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Silica Microspheres Containing High Density Surface Hydroxyl Groups as Efficient Epoxidation Catalysts†

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Uniform sized silica microspheres were synthesized by hydrolysis-condensation method. The obtained material was etched with mild aqueous potassium hydroxide solution for different periods of time to break their Si-O-Si bonds and increases the density of hydroxyl groups on their surfaces. The resulting materials were then used as transition metal-free catalyst for oxidation of olefins in presence of hydrogen peroxide as a green oxidant. The materials were thoroughly characterized using various physicochemical techniques. These highly populated hydroxyl groups on the surface of silica microspheres were proven to be responsible for excellent conversion (up to 93%) and epoxide selectivity (up to 100%) for various olefins. Quantum mechanical calculations also corroborate the experimental findings. Furthermore, both experimental and theoretical studies show that tertiary silanols were present at the active sites of the catalyst surface and were responsible for olefin epoxidation.

Introduction

Silica-based nanomaterials have been extensively explored in catalysis, especially as reports of various synthetic methods to a range of meso- and micro-pororous silica materials have continued.[1] Besides porous silica materials, self assembled silica microspheres with different core-shell and hollow core-shell structures have been widely studied due to their intersting morphology, low density, high thermal and mechanical stability, and short diffusion lengths for reactants to reach desired sites in them. Generally, all these silica-based materials are mainly used as a support materials to produce supported catalysts or shape selective catalysts for a large number of organic transformations.[2] They have also found various potential applications in chromatography, drug delivery vehicle, adsorbents, catalysis, etc.[3-5]

Particularly, silica microspheres with different structures such core-shell, hollow core-shell containing active metals have been effectively used in catalysis with various interesting outcomes.[6,7] Their synthesis with different structure or shape often involves facile procedure such as self-assembly, wet etching, surface coating/modification and/or calcinations. During mild or incomplete etching procedure, for example, using aqueous bases of mild concentrations, their Si-O-Si bonds can be broken and the surface density of hydroxyl on the silica microspheres could be increased.[8] High density of such free surface hydroxyl groups can be useful in catalysis. For instance, Berkeseel *et al.*[9] proved this concept by using terminal free hydroxyl groups from the hyperbranched polyglycerol (hPG) of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as efficient metal free olefin epoxidation catalyst. The high catalytic activity exhibited by the materials was attributed to the electronic effect of fluorine atoms, which by virtue of their hydrogen bonding ability, high ionization power and low nucleophilicity aid the catalytic to the HFIP molecule. Adding to these properties, density of functional groups was quite high in the range of 100 per hPG molecule.

The olefin epoxidation reaction is exceedingly important in the petrochemical industry as relatively easy way to convert available crude oil fraction into versatile synthetic intermediates and commodity chemicals.[10] However, it remains

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Notes and references

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an enormous challenge to achieve high performance of these reactions. Till date the chlorohydrin (non catalytic) route is a well known industrial process for synthesis of epoxides.[11] In the recent years after development of Halcon-Arco process, peroxides of group 4-7 metals have been employed for olefin epoxidation.[12, 13] The major disadvantage from the economic point of view with these processes is that they are expensive. Furthermore many heterogeneous catalysts have also been explored for epoxidation reaction.[14] In the recent past, metal organic framework (MOF) have been used for olefin oxidation.[15]

While transition metal based catalysts are commonly used for epoxidation reaction, a number of non transition metal based catalyst have also been found to catalyze the reaction. The first such type of catalytic system was demonstrated by Schuchardt *et al.* [16], where γ-Al_2O_3 prepared by sol-gel method was shown to be an effective catalyst for nucleophilic olefin epoxidation. Also, it has been investigated the actual catalytic species by ^{27}Al MAS NMR and hydroxyl groups of γ-Al_2O_3, whose global charge is equal to -0.50, are responsible for the catalytic epoxidation reaction.[17] The same group also found that the same species to be responsible for catalytic H_2O_2 decomposition exhibited by the material and decreased oxidant selectivity. Shul'phin and co workers predicted the detailed mechanism of Al^{3+}-catalyzed oxidations of hydrocarbons by DFT calculations.[18] They found that the activation of H_2O_2 occurred by homolytic cleavage forming the intermediate $[Al(H_2O)_4(OOH)(H_2O_2)]^{2+}$ without change of metal oxidation state due to the presence of the easily oxidizable -OOH co-ligand and it generates the HO• radicals, which then responsible for oxidation of hydrocarbons. In the recent past Asefa *et al.*[19] have reported the use of mesoporous SBA-15, MCM-41 and silica microspheres as oxidation catalyst in pH dependent epinephrine oxidation by electrochemical method. Hence, the use of such modified silica materials in metal free catalysis would be very interesting. Herein, we explored synthesis of the assembled silica microspheres with increased hydroxyl population by breaking the Si-O-Si bond and these free hydroxyl groups were used as an efficient epoxidation catalyst using 50% H_2O_2 as an oxidant. Furthermore, our experimental results were confirmed by DFT calculations.

