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Facile synthesis of a sulfonated carbon–silica-meso composite and mesoporous silica†

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In this study we report a novel and simple method for preparing a sulfonated carbon–silica-meso composite showing high acidity and porosity useful for transformation of bulky molecules, where glucose was used as a carbon source as well as a non-surfactant templating precursor and the resultant composite upon calcination yielded the mesoporous silica.

The concentration and pK_a values of catalysts play a vital role in organic transformations, where a high density of accessible strong Brønsted acid sites possessing stability in aqueous environment is desired for catalyst development.[1] The use of liquid acids such as sulfuric acid suffers from energy inefficiency and requires separation and recycling steps of acid waste residue. The usability of recyclable solid materials as replacement to homogeneous acid catalysts is usually limited due to the low density and strength of the acid sites on the solid surface.[2] The method of immobilization of homogeneous catalysts onto solid supports such as sulfonation of activated carbon resin and metallic oxide has come up to solve the problem of acid density, but the procedure is time consuming and involves several preparation steps.[3,4] Moreover, the immobilization of acidic functional groups is difficult and also yields low acid density.

In the preparation of an efficient alternative solid acid catalyst for acid attributed reactions, herein we report a simple one-step method for the synthesis of a new class of sulfonated-carbon–silica composite catalysts. The composite material containing an organic inner core and mesoporous silica shell with its high surface area and acidic properties is not only suitable for further functionalization with acid or metal ions but also provides good mechanical and thermal stability for catalytic applications.

Herein we used glucose as a cheaper and green carbon precursor alternative to the commonly used high cost resins, ionic surfactants and P123 block co-polymers.[5] In order to avoid the limitations involved in the functionalization of an organic moiety in two step partial carbonization and sulfonation methods reported in known prior art,[6,7] herein we adopted a novel synthesis approach of simultaneous carbonization and sulfonation in a single step.

The synthesis involves drop by drop addition of sulfuric acid to the solution of glucose and tetraethyl orthosilicate (TEOS) with the molar ratio of TEOS : 0.385 glucose : 4.8 H_2O : 0.88 H_2SO_4, followed by carbonization of the resultant mixture in a nitrogen atmosphere at 573 K (ESI†) to facilitate the decomposition and transformation of the glucose moieties into hydrophobic carbon residue bearing sulfonyl groups as the inner core that is in close contact with the stabilizing hydrophilic silica matrix shell designated as sulfonated carbon silica (SCS) composite material.

The amorphous mesoporous silica (Fig. S1, ESI†) designated as MS is obtained by calcination of SCS at 873 K to remove the carbon template including sulfonyl groups. The resultant MS particles have wide applications in organic mass transformations,[8] adsorption of gases[9] and immobilization of different organic moieties and inorganic metals for various catalytic applications.[10] Though, there are many methods available for the preparation of mesoporous silica in the literature, the procedures are lengthy, time consuming and use costly surfactants as templating agents.[11,12] The present work gains advantage over the existing methods as it provides a simple one-step synthesis of MS using a low cost, non-surfactant common chemical "glucose" as a template precursor. To the best of our knowledge, this is the first of its kind to synthesise mesoporous silica in a simple method using glucose as a template precursor.

The small-angle X-ray scattering (SAXS) patterns of the as-synthesized (SCS) and calcined (MS) samples are shown in Fig. 1. One broad peak signifying the average pore-center-to-pore-center correlation length is observed in both the samples.[13] However, the peak is highly intensified in MS and indicates the

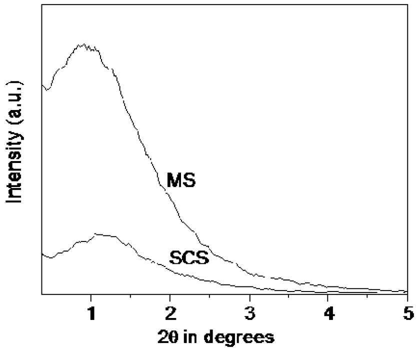

Fig. 1 Small angle XRD patterns of MS and SCS.

