Abstract

Mesoporous materials are important class of porous materials, which include high specific surface area, large pore volume and uniform pore size distribution having pore diameter 2-50 nm. These materials possess great promises and opportunities with improved and tailored properties for applications in adsorption, membranes, sensors, energy storage, catalysis and photocatalysis, biotechnology etc. However, the syntheses of these materials are mostly carried out through the hydrolysis of the respective metal alkoxide, which is not only expensive but also difficult to control the rate of hydrolysis.

In this research work, various mesoporous materials have been synthesized successfully via a surfactant templated route using non-alkoxide precursors through simple, convenient syntheses procedures. Either anionic or cationic surfactant has been applied depending upon the nature of the ionic species present in the reaction mixtures. Two new mesoporous materials have been prepared and described, which are: (i) amino functionalized mesoporous silica-zirconia mixed oxide with Si/Zr= 2, that has shown its ability as an arsenate and anionic dye absorbent, and (ii) mesoporous chromium(III) phosphate which has been reported as an excellent catalyst for oxidation, isomerization, hydration, alkylation, polymerization, decomposition etc.

Mesoporous silica-zirconia mixed oxides with high zirconia content, which is an excellent acid catalyst, have been synthesized and their acidic nature have been studied. Few other mesoporous phosphate materials have been synthesized using new synthesis strategy. These are: (i) mesoporous zirconium phosphate with spherical

structure, which is an ion exchanger and an excellent acid catalyst, (ii) mesoporous zirconium phosphate-silica composite, which has potential practical applications in ion exchange, ionic conductance and catalysis, and (iii) mesoporous tin(IV) phosphate, which is a good acid catalyst and an excellent ion exchanger and thus used for the separation of various inorganic cations.

Zirconium based mesoporous materials have been synthesized using inexpensive, metastable zirconium carbonate complex, which has been prepared from zirconium oxychloride. In presence of heteroatom and suitable surfactant the metastable precursor undergoes gelation or gelatinous precipitation under certain conditions giving rise to desired mesophase. Mesoporous chromium(III) phosphate has been prepared through supramolecular templating mechanism involving the reduction of ammonium dichromate to chromium (III) ionic species in the first step. In presence of phosphate anion, *in-situ* prepared Cr(III) produces "gel" through the formation of Cr–O–P linkage in the basic medium. Urea has been used as pH controlling agent, which produces ammonium ion on heating and increases pH of the solution slowly and homogeneously. Tin(IV) phosphate has been synthesized by homogeneous oxidation of tin(II) chloride in acidic medium in presence of surfactant and phosphate ion using hydroxylamine hydrochloride solution as oxidant.

Depending upon the nature of the synthesized materials, the surfactant has been removed carefully either by (i) solvent extraction or (ii) calcination at elevated temperature.

For solvent extraction, depending upon the nature of the synthesized materials, three techniques have been employed: (i) extraction of surfactant by hot ethanol, (ii) extraction of surfactant by ethanolic HCl solution, and (iii) extraction of surfactant by sodium acetate-ethanol solution.

The synthesized materials have been characterized through low angle X-ray diffraction (XRD), BET (Brunauer, Emmett and Teller) surface area analysis, BJH (Barrett, Joyner, Helenda) pore size distribution, Transmission Electron Microscopy (TEM), Fourier Transformed Infrared (FTIR) spectroscopy, Solid State Nuclear Magnetic Resonance (NMR) spectroscopy. In addition to the above mentioned characterization techniques except NMR spectroscopy, mesoporous Cr(III) phosphate has been characterized by UV-Visible spectroscopy and Electron Spin Resonance (ESR) spectroscopy. The acidity of some of the prepared sample have been measured by Ammonia-Temperature Programmed Desorption (NH_3-TPD) and the nature of the acidic sites of the synthesized mesoporous acid catalyst have been determined by pyridine desorbed FTIR.

The applications of these synthesized mesoporous materials in the field of catalysis or separations have been studied. Mesoporous aminosilane functionalized ZrO_2-$2SiO_2$ mixed oxide has shown absorption property towards arsenate ions and anionic dye molecules. All mesoporous phosphate materials show good acidic nature. Spherical mesoporous zirconium phosphate responds well as a catalyst in the hydrolysis of ethyl acetate ester. H_3PO_4 treated zirconium phosphate-silica composite (Si/Zr = 2) and tin(IV) phosphate are potential candidates for secondary alcohol dehydration. Chromium(III) phosphate and tin(IV) phosphate show good catalytic behavior towards esterification reaction.