05–0.3. The pore diameter was calculated using non local density functional theory (NLDFT) and BJH methods. SEM measurements were carried out on a JEOL JSM-6610LV to study the morphology of the materials. High resolution transmission electron microscopic (HR-TEM) investigations were made using FEI, Tecnai G2, F30 (300 KV) at RSIC, IIT Bombay. X-ray photoelectron spectroscopy (XPS) measurements were carried out on PHI 5000 Versa Prob II, FEI Inc. at ACMS, IIT Kanpur. Thermograms were recorded using TGA/DSC 1 STAR^e SYSTEM from Mettler Toledo instrument with a temperature increments of 10 K/min in air stream from 300 K to 1073 K. Metal content was determined using MP-AES 4200, Agilent technologies, USA. Fourier transform infrared (FT-IR) spectra were recorded using Bruker FT-IR instrument. Solid-state NMR was carried using a 4 mm MAS probe using 400 MHz ECX JEOL NMR spectrometer. ^{27}Al, ^{29}Si, and ^{13}C cross-polarization magic-angle spinning (CPMAS) spectrum was measured at room temperature.

Single Crystal X-ray Diffraction (SCXRD) data were collected on a Bruker diffractometer equipped with a Platform 3-circle goniometer and an Apex II CCD area detector

(Bruker-AXS, Madison, WI) using graphite-monochromated Mo-Kα radiation. Suitable crystals were isolated under an optical polarizing microscope, mounted on a nylon loop, and cooled to the collection temperature under a stream of N_2 gas using an Oxford N-helix cryostat (Oxford Cryosystems, Oxford, UK). Unit cell determination, data collection, integration, absorption correction, and scaling were done using the Bruker Apex2 software suite [APEX 2 AXScale and SAINT, version 2010; Bruker AXS, Inc.: Madison, WI.].

Synthesis of BMIMCl

Butyl chloride (0.1 mole) was added to 1-methylimidazole (0.12 mole) in a 100 mL round-bottom flask and stirred for 2 h at ambient temperature. Afterwards, flask was fitted with a condenser and stirred for 48 h at 343 K. Flask was cooled to ambient temperature and the reaction mixture was washed many times with diethyl ether to remove un-reacted butyl chloride and 1-methylimidazole. Flask was vacuum dried at 323 K to obtain pure BMIMCl.

Chloropropyl silylated imidazolium chloride

1-Methylimidazole (10 mmol) was dissolved in 30 ml of dry toluene in 100 mL round bottom flask fitted with a condenser. 3-Chloropropyltriethoxy silane (10 mmol) was added to the above reaction mixture and the resulting solution was refluxed for 1 day, followed by washing with diethyl ether to get chloropropyl silylated imidazolium chloride IL (Scheme 1). The formation of chloropropyl silylated imidazolium chloride IL was confirmed with the help of ^{1}H NMR.

Synthesis of MnO_2

MnO_2 was synthesized by following the reported procedure.[a] 100 mL round bottomed flask was charged with 1.5 mmol $Mn(OAc)_2.4H_2O$ and 20 mL of distilled water to form a homogeneous and transparent solution and stirred for 30 min. Then, 1.0 mmol $KMnO_4$ was added into the above solution in drop wise manner under stirring for 30 min at room temperature. The resulting solution was then subjected to hydrothermal treatment at 433 K for 6 h in a stainless steel autoclave (25 mL capacity) with an inner Teflon liner. After completion of the reaction, the autoclave was cooled to ambient temperature and the precipitate was washed with distilled water. The products were then dried at 343 K in air overnight.

Synthesis of SiO_2-Al_2O_3

SiO_2-Al_2O_3 composite was prepared using co-precipitation method.[b] 10 mL $CO(NH_2)_2$ (1.5 M) and 10 mL $Al(NO_3)_3.9H_2O$ (0.3 M) solutions were mixed in a 100 mL beaker. Then, resulting homogeneous mixture was added in drops fashion into 10 mL of 5 wt.% colloid SiO_2 solution (Ludox, 40 wt% SiO_2 source) under continuously stirring at 373 K, and then resulting solution was reflux for 2 h. After cooling the mixtures to ambient temperature, resulting colloidal solution was centrifuged, and washed with water. The white pasty mass was dried at 353 K under vacuum for 10 h followed by calcinations at 823 K for 2 h using a heating rate of 5 ^{o}K /min.