Results and Discussion

Silica microspheres were prepared by hydrolysis-condensation (HC) method[4,8,21] and etched by aquous potassium hydroxide solution at different time and concentration. The prepared silica microspheres were characterized by various physicochemical methods. The Brunauer–Emmett–Teller (BET) surface area and pore diameters of the silica microspheres and etched silica's were determined by N_2 adsorption measurements (ESI fig. S1†). The BET surface area of the 0, 2, 3, and 4 h, etched silica microspheres was found to be 28.2, 29.8, 33.4, and 38.2 m^2/g respectively. This result indicated that the surface area of the silica microspheres increased with the etching time. FTIR analysis showed the broad band 2500-3600 cm^{-1} which was due to the surface hydroxyl group (ESI fig. S2†). The band intensity increased after etching the silica microspheres for 4 h which indicats an increase in the density of hydroxyl groups over silica surface. Similar fact was also found out by Asefa *et al.* by geometrical calculation.[20]

The environment around the Si framework was determined by solid state ^{29}Si-NMR (fig.1). As synthesized silica spheres showed peak at -88, -105.0 and -113.1 ppm Q^2, Q^3 and Q^4 clearly showing $[(Si\text{-}O\text{-})_2\text{-}(OH)_2]$, $[(Si\text{-}O\text{-})_3\text{-}OH]$ and $[Si(\text{-}O\text{-}Si)_4]$ species respectively are present on the surface.[21,22] It was observed that with the increase in etching time period of silica microspheres with 0.01 M KOH solution resuted in an increase in broadening of the Q^2 and Q^3 peak at -88 ppm and -104.3 ppm respectively. Broadening of Q^3 peaks was due to increase in tertary silanols on silica microspheres surface.

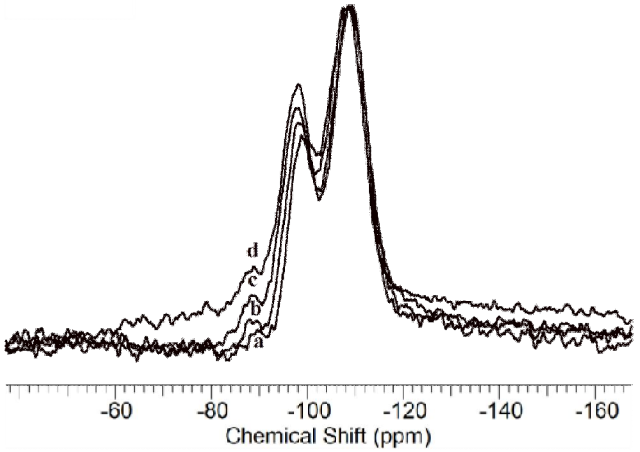

Figure-1: ^{29}Si-NMR spectra of (a) silica microsphers (b) silica microsphers etched for 2h, (c) silica microsphers etched for 3h and (d) silica microsphers etched for 4h.

The SEM and TEM images (ESI fig. S3-S7†) clearly showed the mono dispersed silica microspheres with a diameter of about 350 nm. When these silica particles were etched for two hours using 0.01 M KOH solution, then silica microspheres did not show any significant etching of the surface. However after prolonged etching times (3 and 4h) the silica was etched extensively (fig. 2 B & C).

