Electronic Supplementary Information

1. Materials

For the preparation of the CPSA functionalized mesoporous silica catalysts, all chemicals, i.e. triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123; molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$), cetyltrimethylammonium bromide (CTMABr, $C_{16}H_{33}N(CH_3)_3Br$), sodium metasilicate (44–47% SiO_2), tetraethylorthosilicate (TEOS; 98%), sulphuric acid (99.99%), hydrochloric acid (HCl; 37%), aminopropyltriethoxysilane, salicylaldehyde, chloroform, dichloromethane, methanol and copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), were purchased from Aldrich Chemical Inc. and used as received without further purification. Deionized water was used throughout the syntheses.

For the selective synthesis of aromatic ketones, all the chemicals, i.e. ethylbenzene (EB, 99.8%), *t*-butylhydrogen-peroxide (TBHP, 70%), hydrogen peroxide (HP, 30% H_2O_2), urea hydrogen peroxide (UHP, 97%), acetonitrile (MeCN, 99.8%), 1,2-Dichloroethane (DCE) and methanol (MeOH, 99.8%), 4-methyl-ethylbenzene (>99%), 4-*tert*-butyl-ethylbenzene (98%), propylbenzene (98%), tetralin (>99%), indane, fluorene (98%), diphenylmethane (99%) and 4-methoxy-diphenylmethane were also purchased from Sigma-Aldrich (USA) and TCI (Japan) Chemical Inc. and used as received without further purification.

2. Synthesis of SBA-15 and MCM-41

The well-ordered mesoporous SBA-15 molecular sieve material was synthesized using the pH-adjusting direct hydrothermal method according to our published procedure. In a typical synthesis, 4 g of Pluronic P123 with 25 ml of water was stirred to obtain a clear solution. Thereafter, a required amount of dilute HCl solution was added, and the mixture solution was again stirred for another 1 h for the hydronium ions to be associated with the alkylene oxide units. Next, 9 g of TEOS was added, and the resulting mixture was stirred for 24 h at 313 K. The product was recovered by filtration, washed several times with water and dried overnight at 373 K. Finally, the obtained SBA-15 was calcined in air at 813 K for 6 h for the complete removal of the surfactant template.

The mesoporous MCM-41(40) was alkaline hydrothermally synthesized using cetyltrimethylammonium bromide (CTMABr) as the structuring agent according to a well-known synthetic procedure published by our research group [1].

3. Synthesis of CPSA-containing mesoporous silica catalysts

The mesoporous p-CPSA-SBA-15 catalysts, p-CPSA-SBA-15(0.1) and p-CPSA-SBA-15(0.2), were synthesized by the post-grafting method, using amino-functionalized SBA-15 (APTES-SBA-15) with appropriate amounts of salicylaldehyde and $Cu(NO_3)_2 \cdot 3H_2O$ according to our published procedure [2]. In a typical synthesis of p-CPSA-SBA-15(0.2), one gram of SBA-15 was stirred with 1.8 g of aminopropyltriethoxysilane (3-APTES) in chloroform at room temperature for 15 h under an N_2 atmosphere. Thereafter, the stirred mixture was filtered and washed using the solvents such as chloroform and dichloromethane, and a white solid of APTES-SBA-15 was collected. APTES-SBA-15 was then refluxed with 5 g of salicylaldehyde in methanol (150 cm3) for 4 h at 333 K. The yellowish solid was then collected by the filtration of the refluxed mixture. The obtained solid material was dried in a desiccator. Thereafter, 1.22 g of yellowish solid was stirred with 0.5 g of $Cu(NO_3)_2 \cdot 3H_2O$ solution (it was dissolved by the appropriate amount of methanol) at room temperature for 15 h. The formation of a green solid product was filtered and washed with methanol using Soxhlet. The obtained product was dried under vacuum and is designated as p-CPSA-SBA-15 (0.2).

This typical procedure was adopted for the preparation of thin walled mesoporous CPSA-MCM-41(0.2). Bulk amounts of catalysts, p-CPSA-SBA-15(0.2), p-CPSA-SBA-15(0.1) and CPSA-MCM-41(0.2), were synthesized using the above synthetic procedures for the selective synthesis of aromatic ketones as edited in main manuscript.

