Mesoporous Silica Nanomaterials Applications in Catalysis

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Mesoporous silica materials benefit from unique features that have attracted substantial interest for their use as catalyst-immobilization matrices. These features include high surface area, chemical, thermal, and mechanical stability, highly uniform pore distribution and tunable pore size, high adsorption capacity, and an ordered porous network for free diffusion of substrates and reaction products. Solid supported catalysts are of great interests in both academic and industrial arenas due to their recyclability, enhanced catalytic reactivity, and selectivity. Inorganic, organic end enzymatic catalysis fields have been revolutionized by introduction of mesoporous silica nanomaterials as support due to dramatic increase of contact area and thus contributing to overall reaction yield [1-4]. Furthermore, mesoporous silica offers the opportunity of multifunctionalization and therefore, multiple catalyst immobilizations. The ability to sequester selectively molecules buy their functionality makes mesoporous silica catalyst championing high selectivities. This editorial will highlight the most important achievements in the field of mesoporous silica-supported catalysis.

The first mesoporous silica material was first reported as early as 1971, where a material described as low-bulk density silica was obtained from hydrolyzing and condensing tetraethoxysilicate (TEOS) in the presence of cationic surfactants [5]. This result did not gain much attention at the time it was published because the porosity and structural properties were not reported. It was not until 1992 that the chemistry society started to realize the potential of this field, when scientists in oil giant Mobil Corporation laboratories published a series of ordered mesoporous materials (M41S) with pore sizes ranging from 1.5-10 nm. The variant called MCM-41 with 1000 m^2g^{-1} and pore volumes up to 1 cm^3g^{-1}, has been comprehensively studied and widely applied in many fields such as drug delivery, biosensors and catalysis [6-12]. The morphological transformations that lead to converting bulk MCM-41 mesoporous silica to functionalized mesoporous silica nanospheres (MSNs) by Lin's group represented a step forward toward increasing control of kinetics in catalytic reactions occurring in functionalized MSN [10].

The first report of utilizing mesoporous silica in polymer synthesis catalysts initiated by Aida's group in Japan, has opened new avenues toward modern solid-supported catalysis. The authors reported crystalline nanofibers of linear polyethylene with an ultrahigh molecular weight (6,200,000) and a diameter of 30 to 50 nanometers, formed by the polymerization of ethylene with mesoporous silica fiber–supported titanocene, with methylalumoxane as a cocatalyst. Small-angle x-ray scattering analysis indicated that the polyethylene fibers consist predominantly of extended-chain crystals. The Science article highlighted the potential utility of the honeycomb-like porous framework as an extruder for nanofabrication of polymeric materials [13].

Ever since this publication, catalytic applications of mesoporous silica have exponentially increased. A variety of functionalities have been pursued, and a few examples in each category are provided as follows.

Organic and organo-metallic catalytic functionalities

Several molecular moieties that serve as catalytic groups in solution could be "anchored" on pore surface of mesoporous silica materials without compromising their catalytic ability.

For example, a nucleophilic catalytic system comprised of dialkylaminopyridine-functionalized mesoporous silica nanosphere (DMAP-MSN) has been synthesized and characterized by Lin's group. This material was proved to bean efficient heterogeneous catalyst for Baylis-Hillman, acylation, and silylation reactions with good reactivity, product selectivity, and recyclability. The authors highlighted that the DMAP-functionalized mesoporous silica material can also serve as an effective heterogeneous catalyst for many other catalytic nucleophilic reactions [6].

Maschmeyer et al. reported that direct grafting of an metallocene organo metallic complex onto the inner walls of mesoporous silica, generates a shape-selective catalyst with a large concentration of accessible, well spaced and structurally well defined active sites. Specifically, attachment of a titanocene-derived catalyst precursor to the pore walls of MCM-41-type material produced a catalyst for the epoxidation of cyclohexene and more bulky cyclic alkenes [14].