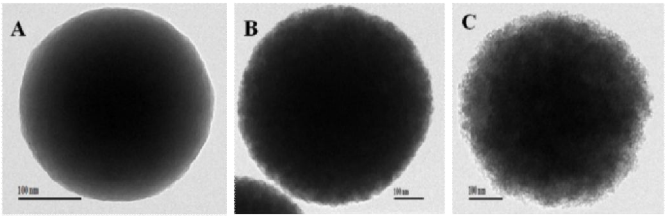

Figure-2: TEM micrograph of silica microspheres etched with 0.01 M KOH for (a) 2 h (b) 3 h and (c) 4 h.

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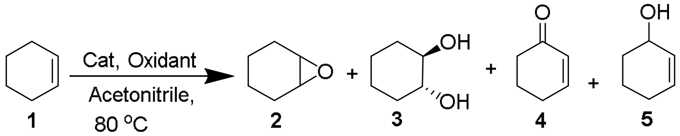
To test the oxygen transfer efficiency of surface hydroxyl group of silica microspheres, cyclohexene epoxidation was carried out as a model reaction (Scheme 1**)**. The reaction was carried out at 80 °C using aqueous 50% H_2O_2 as an oxidant and acetonitrile as a solvent. The reaction was monitored by withdrawing the samples after regular interval of time and analyzed using GC and product were confirmed by GC-MS.



Scheme 1: Epoxidation of cyclohexene and it's possible products.

To find out the best catalyst various experiments were carried out. First, the epoxidation reaction was carried out without using the silica microspheres; it gave 13% cyclohexene conversion in 24 h, with 47.7% cyclohexeneone as a major product which could be due to the auto catalysis by thermal reaction. Then the silica microspheres were used as catalyst, it gave significant increase in the cyclohexene conversion (49.7%) with very high selectivity towards cyclohexene epoxide (93%) (Table 1 entry 2). When 2h etched silica microspheres were used as a catalyst, further increase in the cyclohexene conversion (59.2%) was obtained with 96% selectivity for epoxide. Further increase in etching time of silica microsphere gave 72.3% conversion without much change in selectivity of epoxide. It was found that the formed surface silanol groups assists for further conversion without losing much selectivity (Table 1 entries 4, 5).

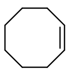
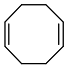
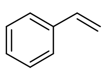
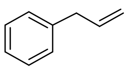
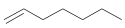
Table 1. Results of epoxidation of cyclohexene using different silica as catalysts[a].

Entry	**Catalyst**	**% Conv.**	**% Sel.**			
		1	**2**	**3**	**4**	**5**
1.	No Catalyst	13.7	23.3	-	47.7	29
2.	Stobber SiO_2	49.7	93.1	2.6	4.3	-
3.	Etched SiO_2 [2h]	59.2	96.0	-	4.0	-
4.	Etched SiO_2 [3h]	66.3	90.4	4.1	5.5	-
5.	Etched SiO_2[4h]	72.3	90	7	3	-

[a]**Reaction condition:** Cyclohexene: 0.01 mol; 50% H_2O_2: 0.04 mol; Temperature: 80 °C; Solvent: Acetonitrile (10 g); Catalyst: 0.08 g; Time-24 h.

The catalytic activity of silica increased singnificatlly because of the increase in density of surface on to the etched silica spheres. The increase in surface hydroxyl groups was due to the breaking of Si-O-Si bond in silica sphere and formation of corrugated and nanoporous structure in the etched sample.[8,20] To prove the increased catalytic activity due to increase in hydroxyl groups, we have carried out series of experiments. First, after 8 h reaction time, the catalyst was removed from reaction mixture by filtration and reaction was continued till 24 h. It gave only additional 12% cyclohexene conversion which could be due to autocatalysis (ESI TS1†). Furthermore, surface hydroxyl groups of 4 h etched silica spheres were killed by calcining the sample at 500 °C. This calcined sample when used for cyclohexene oxidation it gave only 25.1% conversion and 62% selectivity under identical condition. These results indicated decrease in catalytic activity due to reduction of surface silanol groups. The increase in catalytic activity can be attributed to the *in-situ* generation of silica-peroxy species and direct transfer of oxygen via hydrogen bonding. Bednarz and co-workers[24] have shown in silica-H_2O_2 xerogel similar type of strong coordination between surface hydroxyl and H_2O_2 hence similar type of interactions are possible on silica surface with H_2O_2. Furthermore, reaction was carried out at different substrate to oxidant ratio to find out the amount of oxidant required for complete oxidation. When two equivalents oxidant was used then it gave 25% cyclohexene conversion without changing the selectivity in 24 h. Also upon increasing the oxidant ratio to six equivalents it gave 95% cyclohexene conversion without changing the selectivity (ESI Table ST2†).