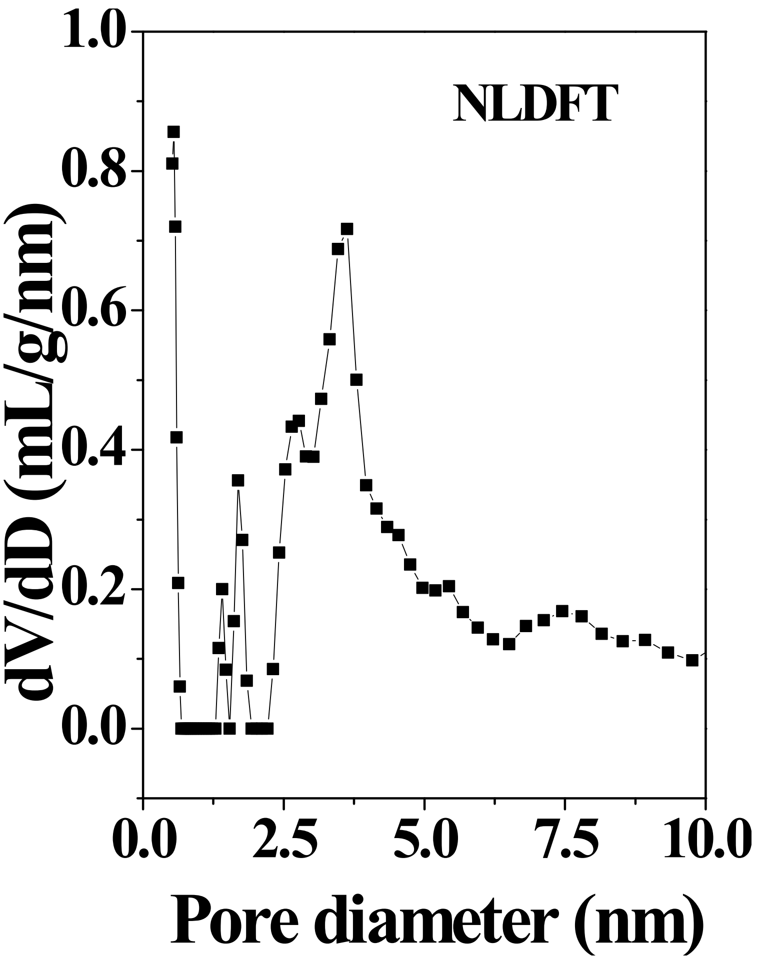
Procedure of catalytic reduction

Styrene (5 mmol), hydrazine hydrate (7.5 mmol), and catalyst (5 mol %) were stirred in 4 mL ethanol at ambient temperature for 12 h. For the heterogeneous catalyst, styrene (2 mmol), hydrazine hydrate (3.0 mmol), and catalyst (50 mg) were stirred in 4 mL ethanol at ambient temperature for 12 h. After the reaction, catalyst was separated from the reaction mixture using centrifuge machine. Organic portion was passed through anhydrous sodium sulphate and a small aliquot was subjected to GC analysis (Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 µm) to monitor the progress of reaction. Products were identified using GC-MS (Schimadzu GCMS-QP 2010 Ultra; Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 µm). Besides, all the standards (substrates and products) required for the analysis were also injected in GC. Most of the products investigated in this study are commercially available. They were procured from Sigma-Aldrich, India. Standard mixtures were prepared and analyzed by GC. Calibration curves were constructed by plotting the concentration and area under the peak obtained from the GC analysis (Standard addition method). The conversion was determined based on the results obtained from the GC analysis and these calibration curves. Each sample was measured three times and the standard deviation was calculated. The standard deviation was in the range of 0 to ±1.3. Similarly, reduction of alkynes was also performed by following the reaction condition given in Table 5.

Procedure of the complex synthesis between ILs (BMIMCl.$MnCl_2$ and BMIMCl.$FeCl_3$) and hydrazine hydrate

BMIMCl.$MnCl_2(NH_2NH_2)_x$: In a two-necked round bottom flask, BMIMCl.$MnCl_2$ (1.5 mmol) was taken. To it hydrazine hydrate (99%, 15 mmol) was added slowly over a period of 20 min under the nitrogen atmosphere and vigorously stirred for 12 h at 300 K. Exothermic reaction was observed while adding hydrazine hydrate to the halometallate salt, indicating the formation of complex. After 12 h, resultant mixture was centrifuged, washed with chloroform three times, and finally dried in oven at 323 K for 10 h.

Similarly, **BMIMCl.$FeCl_3(NH_2NH_2)_x$** was also prepared using BMIMCl.$FeCl_3$ as halometallate source. In this case also, during the addition of hydrazine hydrate, initially exothermic reaction occurred and after that brownish precipitates was observed, indicating the formation of complex. After 12 h, the resultant mixture was centrifuged, washed with chloroform, and dried in oven at 323 k for 12 h.



