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Mesoporous materials: synthesis, characterization and possible applications

Thesis Submitted

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ABSTRACT

The formation of liquid-crystal-like arrays made up of molecular complex formed between molecular inorganic species (TEOS) and neutral, cationic, non-ionic, and linear anionic surfactants are convenient approach for the synthesis of mesostructure materials. Mesoporous silicates structure with controlled pore sizes (2- 17 nm) were successfully synthesized from tetraethoxysilane (TEOS) or sodium silicate using previous organic materials mixture as template. By adjusting the initial molar ratio of surfactants/TEOS, pore sizes of the final disordered or ordered hexagonal mesoporous silicas could be precisely tuned in the ranges of 2-17 nm. Incorporation of Al^{3+} into silica framework using direct method has been successfully prepared in high acidic medium.

Results show that the materials have high surface area, narrow pore size distribution and high total pore volume. The mesoporous materials were characterized and confirmed by using X-ray, N_2 sorption, SEM, TEM, AFM, FTIR, pyridine-FTIR, TGA, DSC, TPR and NH_3-TPD.

The activity of different supports and catalysts were carried out on paraffinic wax, cumene cracking, n- heptane, n-hexane and cyclohexane hydroconversion, which gave great catalytic activities toward catalytic cracking, hydrocracking and hydroisomerization.

Key words: mesoporous materials; Al-mesoporous materials; HMS; AlHMS; SBA-15; AlSBA-15; MCM-41; AlMCM-41; anionic surfactants; paraffinic wax cracking; cumene cracking; isomerization.

SUMMARY

Nanoporous materials have become more and more important in either science or technology. They can be grouped into three classes based on their pore diameter (d): microporous, $d < 2.0$ nm; mesoporous, $2.0 < d < 50$ nm; macroporous, $d > 50$ nm. Among them, mesoporous materials have attracted more attention due to tailoring ability of the pore structure over a wide range, and the potential applications in catalysis.

Designing a heterogeneous catalyst involves both the proper control of the surface chemistry and a rigorous control of the surface geometry at the micro-, meso- and macroscales. This is because high surface areas or high active phase dispersions as well as fast mass transfer of the reactants that are required from any active catalyst.

Four groups of ordered and disordered hexagonal structural mesoporous molecular sieves Si-HMS, Si-SBA-15, Si-MCM-41,Si-MFG and have been prepared and successfully controlled by optimizing the gel compositions using tetraethylorthosilicate and sodium silicate have been used as silica sources while aluminium isopropoxide is used as alumina source. In addition, decylamine, nonionic (poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, Mwt = 5800), cationic cetyltrimethylammonium bromide, and commercial alkylbenzene sulphonic acid have been used as structure directing agents (templates).

HMS molecular sieve has been synthesized via hydrogen bonding self-assembly in microemulsion of ethanol/water, dioxane/water and benzene/water mixtures in order to obtain the hexagonal mesoporous materials. Homogeneous solutions of the structure directing surfactant in water/ethanol and water/dioxin co-solvents completely dissolve the

surfactant and allow for the formation of HMS derivatives with high textural mesoporosity. The pore size distribution and particle size of the final disordered hexagonal mesoporous silicas could be precisely tuned depending on nature of solvent and TEOS/DA ratios.

AlSBA-15 materials with different *n*Si/*n*Al ratio have been synthesized by simply adjusting the molar water to hydrochloric acid ratio ($nH_2O/nHCl$).

MCM-41 and AlMCM-41 have been synthesized from low cost sodium silicate and sodium aluminate via cationic templating. Substitution of high cost silica sources by low cost sodium silicate is the first target of this work.

Large-pore mesoporous silica and silica-alumina with 3D wormhole framework structures (denoted as MFG) have been prepared using novel and inexpensive commercially available linear alkylbenzene sulphonic without using both acid catalyzed hydrolysis of silica source pathway and swelling agents for core micelle. Substitution of high cost templates by inexpensive, low toxicity and locally commercial is the second target of this work.

Direct incorporation of heteroatoms (Al^{3+}) has a negative effect on structure ordering, total pore volume and pore size distribution. The negative effect is directly proportion to amount of Al^{3+} incorporated. On the other hand, incorporation of $Al3^{+}$ has a positive effect on enhancement of acidity, dispersion of $NiMoO_3$. The acidity and dispersion of active phases is directly proportional to amount Al^{3+}. The loading of Mo in highly acidic medium preserve the mesostructure ordering. The preservation of structure ordering after Mo loading is the third target of this work.

The physical and chemical compositions of the prepared materials have been characterized by adequate analysis that proves the physical and chemical composition is identical for mesoporous materials.

The high performance catalytic activity of mesoporous material have been studies on different petroleum fraction such as, wax cracking, cumene cracking and hydroconversion of n-heptane, n-hexane and cyclohexane.

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Mohamed A. Betiha

Dedicated

To the two most important people in the world, my parents Ahmad and Fatma, who sacrificing their lives to provide me with everything that I wished.

They have instilled in me the qualities that have brought me to where I am today.

“رب ارحمهما كما ربياني صغير”

"My Lord! Bestow on them your Mercy even as they cherished me in childhood. " (The Holly Quran, Chapter 17, Verse 24)

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