Table 2. Results of epoxidation of different olefins using 4h etched silicasphere.[a]

Entry	**Substrate**	**% Conv.**	**% Sel.**				
			6	**7**	**8**	**9**	**10**
1.		51.6	100	-	-	-	-
		93[b]	100	-	-	-	-
2.		56[c]	89	-	11	-	-
3.		32	15	46.6	-	37.4	-
4.		19	100	-	-	-	-
5.		42	60.6	-	-	-	39.4

[a]**Reaction condition:** Substrate: 0.01 mol; 50% H_2O_2: 0.04 mol; Temperature: 80 °C; Solvent: Acetonitrile (10 g); Catalyst 4h etched silica sphere: 0.08 g; Time-24h. [b]Time: 20 h and 1:6 substrate to oxidant ratio; [c]Time: 20 h and oxidant 1:8; **6** = mono epoxides of the respective substrate; **7** = benzaldehyde; **8** = (1Z,5Z)-cycloocta-1,5-diene; **9** = 1-phenyl ethanol-1; **10** = hexanal.

To study the scope the silica microspheres as epoxidation catalyst, variety of olefins were oxidadized under optimized

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reaction condition. When cyclooctene was used as substrates, it gave 90% conversion and 100% selectivity for epoxide (Table 2 entries 1,). Also, when cycloctadiene was used as substrates then it gave 56% conversion in same time with 89% monoepoxide product and 11% diepoxide product. As expected styrene gave poor conversion (32%) and 15% selectivity for epoxide and main product was benzaldehyde (46.6%). Whereas, allyl-benzene gave further less conversion (19%), with 100% epoxide being the exclusive product. Importantly, even n-heptene could be oxidized with 42% conversions and 60.6% selectivity for epoxide and. 39.4% hexanal proudct. From all these studies we conclude that these silica spheres can be usefull oxidation catalyst.

Mechanistic study using DFT calculations

We investigated the mechanism of the above reaction catalyzed by high density hydroxyl consiting silica spheres with density functional theory (DFT) studies. The DFT calculations were performed using the Turbomole 6.4 suite of programs.[25] The TZVP basis set was used,[26-28] along with the B-P 86 functional.[29,30] Solvent effects have been considered with single point calculations on the optimized geometries, with acetonitrile (ε = 37.5) employed as the solvent. For further details, please see the computational details.

We have assumed that silica microspheres are composed of bulk Si-O-Si and surface silinols (Si-OH). However, the bulk silica atoms are not available for the catalytic reaction as they do not interact with the reaction medium. The synthesized silica microspheres surface is composed of mainly tertiary and quarternary silanols, whereas secondary silanols are completely absent or at low concentrations, as shown by ^{29}Si NMR spectroscopy. Model systems (a-1) for the secondary silanol (fig.3), and (a-4), for the tertiary silanol (fig. 4) have been employed in the DFT calculations. The choice of these models for the surfaces has been dictated by the fact that bulk and surface Si-O-Si are inert and do not participate in the epoxidation chemical reaction on the surface, and, hence, the secondary and tertiary silanol sites chosen in a-1 and a-4 are the only active sites on the catalyst surface. Therefore, employing a-1 and a-4 is appropriate for determining the most likely mechanism of cyclohexene epoxidation.