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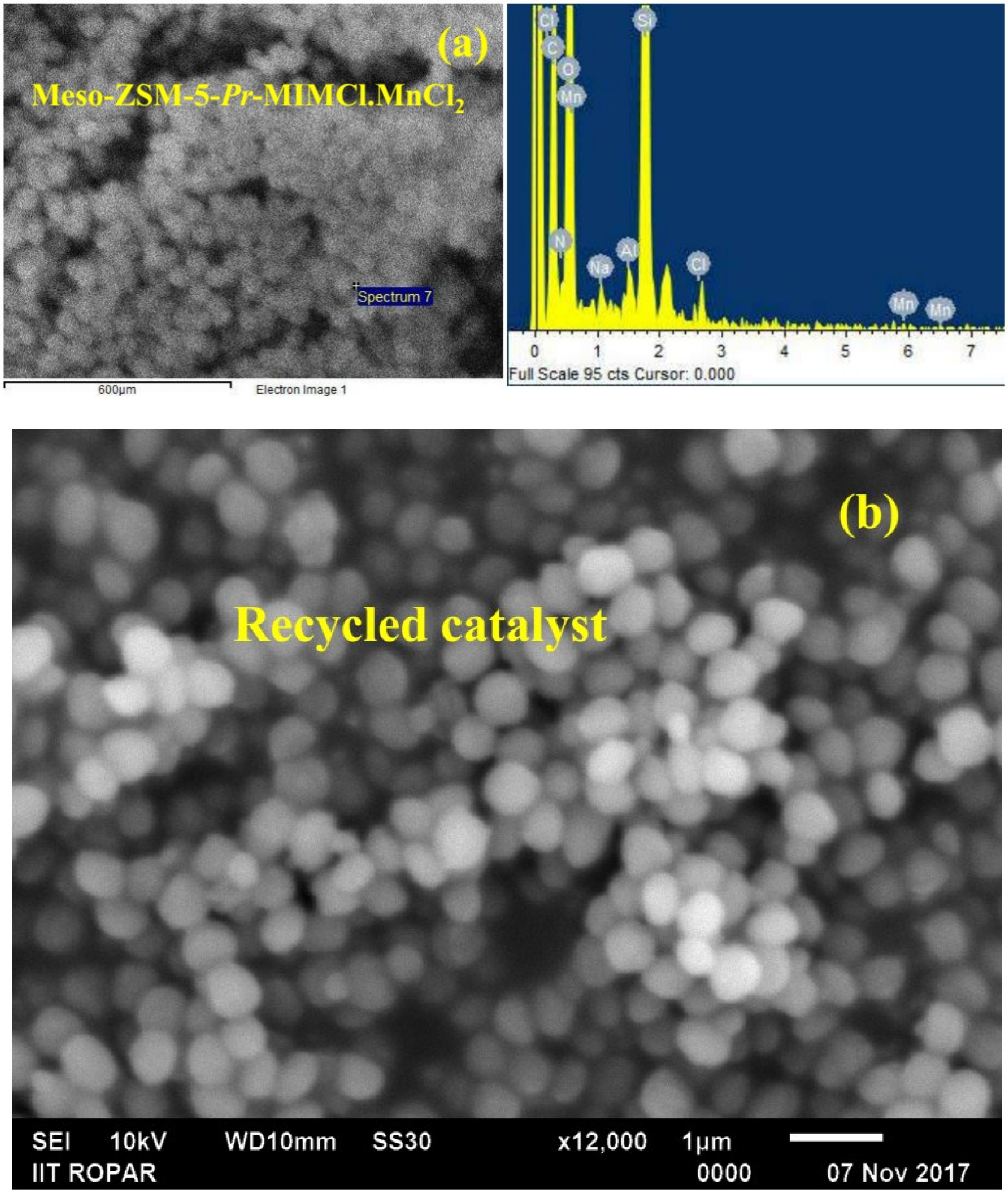