4. Investigation of catalytic stability

The mesoporous p-CPSA-SBA-15 catalysts, e.g., p-CPSA-SBA-15(0.2) and p-CPSA-SBA-15(0.1), used in oxidation reactions were regenerated by washing and drying at ambient temperature [2]. For an example, 0.1g of p-CPSA-SBA-15(0.2) catalyst used for these reactions was reactivated by filtration from reaction mixture, and then the catalyst was thoroughly washed by the corresponding solvents (50 ml) such as acetonitrile and dichloromethane and dried using

vacuum oven at an ambient temperature. The similar procedure was used for recovering of p-CPSA SBA-15(0.1) used for this reaction.The treated catalysts are denoted as recyclable CPSA-SBA-15 (R-CPSA-SBA-15) catalysts, i.e. R-CPSA-SBA-15(0.2) and R-CPSA-SBA-15(0.1) and used in recycling studies.

Before using in benzylic oxidation of various aromatics, 0.1g of p-CPSA-SBA-15(0.2) was simply washed several times using 100 ml of solvents, such as acetonitrile and dichloromethane, to improve the catalytic activity through the removal of any non-framework CuO nanoparticle species deposited on the active surfaces of the catalysts [2]. This treated catalyst is named as W-CPSA -SBA-15(0.2).

5. Solvent-free benzylic oxidation of aromatics

All the chemicals, for solvent-free benzylic oxidation of aromatics, were purchased from Aldrich Chemical Inc., and used as received without further purification. In order to explain about the solvent-free benzylic oxidation of aromatics, oxidation of EB to acetophenone (APC=O) was taken as an example and performed under a vigorous stirring thermostatted quartz vessel reactor with various reaction parameters. In a typical experimental procedure, 50 mg of p-CPSA-SBA-15(0.2) was taken in the reactor with 10 mmol of EB. After that, the reactor was stirred under constant stirring with slowly raising temperature to 353 K. Then, the reactant mixture was continuously refluxed for 180 min after adding 30 mmol of *t*-butylhydroperoxide (TBHP) through the septum. After completion of the reaction, the products were collected by the recovering of p-CPSA-SBA-15(0.2). To find the best catalyst, the diverse CPSA functionalized mesoporous silica catalysts were used for the oxidation of EB under the similar reaction condition. Various reaction parameters such as time, temperature, stoichiometric molar ratios of reactant (EB-to-TBHP) were conducted to find the best reaction conditions over W-CPSA-SBA-15(0.2). For the identification of a better solvent over W-CPSA-SBA-15(0.2), the oxidation of EB was carried out with different solvents like MeCN, DCE, H_2O and MeOH. The oxidation of EB was also carried out with different oxidizing agents, viz. HP (H_2O_2, 30%), molecular oxygen (O_2) received from saudi industries and UHP. Furthermore, using a variety of CPSA functionalized mesoporous silica catalysts, p-CPSA-SBA-15(0.2), R-CPSA-SBA-15(0.2) and W-CPSA-SBA-15(0.2), the solvent-free benzylic oxidation of other aromatics was extensively performed using a vigorous stirring thermostatted glass vessel reactor under various reaction conditions.

References

1. M. Selvaraj, S.W. Song, S. Kawi, Epoxidation of styrene over mesoporous Zr-Mn-MCM-41, Microporous and Mesoporous Materials, 110 (2008) 472-479.
2. M. Selvaraj, M.A. Assiri, Selective synthesis of benzoquinones over Cu(ii)-containing propylsalicylaldimine functionalized mesoporous solid catalysts, Dalton Transactions, 48 (2019) 3291-3299.