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significant increase in the order of the mesostructure due to the removal of the sulfonated-carbon moiety during calcination. This is further reflected in nitrogen adsorption–desorption isotherms of SCS and MS (Fig. 2A). The isotherms of both the samples are of type IV, characteristic of mesoporous materials according to IUPAC classification, but the hysteresis loop of the MS sample appears to be H2 type indicating that the MS has good pore connectivity than usually observed for large mesopores resulting from removal of the sulfonated-carbon moiety.[14] The pore volumes of SCS and MS are 0.52 cm^{3} g^{-1} and 0.87 cm^{3} g^{-1}, respectively, that confirms the removal of the sulfonated-carbon moiety in SCS and is responsible for significant increase in pore volume in MS (ESI†, Table S1). This phenomenon is further reflected in the increase in average pore diameter of the SCS from 2.6 nm to 5.3 nm after calcination (MS) (Fig. 2B). The EDX elemental analysis of samples also supported the removal of the carbon moiety after calcination (Fig. S2, ESI†).

The SEM images of samples also support the phenomenon of removal of the carbon moiety during calcination of SCS, where the black spots representing the carbon moiety observed in SCS are disappeared in MS (Fig. 3A). TPD analysis of samples reveals that SCS has high acidity than MS (Fig. S3, ESI†) as SCS contains the acid group bearing a carbon moiety which disappears during calcination and is absent in the resulting MS. Moreover, the SCS exhibited acidity similar to sulfonated zirconia.[15] The IR spectra of the samples show the interaction between the sulfonated-carbon moiety and mesoporous silica in SCS (Fig. 3B). It is known that sulfonated carbon exhibits two characteristic bands representing the –OSO$_3$H group at 1712 cm^{-1} and 1207 cm^{-1}.[16] In our study, the SCS also exhibited a band at 1712 cm^{-1}, but the second one at 1207 cm^{-1} is not distinct as it is merged with the band at 1090 cm^{-1} related to silica. The additional bands obtained at 3447 cm^{-1} and 803 cm^{-1} are due to presence of –OH and SiO$_2$ stretching vibrations. The TGA analysis of SCS (Fig. S4, ESI†) shows weight loss at two places: (1) about 8% weight loss below 392 K and (2) about 14% weight loss between 573 K and 1023 K which can be ascribed to the removal of water/moisture and carbon material respectively. This envisions that the catalyst is stable at the chosen reaction temperature *i.e.* 393 K under solvent free conditions.

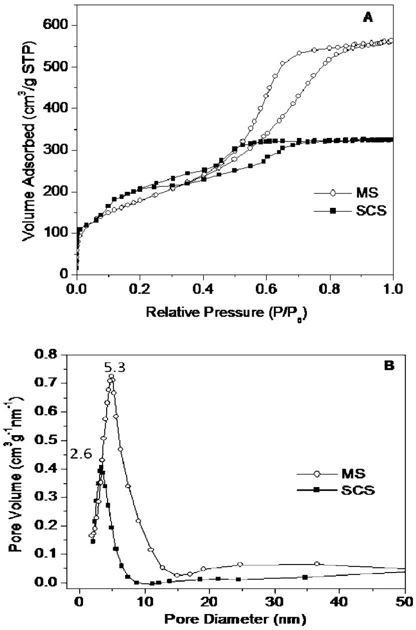

Fig. 2 (A) N$_2$ adsorption–desorption isotherms of MS and SCS. (B) The respective pore size distribution using the BJH method is shown.