Inorganic catalytic functionalities

Derivatization of mesoporous silica materials with inorganic catalytic units could be achieved through impregnation or substitution of the metal in the silica framework. This category is often overlapping with the inorganic nanoparticle catalysts, provided that often, impregnation or encapsulation give rise to inorganic nanoclusters; however, we will present the two categories separately.

An encapsulation process of Pd, using mercaptopropyl functionality, lead to a material that catalyzed the Mizoroki-Heck and Suzuki-Miyaura reactions without leaching Pd into solution. Analytical tests have demonstrated that the catalysis occurs on the surface or in the pores of the silicate [15].

Metal organic chemical vapor deposition (MOCVD) has been employed to generate active Cu- and ZnO-containing methanol-synthesis catalysts by vaporizing suitable organometallic precursors into mesoporous silicates, followed by thermal treatment. The catalytically active components in the final material have nanoscopic dimensions. The methanol production by the catalysts is similar to that of systems synthesized by the classical route [16].

A recent trend in mesoporous silica materials arena involves

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supramolecular templating, aiming to obtain large pore materials. Large pores materials allow large molecules to be catalytically converted in the pores, thus avoiding pore obstruction. Ma and co-workers demonstrated that gold nanoparticles (AuNPs) within the extra-large pores exhibit dramatically increased lifetime compared to those located within relatively small mesopores due to the enhanced mass diffusion that suppresses coke deposition on AuNPs [17].

Titanium silicalite is an effective molecular-sieve catalyst for the selective oxidation of alkanes, the hydroxylation of phenol and the epoxidation of alkenes in the presence of H_2O_2. The range of organic compounds that can be oxidized is greatly limited, however, by the relatively small pore size (about 0.6 nm) of the host framework. The group of Pinnavaya describe the use of the templating approach to synthesize mesoporous silica-based molecular sieves partly substituted with titanium. The materials showed selective catalytic activity towards the oxidation of 2,6-ditert-butyl phenol to the corresponding quinone and the conversion of benzene to phenol [18].

Nanoparticle-based catalyst immobilization

Nanoparticles are key to miniaturization and nano-confinement-related effects and properties. Achievement of nanoparticle and porous materials fusion is leading to a rapidly growing technology. Harnessing the nanoscale activity and selectivity of a catalytic nanoparticles along with their confinement in mesoporous silica nano-reactors, provide efficient catalytic materials for producing commodity chemicals, and energy needed for a future sustainable society. Several research groups reported high catalytic performances of metal and metal alloy nanoparticles in mesoporous silica. Supported metal nanoparticle catalysts have also been used in various energy-related applications such as biomass conversion and water splitting [19].

One of the challenges in elaborating multi-catalytic sites when using nanoparticles catalysis on mesoporous silica support is achieving near-maximum interparticle spacing. A recent success was reported for a $Cu/ZnO/Al_2O_3$ catalyst, where the desired spacing was obtained as accessed quantitatively by electron tomography. The catalyst deactivation is slowed down up to an order of magnitude compared with a catalyst with a non-uniform nanoparticle distribution, or a reference [20].

Bifunctional mesoporous silica based catalysts

Conversion toward a desired product oftentimes demands multiple step reactions. Mesoporous silica versatility allowed a few research groups to demonstrate him possibility of incorporating multiple catalytic groups in the same mesoporous silica particle.

Mesoporous silica nanosphere (MSN) materials bifunctionalized with a general acid group and a base group in various relative concentrations are described and shown to function as cooperative catalytic systems. The turnover numbers observed indicate that the acid groups can activate substrates in cooperation with the base groups to catalyze reactions that involve carbonyl activation [8].

Bifunctional mesoporous silica nanoparticles (MSNs) bearing Pd-complexes and additional basic sites were also prepared and tested as cooperative active catalysts in the Tsuji–Trostallylation of ethyl acetoacetate. Functionalization of the MSNs was realized by post-modification using click-chemistry. The selectivity of mono *versus* double allylation was achieved by control of reaction temperature and the nature of the catalyst [21].

