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Review

Versatile design and synthesis of mesoporous sulfonic acid catalysts

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ABSTRACT

Mesoporous sulfonic acid catalysts (MSAC) are widely used in acid-catalyzed reactions, including biomass conversions with plenty of polar solvents and precursors. The catalytic efficiency of MSAC is greatly affected by the microenvironment around the sulfonic acid sites. In this review, the progress on modification of microenvironment of MSAC is reviewed over the past decade. Hydrophobic modification allows MSAC prevent the adhesion of water molecules onto sulfonic acid sites, to abate the risk of reduced acid strength and catalytic efficiency. In comparison, hydrophilic properties can bring positive effect on acid-catalyzed reactions with the aid of hydrophilic interaction between polar functional groups on MSAC and hydrophilic groups of specific substrates. Amphiphilic MSAC with tunable wettability for specific substrates and solvents tend to improve the efficiency in certain reactions with mixed solvents or reactants of different polarity, especially for biphasic systems of immiscible liquids. Furthermore, much attention has been attracted on modification of surface to simulate the microenvironment of homogeneous solvents and enzyme biocatalysts in recent research. New trends of this field are also highlighted.

1. Introduction

Liquid homogeneous acids (e.g., H_2SO_4, H_3PO_4 and triflic acid) play a highly important position in numerous important chemical industrial processes. However, chemical industry reactions based on liquid-phase acid catalysis generally have some defects, such as toxic reagents, acid corrosion on reaction plants, and a large volume of poisoned and harmful wastes [1]. Furthermore, technical difficulties also exist in quenching liquid acids and separation products from reaction systems. In order to develop greener chemical processes, the synthesis and application of solid acids have been extensively explored according to the requirements of environmental protection laws [2–4]. With the advantages of easy separation and facilitated recycling, solid acids are in accordance with the future development of "green chemistry" and "sustainable development", which can protect existing resources assigns environmental value to conserve existing resources and avoid the production of toxic and harmful wastes [5,6]. As alternative catalysts for homogenous acids, solid acids including zeolites, polymers, and metal oxides, have been widely applied in the past decades [3]. Among various solid acids, sulfonic acid functional catalysts (SACs) become a rising concern due to their strong acid strength, convenient preparing method and easy handling. SACs act as efficient and eco-friendly replacers to their homogeneous analogs [7]. As pioneers in commercialized SACs, polymers supported sulfonic acids have been widely used in research due to easy recovery and strong acidic property. Nevertheless, the application of polymer based sulfonic acids is limited, because of their poor thermal and mechanical stability, as well as limited surface areas. Recent research efforts have been focused on immobilization of sulfonic acid groups onto nanoporous materials, to improve the stability of catalysts and the efficiency of mass transfer [8]. Mobil company materials (MCMs) series of mesoporous silica were reported by Mobil Oil Company in 1992, and these ordered mesoporous silicas (OMSs) were composited of an array of uniform mesopores. The highly ordered structure provides OMSs with distinguishing features: high surface area, mesopores with adjustable pore size, well-organized nano-sized pores and frameworks, as well as mild and controllable synthesis conditions [9–11]. With above advantages, OMSs are intended to be designed as solid acid catalysts to replace microporous zeolite for accommodation of bulk molecules [12]. After over two decades' development, prominent progress has been achieved in the synthesis and application of mesoporous SAC (MSAC) [13]. The scope of MSAC has expanded from OMSs to periodic mesoporous organosilicas (PMOs), metal organic frameworks (MOFs), carbons, polymers, metal-oxides and so on. There are a few

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comprehensive reviews on the new types and synthesis methods of MSAC in recent years [14–16], which will not be re-detailed in this progress review. The main topic of this report is focused upon recent development progress on the construction of microenvironment of MSAC in the past ten years.

Previous application of MSAC mainly centers on the acidic catalytic synthesis of fine chemicals and petrochemical products in gaseous and liquid phases [12]. With the increasing demand of energy consumption and rapid elimination of fossil oil, conversions from biomass resources into biofuels and value-added platform chemicals have attracted much attention from the public and research groups [17,18]. Among various renewable biomass, lignocellulose (including cellulose, hemicellulose and lignin), the main components of plant and woody biomass with rich reserves, has attracted significant attention as the alternative replacement of current fuels and chemical intermediate products [19–22]. Many biomass precursors are composited of molecules with high molecular weight and large molecular size, and the traditional solid acids with micropores (such as zeolites) encounter obstacles of restricted mass transfer efficiency for large reactant particles. Mesopores can accommodate the reactants with large sizes to diffuse into the internal area of abundant active sites, which has been proved in some cases of biomass conversions, such as esterification of free fatty acid feedstocks and biodiesel production [23,24]. On the other hand, all these natural macromolecules contain plenty of oxygen functional groups which should be eliminated in conversion of lignocellulose into hydrocarbon-based biofuels [25]. Furthermore, most of these biomass precursors can only be dissolved and depolymerized in polar solvents, such as ionic liquids and water [26].