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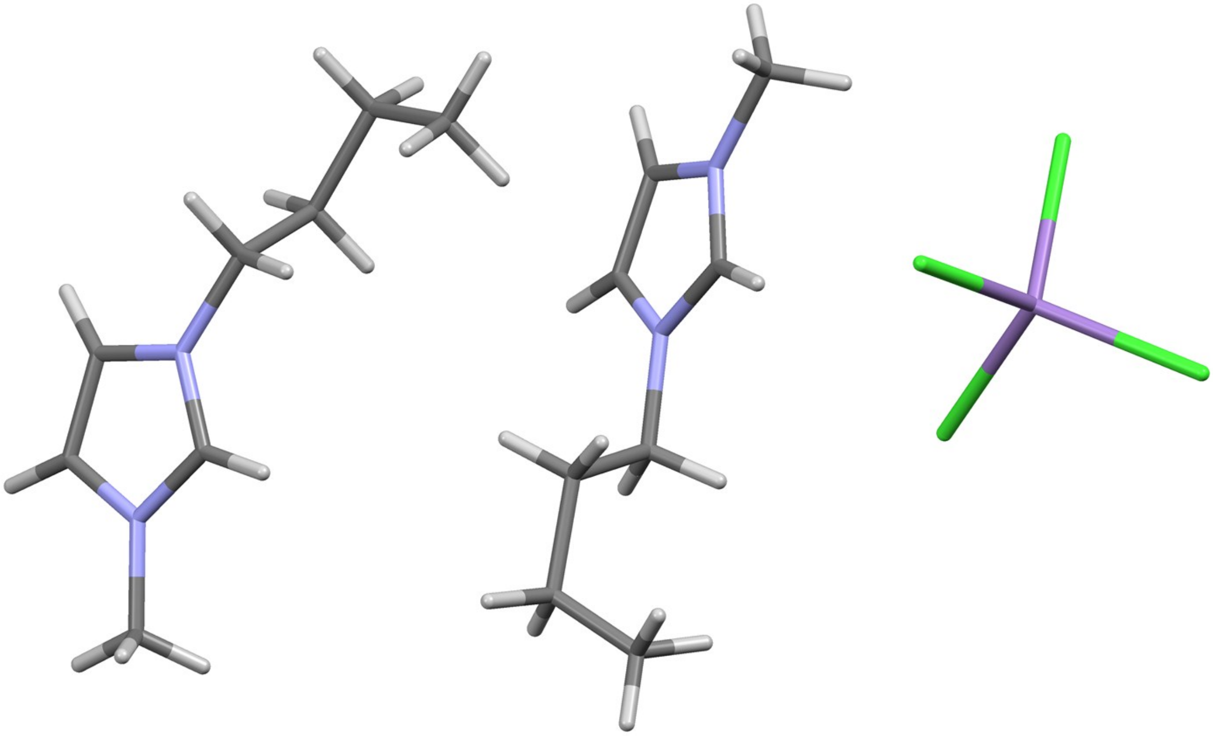

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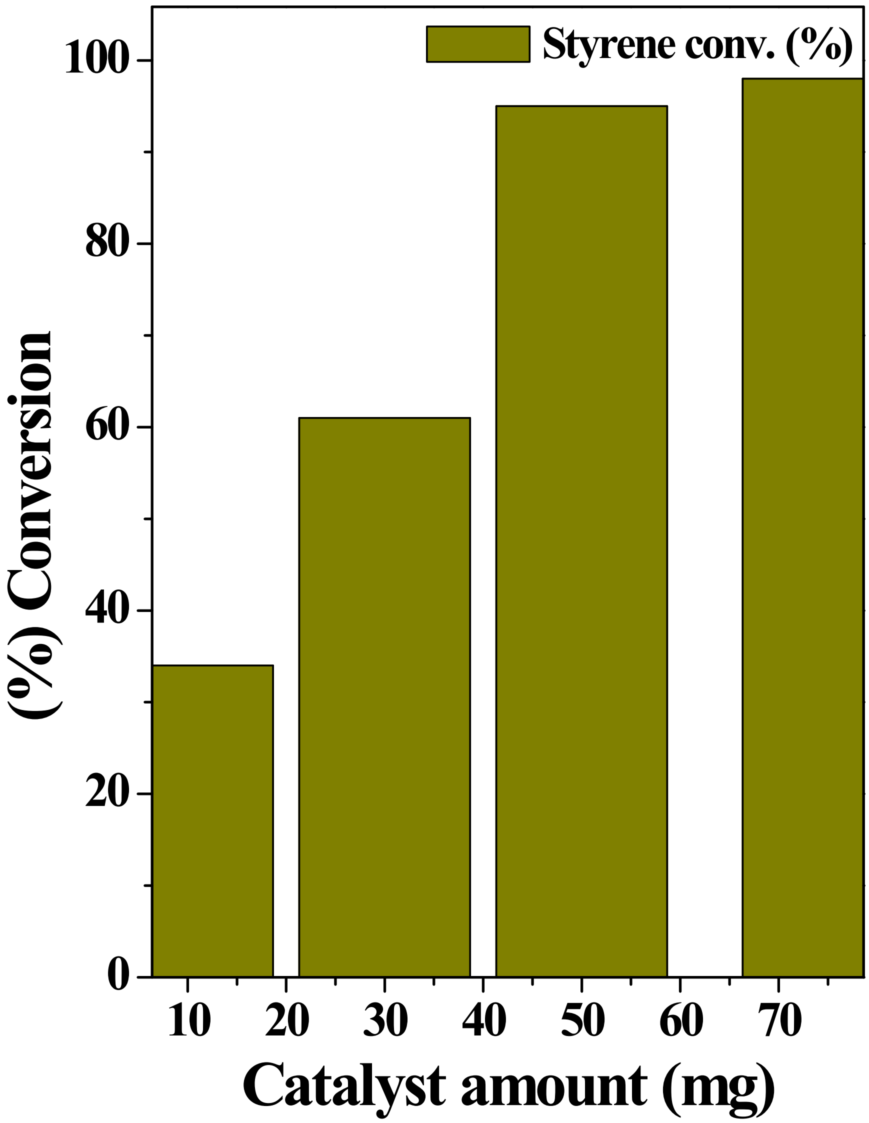