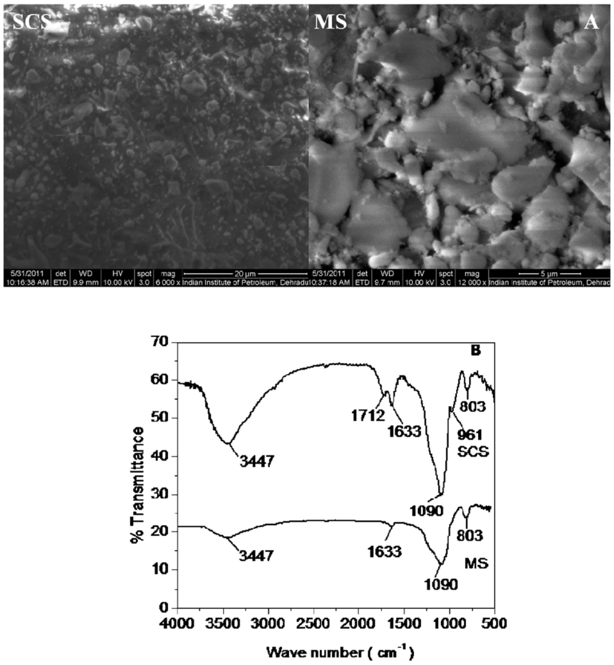

Fig. 3 (A) SEM images of SCS and MS. (B) IR of SCS and MS.

Based on the textural properties of the materials obtained (Table S1, ESI†), we have proposed a schematic model for the synthesis of SCS and MS (Fig. 4). Tetraethyl orthosilicate and glucose vigorously hydrolyse under the synthetic conditions to give –SiOH groups and sulfonyl groups bearing an aromatic organic moiety. This supramolecular assembly of glucose molecules helps to form the cage-like structure inside the SiO$_2$, where the –SO$_3$H group acts as a hydrophilic agent that can facilitate the interaction between the hydrophobic carbon moiety and the hydrophilic silica moiety for the successful formation of the SCS composite, which upon calcinations expels the sulfonated-carbon moiety to give MS with increased average pore diameter and pore volume (Fig. 2B). Aggregation or even close-packing of SiO$_2$ can also result in the formation of a mesoporous structure.[17]

Thus, SiO$_2$ units are self-assembled, and their structure effectively sustains the local strain caused during the carbon removal and mesopore formation. Upon calcinations, the

Fig. 4 The proposed templating and sulfonation pathway for the synthesis of SCS and MS.

supramolecular assembly of sulfonated glucose molecules breaks from the SiO_2 structure. Contrary to the previously reported templating pathways using surfactants or block-co-polymers where the interaction between the template molecules and the silica framework is through hydrogen or ionic bonding,[18,19] in the present study covalent bonding is observed to exist between the carbon moiety and SiO_2 of the SCS composite as it is confirmed by the presence of two IR bands at 1712 cm^{-1} and 1633 cm^{-1} representing the $–OSO_3H$ ester bond and aromatic ring respectively. As a result, the SCS of the present study exhibits pore expansion (Fig. 2) rather than the pore contraction (as conventionally observed for surfactants or block-co-polymer templated materials), up on calcination.

In general, the tertiary butylation of phenol is conventionally carried out in the vapour phase reaction at higher reaction temperatures (above 413 K) (Table S2, ESI†). However, the recent developments in novel materials provide opportunity for low temperature liquid phase catalytic reactions.[20,21] The SCS material synthesized in the present study exhibiting mesoporosity along with strong acidity is expected to be suitable for catalytic applications involving bulky molecular transformations and the material is tested for its performance in liquid phase butylation of phenol. The studies indeed indicated the promising catalytic functionality of the SCS, where the catalyst exhibited as high as 50% conversion based on phenol ($>97\%$ conversion based on alcohol) with product selectivity of 52%, 30% and 18% to 2-tertiary butyl phenol, 4-tertiry butyl phenol and 2,4-ditertiary butyl phenol respectively (Table S3, ESI†). The results indicate comparable or better performance of the SCS catalyst with the reported results (Table S4, ESI†). The reusability of the catalyst (SCS) synthesized in this work was investigated by filtering the reaction solution, washing with ethanol and drying at 393 K between consecutive cycles.

The results confirmed that the acidity-bearing carbon composite in combination with mesoporosity of the SCS catalyst successfully provides the required activity and stability to the catalyst. Moreover, due to its high surface area and pore volume, the MS obtained after removal of the sulfonated-carbon moiety is a vital host material for immobilization and functionalization useful for various mass absorption and catalytic transformations.

In conclusion, we have demonstrated a facile and single step synthesis method for the preparation of high surface area acidic SCS and MS materials through a novel approach of simultaneous carbonization and sulfonation of glucose in an organic silica medium, where glucose acts as a carbon source as well as a template precursor.

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