A hybrid version on mesoporous silica-based bifunctional catalysts involve acid functionality combined with metal nanoparticles, playing a key role for the hydrolysis and reduction of cellulose.[19]

Enzymatic catalytic functionalities

Research demonstrated that enzymes encapsulated or entrapped in mesoporous silica materials retain their biocatalytic activity and are more stable than enzymes in solution. Different types of mesoporous materials with varied their morphological and structural characteristics, and strategies used for their functionalization with enzymes are reported in plethora of publications [22]. Enzyme attachment could be attained by physical and chemical methods, from simple physical absorption to covalent attachment. Studies demonstrated that stability is tremendously improved with covalent attachment of enzymes in mesoporous silica.

Mesoporous materials applications in catalysis have seen an exponential growth in the past decade. The versatility of functionalization techniques of mesoporous materials along with ability to readily separate the products upon reaction completion allow for continuous innovation in the catalysis field with recent applications in high-demand fields such as renewable bio-fuels, carbon-dioxide capture and solar water splitting. The tremendous potential of mesoporous materials has expanded into templating carbon structures on their framework, offering new catalytic scaffolds to be further exploited.

References

1. Thomas JM (2009) Angewandte Chemie International Edition. 48: 3390-3391

2. Martínez C, Corma A (2011) Coordination Chemistry Reviews. 255: 1558-1580.

3. Corma A, García H (2003) Chemical Reviews 103: 4307-4366.

4. White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ (2009) Chemical Society Reviews. CSR 38: 481-494.

5. Chiola V, Ritsko JE, Vnderpool CD (1971) US Patent 3: 556-725.

6. Chen HT, Huh S, Wiench JW, Pruski M, Lin VSY (2005) Journal of the American Chemical Society. JACS 127: 13305-13311.

7. Radu DR, Lai CY, Wiench, JW, Pruski M, Lin VSY (2004) Journal of the American Chemical Society. JACS 126: 1640-1641.

8. Huh S, Chen HT, Wiench JW, Pruski M, Lin VSY (2005) Angewandte Chemie International Edition. 44: 1826-1830.

9. Lai CY, Chia-Wen W, Radu Daniela R, Trewyn Brian G, Lin Victor SY (2008) Studies in Surface Science and Catalysis. 170B: 1827-1835.

10. Lai CY, Trewyn BG, Jeftinija DM, Jeftinija K, Xu S, Jeftinija S, Lin VSY (2003) Journal of the American Chemical Society. JACS 125: 4451-4459.

11. Slowing II, Trewyn BG, Giri S, Lin VSY (2007) Advanced Functional Materials. 17: 1225-1236.

12. Radu DR, Lai CY, Jeftinija, Rowe EW, Jeftinija S, Lin VSY (2004) Journal of the American Chemical Society. JACS 126: 13216-13217.

13. Kageyama K, Tamazawa, JI, Aida T (1999) Science 285: 2113-2115.

14. Maschmeyer T, Rey F, Sankar G, Thomas JM (1995) Nature 378: 159-162.

15. Crudden CM, Sateesh M, Lewis R (2005) Journal of the American Chemical Society. JACS 127: 10045-10050.

16. Becker R, Parala H, Hipler F, Tkachenko OP, Klementiev, et al. (2004) Angewandte Chemie International Edition. 43: 2839-2842.

17. Ma G, Yan X, Li Y, Xiao L, Huang Z, et al. (2010) Journal of the American Chemical Society. J Am Chem Soc 132: 9596-9597.

18. Tanev PT, Chibwe M, Pinnavaia TJ (1994) Nature. 368: 321-323.

19. Fukuoka A, Dhepe PL (2009) The Chemical Record. 9: 224-235.

20. Prieto G, Zečević J, Friedrich H, de Jong KP, de Jongh PE (2013) Nat Mater. 12: 34-39.

21. Dickschat AT, Behrends F, Surmiak S, Eckert H, Studer (2013) A Chemical Communications. 49: 2195-2197.

22. Hartmann M, Kostrov X (2013) American Chemical Society. ACS: 6277-6289.