The attack of H_2O_2 at the active site (a-1) having the secondary silanol group [$Si_3O_9H_8$] present on the silica surface results in the formation of [$Si_3O_8H_8OOH$] (a-2) *via* the transition state (t-1) having an energy barrier of 39.0 kcal/mol. There was also the possibility of a competitive reaction between the two germinal diols to form Si=O. However, the DFT calculations indicate that this possibility is less likely because the transition state barrier for the formation of the [$Si_3O_8H_7$] [(S-2) (ESI fig. S8†) was calculated to be 42.6 kcal/mol and is thus 2.6 kcal/mol higher in comparison to the barrier for the H_2O_2 attack at the silicon centre. The resulting species [$Si_3O_8H_8OOH$] (a-2), from the reaction between H_2O_2 and (a-1) reacts with cyclohexene to form cyclohexene epoxide with the regeneration of the catalyst. The transition state barrier (t-2) for the formation of epoxide from cyclohexene was calculated to be 23.7 kcal/mol.

Alternatively, it is also possible that functional groups -OOH and –OH present at the active site [$Si_3O_8H_8OOH$] (a-2) can interact amongst themselves *via* intramolecular rearrgement to form ring peroxo (-O-O-) species (a-4). The transition state barrier (t-4) for this step is 24.5 kcal/mol. This peroxo species can further react with cyclohexene to form epoxide *via* exogeneous attack at the doule bond through a mechanism similar to the Sharpless mechanism[31] (ESI fig. S9†). The transition state barrier for this step was calculated to be 22.7 kcal/mol. Interestingly, DFT calculations show that the energy difference for two competitive mechanism, that is, the breakdown of superoxo species –O-O-H present on active site (a-2) to form epoxide, and intramolecular rearrgement on the same active site to form the peroxo species (a-3) was less than 1.0 kcal/mol. This indicates a probability for the occurence of either of the mechanisms. The species [$Si_3O_9H_6$] (a-4) further reacts with H_2O_2 to form [$Si_3O_{11}H_8$] (a-5) and the catalytic active site is regenerated. The barrier for this step is 18.1 kcal/mol (t-4).

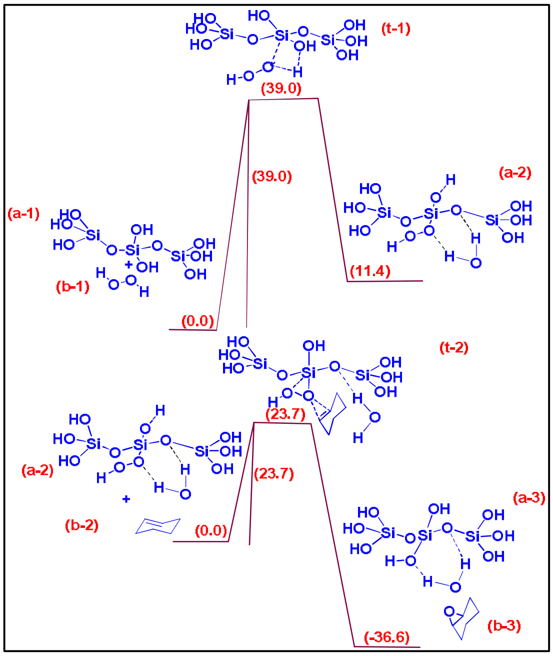

Figure-3: The potential energy surface for olefin epoxidation catalyzed by secondary silanols present on the synthesized silica microspheres; energy values (ΔG) are in kcalmol^{-1}.

The results of the calculations with the active site having the tertary silanol [$Si_4O_{13}H_{10}$], (a-7) on the surface are shown in Figure 4. The interaction of (a-7) with H_2O_2 results in the formation of [$Si_4O_{12}H_9OOH$] (a-8), having a barrier of 32.6 kcal/mol, which is 6.4 kcal/mol lower as compared to the secondary silanol (a-2) case. Now, solid state ^{29}Si-NMR spectroscopy cleary shows that synthesized silica spheres have predominantly a peak at -105.0 and -113.1 ppm Q^3 and Q^4 indicating the presence of [(Si-O-)$_3$-OH] and [Si(-O-Si)$_4$]

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species on the surface, whereas the Q^2 peak is in lower concentration on the silica surface. On further etching, the silica surface with 0.01 M KOH resulted in a resonance peak at -104.3 ppm with broadening of Q^3 peaks indicating the increase of tertiary silanol groups on the silica surface. It was experimentally observed that this led to an increase in catalytic activity, just as the calculations also suggest, as discussed here. The computational studies therefore corroborate the experimental findings. The intermediate species [$Si_3O_8H_8OOH$] (a-8) formed further reacts with cyclohexene to form epoxide (b-3) having a barrier of 23.3 kcal/mol (fig. 4) These studies have helped us to not only investigate the mechanism with these two different active sites, but have also aided in determining the superior active site amongst secondary and tertiary silanols for cyclohexene epoxidation.