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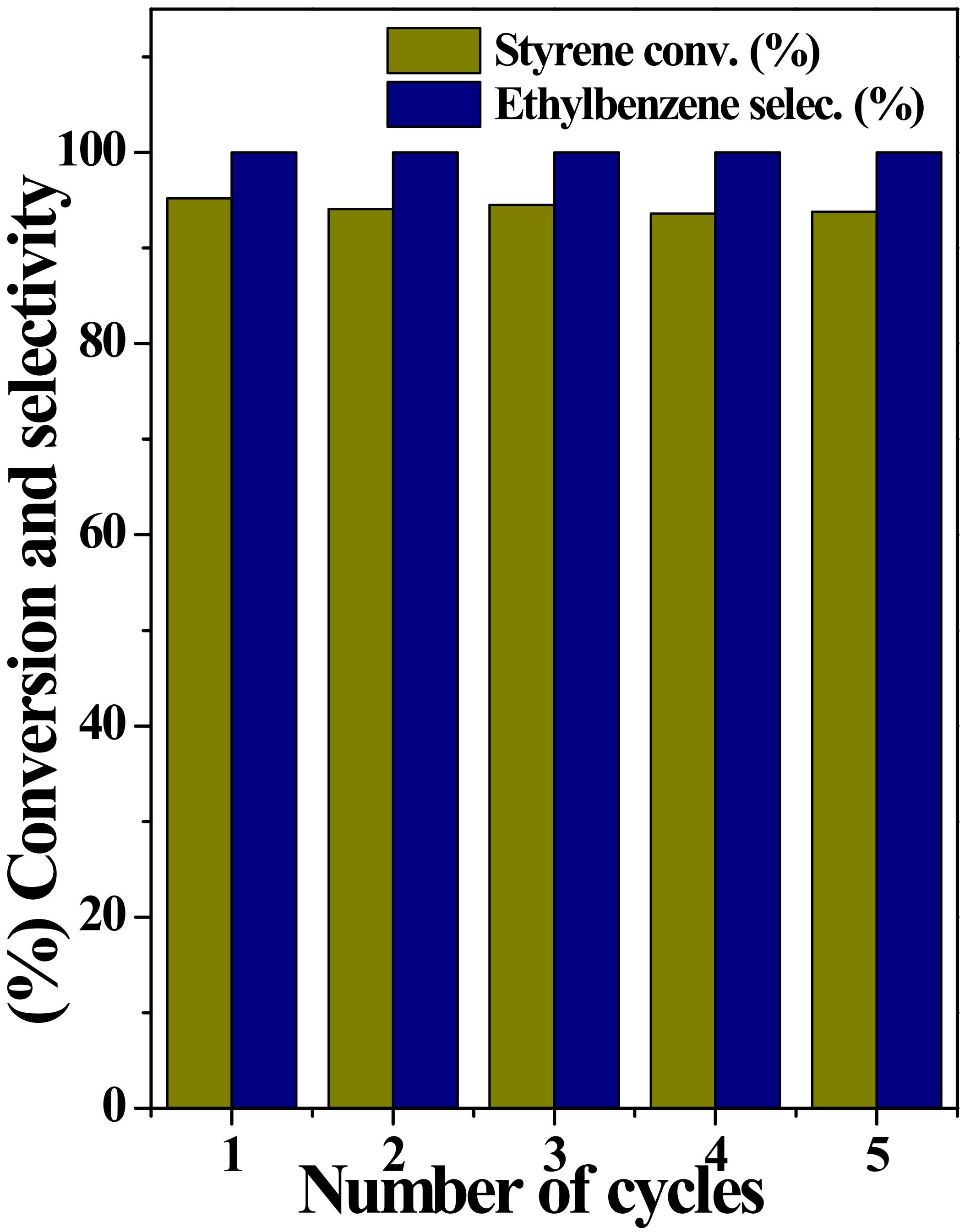
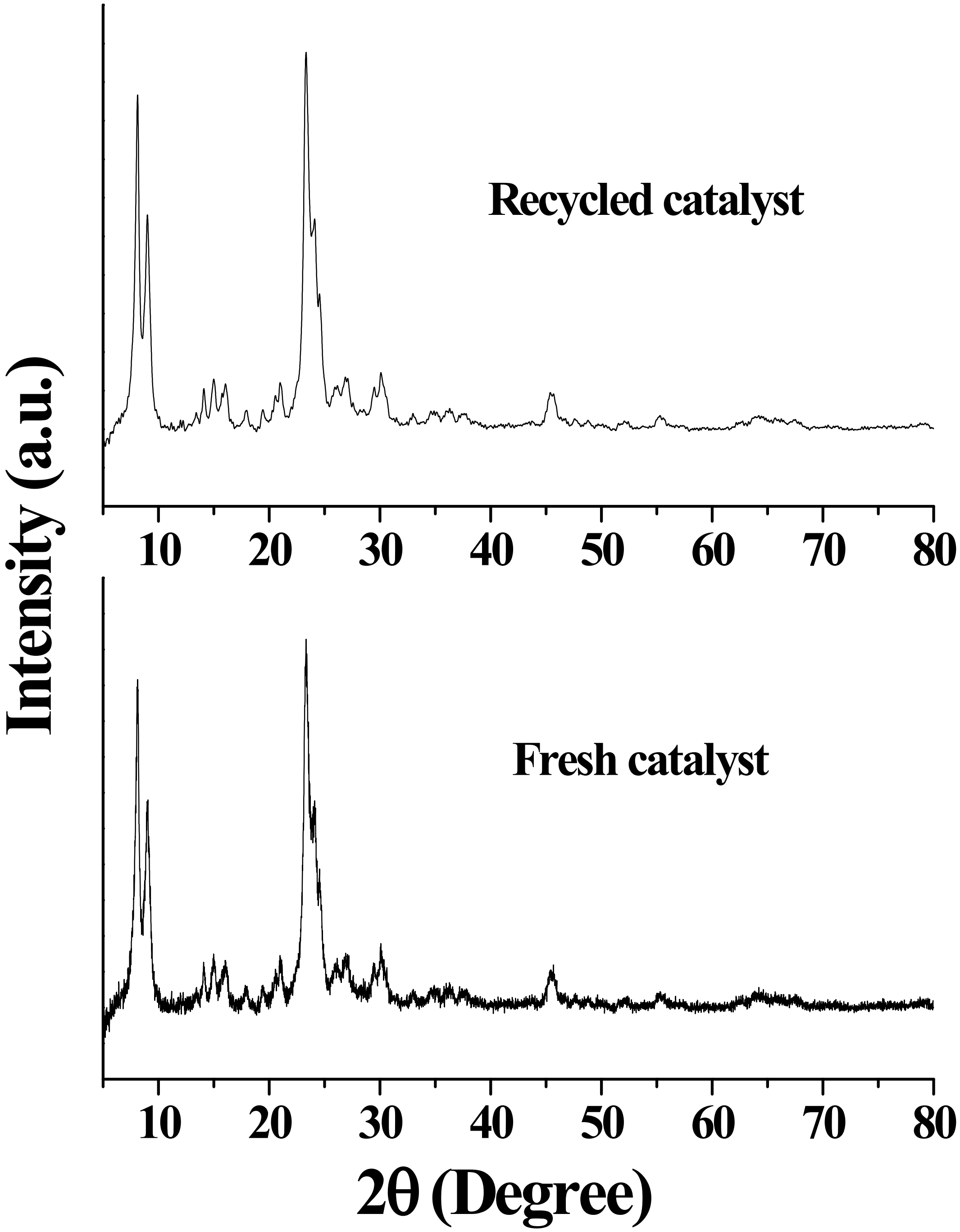