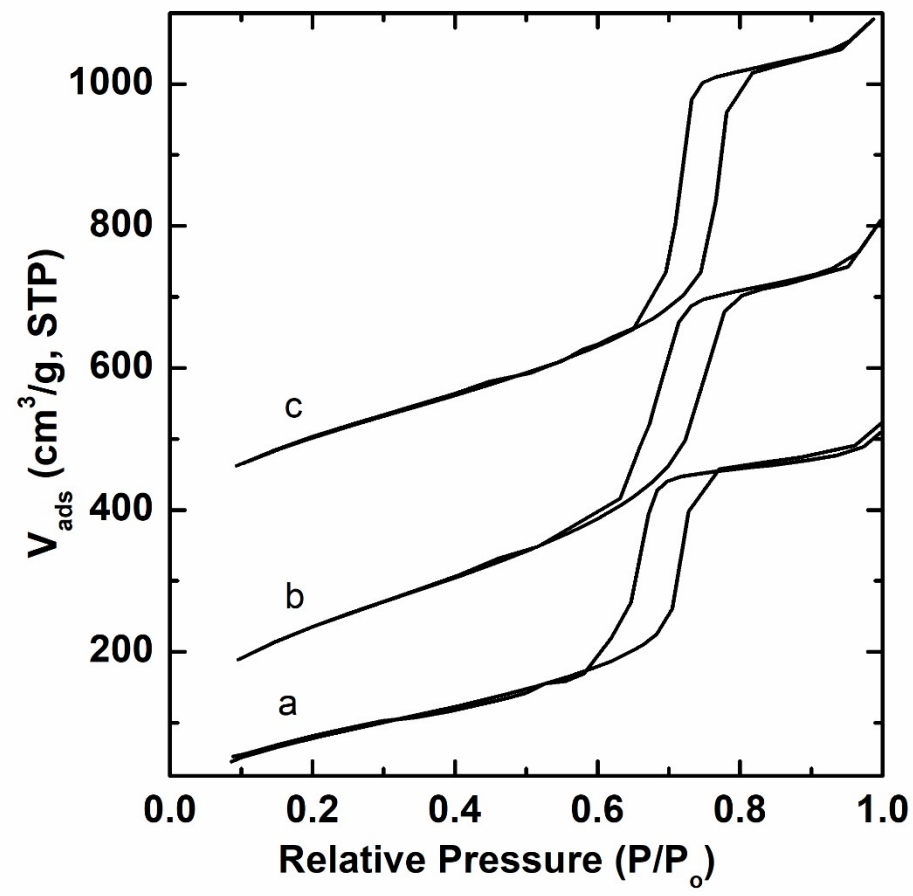


Figure S1 N_2 adsorption isotherms of (a) p-CPSASBA-15(0.2), (b) R-CPSASBA-15(0.2) and W-CPSASBA-15(0.2)

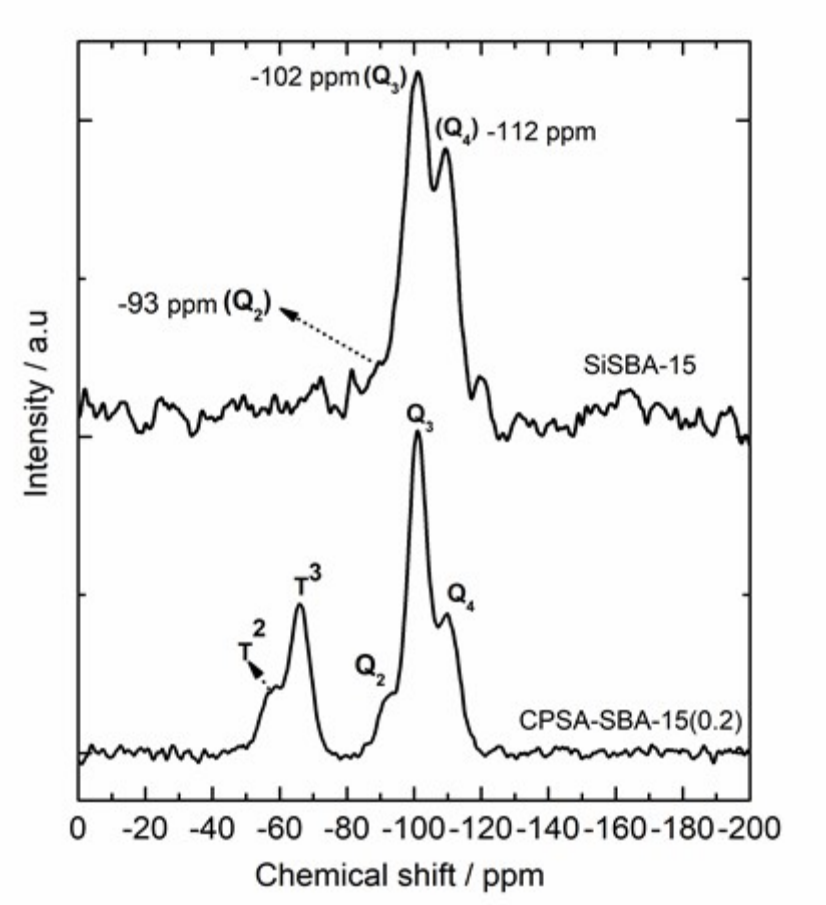
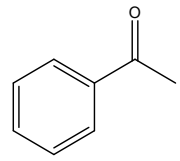