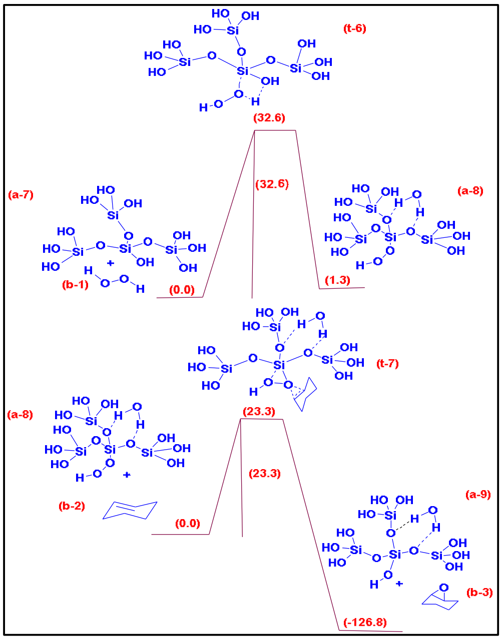
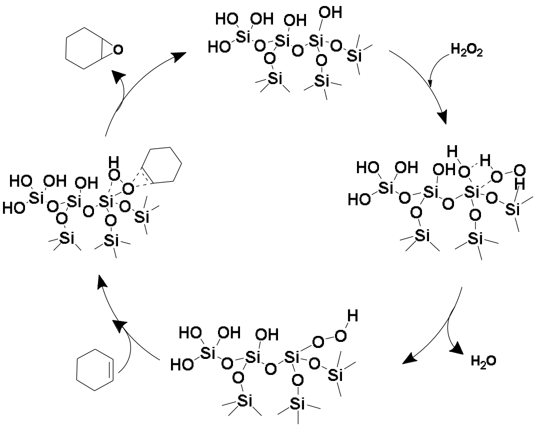


Figure-4: The potential energy surface for olefin epoxidation catalyzed by tertiary silanols present on silica microspheres; energy values (Δ G) are in kcalmol^{-1}.



Scheme 2: Represents the plausible mechanism of olefin epoxidation catalyzed by the silica microspheres.

Based on our experiment and DFT results, the possible route to formation of epoxide is depicted in scheme 2. We belive that surface hydroxyl groups of silica spheres reacted with the H_2O_2 to form superoxo (η^1-OOH) species with elimination of water, which further reacted with the double bond of the olefin to form epoxide, followed by the regeneration of the catalyst.

Conclusions

We have investigated by experimentally and computationally that the silica microspheres containing high density surface hydroxyl groups are very efficient for epoxidation of olefine using hydrogen peroxide as green oxidant. It was further conformed that by controlled etching with time the surface area as well as hydroxyl density increased by breaking the Si-O-Si bond over the surface of silica microspheres. The increased surface hydroxyl group density was further confirmed by different physicochemical method. It was found that the presence of high density surface hydroxyls on the silica surface increases the rate of epoxidation reaction. Also, it showed wide range of olefins such cyclooctene, allybenzene, cycloctadiene, n-heptene could be oxidised being used the etched silica spheres. Furthermore, both experimental and theoretical studies show that tertiary silanols were active sites present on the catalyst surface responsible for olefin epoxidation.

Experimental Section

Synthesis of silica microsphere: The silica microsphere were synthesized by following the reported procedure[4,20]: in brief, a 1000 mL plastic bottle was charged with 400 mL ethanol, distilled water 14.4 mL and 40 mL ammonia solution and stirred vigorously at 1000 rpm for few minutes. Then 23.4 g tetraethylorthosilicate (TEOS) was added slowly into the reaction mixture and reaction mixture was allowed to stir at moderate strring (600 rpm) for 3 h. Then obtained white solid was collected by the centrifugation and washed with ethanol water solution (50%) thrice and allowed to dry at room temperature. The weight of final product was 7g (yield = 97%).