Fig. S5. Recyclability studies during the reduction of styrene in the presence of hydrazine hydrate using *Meso*-ZSM-5-pr-MIMCl.MnCl$_2$.



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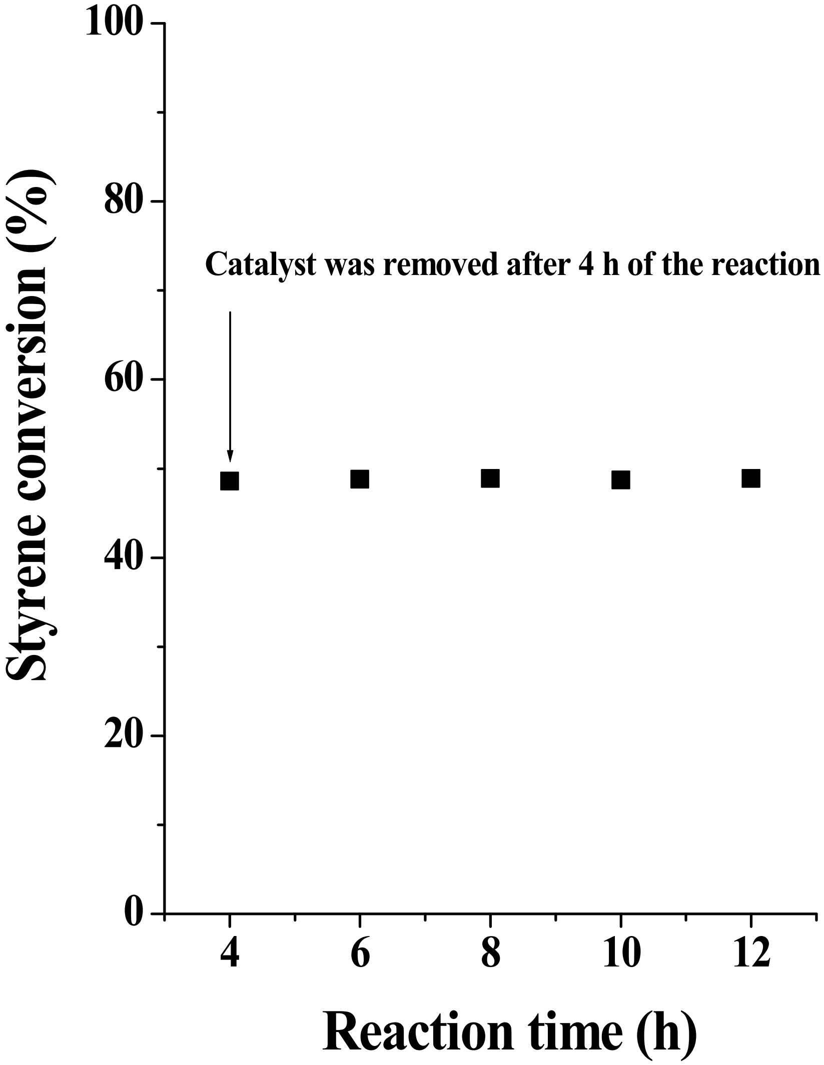

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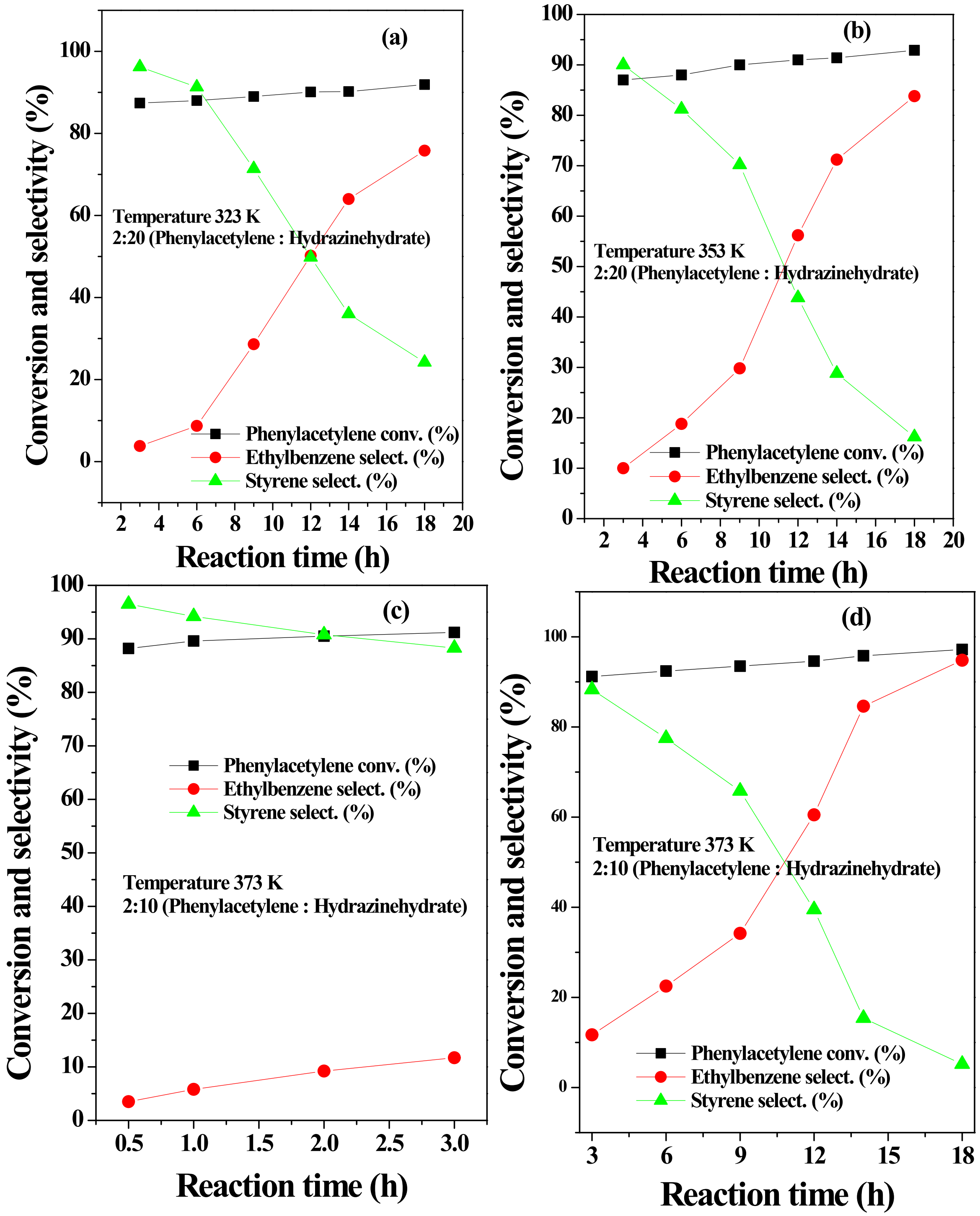