The conversion of biomass resource always contains elimination of functional groups with oxygen atoms, and it leads to the production of a lot of water molecules [25]. When referred to reactions preformed in polar systems, sulfonic acid sites take a risk of water molecules' attacking. Hydrophobic modification of microenvironment around acid sites plays an important role in inhibiting the poisoning effect caused by polar reactants and solvents [24]. Moreover, selectivity of specific products for some biomass conversions can also be affected by the presence of water. For example, the reaction extension of Aldol condensation between aldehydes and ketones can be promoted by removing water which is produced during the reaction [27]. The stability of MSAC under hydrothermal conditions is another hot topic for recent research, and both the frameworks of MSAC and the sulfonic acid groups are designed to be stable under harsh reaction conditions [28]. For above reasons, the synthesis and application of hydrophobic MSAC is the dominant section of recent progress on modulation of MSAC's microenvironment. The hydrophilic/hydrophobic character of MSAC surface can generate interesting influence on inner-particle mass transfer process, as well as catalytic efficiency of MSAC [6]. To this end, it is very important to adjust the polarity equilibrium of MSAC's surface, and suitable modification can optimize the adsorption/desorption process to influence the catalytic performance.

In comparison, hydrophilic surface can also promote acid-catalyzed reaction in specific conditions [29]. The hydrophilicity is commonly induced by polar functional groups on MSAC surface, and substrates with strong polarity intend to approach MSAC's surface by hydrophilic interaction. While hydrophobic products and solvents are co-present in reaction systems, hydrophilic surface can selectively enrich substrates with similar polarity and this adsorption performance is propitious to enhance MSAC's catalytic selectivity and efficiency.

Furthermore, while the balance of hydrophilicity and hydrophobicity is precious controlled, an amphiphilic MSAC can be synthesized to act as the interfacial catalyst in biphasic liquid systems [30]. Very recently, a few groups reported the application of solid particles with specific amphiphilicity to stabilize the micro-emulsion droplets without other surfactants in the systems of two incompatible fluids, and so-called Pickering emulsions show superior catalytic performance in water and oil mixed solvents without using conventional surfactants [31]. With tunable hydrophobic/hydrophilic surface, MSAC can act as emulsifier and interfacial catalyst concurrently for the emulsion.

One of the important research fields for microenvironment modulation is simulation of enzyme-based bio-nanoreactors or specific solvent molecules. Researchers intend to modify MSAC surface with specific functional groups to construct the microenvironment that is similar with the inner space of cellulase or other enzymes, because cellulase can efficiently decompose cellulose into its sugar constituents under mild pH conditions and temperature, and the facile reaction conditions can also postpone the deactivation process of enzymes [32]. Previous research has proved that cooperative effect of binding domains and catalytic domains accounts for the high efficiency for biocatalysis under mild conditions [33]. Recent studies on the biomimetic strategy were focused on creating binding sites on MSAC for specific adsorption. Considering that there are plenty of polar groups (such as carboxyl groups and so on) in active enzyme, modification of MSAC with groups of similar interaction can provide an efficient tool for improving catalytic performance under relatively mild conditions. In addition, although natural reactions are always performed in aqueous solutions, enzymes can enrich hydrophobic oligomers of sugars via CH-π and hydrophobic interactions. A similar strategy can also be utilized in producing biomimetic nanoreactors for adsorbing hydrophobic biomass precursors [18]. In addition, Dumesic's group [34–37] screened plenty of solvents to ascertain the optimized solvent for sugars' conversion into platform chemicals, and the selected solvents have high boiling points which cause great difficulty in separation the products from solvents. Functional groups with similar structure of homogeneous solvents are grafted onto surface of MSAC, aiming at producing recyclable "solid solvent", which are confined in the pores of MSAC to replace the homogenous counterparts.

In bullet points, the recent progress on construction of microenvironment for MSAC will be reviewed in the following four sections: (1) hydrophobic modification of MSAC and related applications; (2) deep research in hydrophilic interactions between acid sites and reactants/products; (3) controlling the balance of hydrophilicity/hydrophobicity to construct amphiphilic surface; (4) functionalization of MSAC surface for specific adsorption with biomimetic strategy.

2. Hydrophobic modification of MSAC and related applications

Hydrophobic modification of MSAC is one of the most important fields in recent research, and there are mainly three synthetic methods to enhance hydrophobicity of MSAC's surface: post-modification method to enhance surface's hydrophobicity, incorporation of hydrophobic components into hydrophilic frameworks of MSAC and direct synthesis of MSAC with hydrophobic or water-tolerant building blocks. The last two methods can modify both the surface and frameworks' components and properties, while the first one can only endow external surface with different degree of hydrophobicity. The influence of hydrophobic modification on catalytic performance mainly presents as following: (1) preventing water molecules from approaching sulfonic acid groups and maintaining the acid strength of MSAC during the reaction; (2) protecting the frameworks and active sites of MSAC under hydrothermal conditions; and (3) selective enrichment of hydrophobic substrates in MSAC. This section will be reviewed according to synthetic