Synthesis of etched silica microsphere: 4 g above synthesized silica microsphere was dispersed in 50 mL of distilled deionized water by sonication. Then 1500 mL (0.01 M) KOH was added into it and the reaction mixture was stirred at slow and constant speed (at 250 rpm) for 2 h and finally etched silica was collect by centrifugation and washed with copious amount of water and this procedure was repeated at least three times. Also the silica was etched at different time i.e., for 3 and 4h following the same procedure.

Catalytic epoxidation reactions: The liquid phase epoxidation of olefin was carried out in a two necked round bottom flask (RBF). The flask was charged with alkene (0.01 mol), oxidant 50% H_2O_2 (0.04 mol) and 10 mL solvent (acetonitrile). The RBF was equipped with water condenser and immersed in a thermostat oil bath at 80 °C. Then reaction mixture was stirred on the magnetic stirrer. The reaction was continued for 24 h.

The samples were withdrawn periodically and analyzed on Agilent 6890 Gas chromatograph equipped with a HP-5 dimethyl polysioxane column (60 m length, 0.25 mm diameter and 0.25 µm film thicknesses with flame ionization detector. Products were confirmed by injecting the authentic on GC and also GC-MS.

Computational Details

The computational procedure adopted is as follows: all the structures reported in the manuscript have been optimized using density functional theory (DFT) with the Turbomole suite of programs, using Turbomole Version 6.4.[25] The geometry optimizations were performed using the BP-86 functional.[27] The electronic configuration of the atoms was described by a triple-zeta basis set augmented by a polarization function (TURBOMOLE basis set TZVP).[26] Since it is possible that the geometry optimization procedure with DFT may be sensitive to the nature of the functional, all the structures were also optimized with the Perdew, Burke, and Erzenhof density functional (PBE),[32] as well as with the B3LYP functional,[33, 34] and the TZVP basis set, in order to make sure that the results did not vary significantly with the change of the functional. The resolution of identity (RI),[35] along with the multipole accelerated resolution of identity (marij)[36] approximations were employed for an accurate and efficient treatment of the electronic Coulomb term for both of the sets of the density functional calculations. A comparison was then done between the corresponding structures obtained with the BP-86 and the PBE and B3LYP functionals. The comparison showed very little difference in bond lengths, angles and dihedral values between the corresponding structures for all the cases (ESI S8-15†). A further corroboration of the smallness of the difference between the structures obtained from the two functional came from the comparison of the potential energy surfaces for the different reactions discussed in the manuscript. The ΔE values for the insertion and termination barriers for the epoxidation mechanism, obtained from the three separate set of calculations, were compared and the results, shown in the supporting information, indicate that there is only slight difference between the corresponding values for almost all the cases for the energies obtained with the BP-86 and the PBE functionals. The energies obtained from the B3LYP functionals were found to be different by 8-10 kcal/mol from the corresponding BP-86 and PBE values. This suggests that changing the functional may result in a change of the absolute values of the barriers in the different mechanisms, but that the essential conclusions reached in the manuscript will remain unchanged. With regard to the transition states obtained from the three sets of calculations, care was taken to ensure that the obtained transition state structures possessed only one imaginary frequency corresponding to the correct normal mode. No other imaginary frequencies were present. Table ST3† in the supporting information file shows the values of the imaginary frequencies that have been obtained for the different transition state structures reported in the manuscript. The contributions of internal energy and entropy were further obtained from frequency calculations done on the DFT structures at 298.15 K. Thus, the energies reported in the figures of the paper are the ΔG values. Solvent effects were incorporated using the COSMO model[37], with acetonitrile (ε = 37.5). Solvent effects were incorporated in the following fashion: single point calculations were done, with COSMO included, on all the structures that had been obtained from the gas phase calculations. The frequency calculations were done on the gas phase optimized structures, and the contribution of the entropy and zero point energy was included from the frequency calculations. The comparison of the ΔH and ΔG values in the gas phase and with COSMO included is shown in (Table ST-3) of the supporting information file. The actual optimized images of all the all the reactants, intermediates and transition states are given in ESI S-16 and 17†.

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