Figure S2 ^{29}Si CP MAS NMR spectra of SiSBA-15 and p-CPSA-SBA-15(0.2)

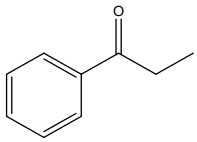
NMR (^{1}H and ^{13}C) data for main ketone products

The NMR (^{1}H and ^{13}C) data for main ketone products were confirmed with their authentic samples, and their experimental prcedure referred as reported in elsewhere [1-2].



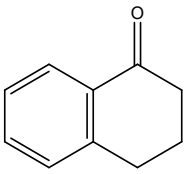
acetophenone

Acetophenone (Entry 1): It is a colourless viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.97 (m, 2H), 7.58-7.56 (m, 1H), 7.48-7.47 (m, 2H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 137.2, 133.2, 128.7, 128.3, 26.5.



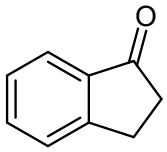
propiophenone

Propiophenone (Entry 2): It is a colourless and sweet-smelling liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.97 (m, 2H), 7.57-7.55 (m, 1H), 7.47-7.45 (m, 2H), 3.02 (q, 2H, J = 7.2 Hz), 1.22 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 137.1, 132.8, 128.4, 128.1, 31.7, 8.1.

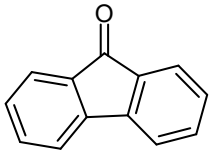


1-tetralone

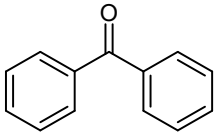
1-Tetralone (Entry 3): It is a colourless oil with a faint odor.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (dd, J = 7.8, 1.2 Hz, 1H), 7.48 (td, J = 7.5, 1.4 Hz, 1H), 7.18-7.36 (m, 2H), 2.98 (t, J = 6.1 Hz, 2H), 2.62-2.72 (m, 2H), 2.08-2.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): C =198.2, 144.5, 133.4, 132.4, 128.8, 127.1, 126.4, 39.1, 29.5, 233.



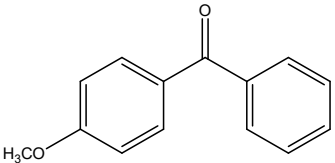
1-Indanone (Enry 4): It is colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.62-2.67 (m, 2H), 3.9 (t, *J* = 6.0 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 25.9, 36.1, 123.5, 126.6, 127.1, 134.5, 137.1, 155.2, 207.2.



9-Fluorenone (Entry 5): It is an aromatic organic compound and yellow colour powder; ^{1}H NMR (400 MHz, CDCl3): δ = 7.62 (d, *J* = 7.3 Hz, 2H), 7.47 (dt, *J* = 14.6, 7.1 Hz, 4H), 7.23-7.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =193.4, 144.1, 134.5, 133.7, 128.7, 124.1, 120.1.



Benzophenone (Entry 6): It is a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75-7.85 (m, 4H), 7.54-7.64 (m, 2H), 7.42-7.53 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 137.4, 132.4, 130.2, 128.3.



4-methoxy-benzophenone

4-Methoxy- benzophenone (Entry 7): It is a white solid. ^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.77-7.85 (m, 2H), 7.72-7.75 (m, 2H), 7.53-7.57 (m, 1H), 7.41-7.47 (m, 2H), 6.91-6.99 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.3, 163.1, 138.2, 132.5, 131.8, 130.3, 129.7, 128.1, 113.5, 55.6.

References

1. Y.Yang and H. Ma, Tetraheran Lett., 57 (2016) 5278.
2. M. H.-Sarvari, T. A.-Kachouei and F. Moeini, RSC Adv., 5 (2015) 9050.