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Table S1. Comparative catalytic activity data reported in literature for the reduction of styrene to ethylbenzene over various reported heterogeneous catalyst using hydrazine hydrate as reducing agent.

S.N	Catalyst	Reaction condition	$Y_{Ethylbenzene}$ (%)	TON/TOF (h^{-1})	References
1	Ni–K10	Substrate (0.9 mmol), hydrazine hydrate (0.4 mL), ethanol (3 mL), catalyst (100 mg), 8 h, 343 K.	82	15.4/1.9 h^{-1}	18
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	0.8/0.03 h^{-1}	10
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), time (8 h), 60^0C.	99	3.2/0.4 h^{-1}	46
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	0.4/0.02 h^{-1}	10
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	1.05/0.04 h^{-1}	10
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	0.21/0.01 h^{-1}	10
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	0.32/0.013 h^{-1}	47
8	Cu(bdc)	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL	8	0.16/0.006 h^{-1}	47

		of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (50 mol%).			
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	6.4/0.26 h^{-1}	47
10	Cu(OH)x@Al$_2$O	styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (6 mol%).	16	2.66/0.11 h^{-1}	47
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	9.66/0.40 h^{-1}	47
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	1.16/0.48 h^{-1}	47
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	1.96/0.081 h^{-1}	47
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	0.44/0.018 h^{-1}	47
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	19	0.38/0.015 h^{-1}	47

		mol%).			
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	6/0.25 h^{-1}	47
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	8.8/0.36 h^{-1}	47
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	0.26/0.01 h^{-1}	47
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	0.50/0.02 h^{-1}	47
20	AlPO-5	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (76 mol%).	31	0.40/0.01 h^{-1}	47
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	0.52/0.02 h^{-1}	47
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	15/0.62 h^{-1}	47
23	Ti–zeolite β	Styrene (0.2 mmol), acetonitrile (5 mL), 40 mL	14	28/1.16 h^{-1}	47

		of 25% aqueous ammonia, 36 mL aqueous hydrazine, 298 K, 24 h, catalyst (0.5 mol%).			
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	13/0.54 h^{-1}	47
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	4/0.16 h^{-1}	47
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	6/0.25 h^{-1}	47
27	Fe_3O_4 catalyst	Styrene (1.0 mmol) and catalyst (40 mol %), EtOH (6 mL) , 353 K, time (18 h).	99	2.5/0.13 h^{-1}	48
28	Fe@g-C_3N_4(10% Fe)	Styrene (1 mmol), catalyst Fe@g-C_3N_4 (10% Fe) (25 mg), $NH_2NH_2\cdot H_2O$ (10 mmol), water (1.0 mL), 40 W domestic light bulb.	98	22.2/2.8 h^{-1}	49
29	*Meso*-ZSM-5-*pr*-MIMCl.$MnCl_2$	Styrene (2 mmol), hydrazine hydrate (3.5 mmol), catalyst (50 mg), reaction time (12 h), ethanol (4 mL).	95	38.5/3.2	This study

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