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Synthesis, functionalisation and characterisation of mesoporous materials and sol–gel glasses for applications in catalysis, adsorption and photonics

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Abstract

In this review, synthesis and functionalisation approaches for ordered mesoporous materials and sol–gel glasses are described. Catalytic and adsorption applications are emphasised for the ordered mesoporous materials, while optical applications are the focus for sol–gel glasses.

Keywords: Ordered mesoporous materials; Sol–gel glasses; Functionalisation; Catalytic materials; Photonic materials

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1. Introduction

A new and fascinating area of research was opened when scientists at Mobil Oil Corporation reported the preparation of mesoporous materials of the so-called M41S family in 1992 [1,2]. Unlike previous mesoporous silica, these materials have ordered and well-defined pore structures with narrow pore size distributions. Different pore structures and pore sizes can be obtained by controlling the ratios of reactants in the synthesis gel [3–7]. Cetyltrimethylethylammonium bromide (CTAB) is a common surfactant in synthesis of the M41S family members, resulting in pore sizes of about 3 nm, and MCM-41 (hexagonal structure) and MCM-48 (cubic *Ia3d* structure) are typical structures [1,2]. The pore sizes can be decreased or increased by varying the chain length of the surfactant, or by adding organic molecules which act as spacers inside the micelles.

Another milestone was reached in 1998 when Zhao et al. extended the range of ordered mesoporous structures by the so-called SBA materials [8,9]. The most prominent of these is the hexagonally ordered SBA-15. The triblock copolymer $(EO)_{20}(PO)_{70}(EO)_{20}$ is usually used as structure directing agent in the synthesis of SBA-15. This provides pore sizes ranging from 5 to 10 nm, depending on the synthesis conditions. By adding organic co-solutes, the pore size may be increased to 30 nm while maintaining the ordered hexagonal structure. Another member of this family is SBA-16, which is normally synthesised using the triblock copolymer $(EO)_{106}(PO)_{70}(EO)_{106}$ as structure directing agent, resulting in a bicontinuous cubic *Im3m* structure [9].

Sol–gel chemistry has long been a research area in itself and, subsequently, it has been combined with surfactant chemistry in syntheses of ordered mesoporous materials. In this review, we will focus on the preparation and functionalisation of these related types of inorganic structures. Initially, a brief introduction to traditional sol–gel chemistry is given. Compared to sol–gel glasses, mesoporous silica materials have the additional benefits of regular pore ordering with narrow, tunable pore size distributions and exceptionally high surface areas (>6–700 m^2/g). Consequently, we will focus on the general synthesis mechanisms of these structures, and place emphasis on surfactant–silica interactions and various other factors that can influence the final mesostructure of the materials.

Both types of materials are well-suited as carriers of various functionalities, either incorporated into the framework or supported on the surface. In the second part, we describe various methods of functionalisation. For mesoporous materials, focus is put on the incorporation of transition metals and how synthesis conditions can influence the properties of cobalt-containing structures. Hydrodesulphurisation (HDS) and NO_x reduction processes are highlighted. Furthermore, preparation of mesoporous alumina and alumina phosphates is described. For sol–gel glasses, we focus on the incorporation of optically active ruthenium and europium sites, and a sensor application is outlined. The last section addresses dendrimer functionalisation of both sol–gel glasses and mesoporous structures.

2. Synthesis

2.1. Sol–gel chemistry

The sol–gel technique is based on the exceptional properties of organosilicon compounds to form siloxane polymers [11]. Hydrolysis and condensation of monomeric silicon alkoxide precursors upon addition of water can be described by the following three equations:

Hydrolysis:

$$\equiv \mathrm{Si} - \mathrm{OR} + \mathrm{H_2O} = \ \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{ROH} \tag{1}$$

Water condensation:

$$\equiv \mathrm{Si} - \mathrm{OH} + \equiv \mathrm{Si} - \mathrm{OH} \ \ \mathrm{C} = \ \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{H_2O} \tag{2}$$

Alcohol condensation:

$$\equiv \mathrm{Si} - \mathrm{OR} + \equiv \mathrm{Si} - \mathrm{OH} \ \ \mathrm{C} = \ \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv + \mathrm{ROH} \tag{3}$$

where R is an alkyl group C_xH_{2x+1}.

The pH of the reaction environment highly affects the outcome. Low pH values yield fast hydrolysis and slow condensation, resulting in a three-dimensional gel. High pH yields slow hydrolysis rates and rapid condensation, resulting in a suspension of particles, in many cases with a monodisperse particle size distribution.

2.2. Ordered mesoporous silica materials

Ordered mesoporous silica materials are typically synthesised by adding a silica source to a micellar surfactant solution at an adjusted pH [12]. The pore structure of the materials, however, resembles the ordering of liquid crystalline phases where water is replaced by the silica framework. This means that there must be interactions between the surfactants and silica species as they undergo reaction, resulting in phase transition into the observed pore structure. The mechanisms behind this have been extensively investigated and recently reviewed [13]. A major advance in this area was made by Firouzi et al. [14]. They suggested a cooperative process where surfactants self-assemble into an ordered mesophase depending on charge density matching between the surfactants and silica species, and finally the silica framework precipitates. MCM-41 and MCM-48 are, for example, often prepared using cationic surfactants as structure directing agents. In aqueous alkaline media, the silica species will be negatively charged, resulting in electrostatic interactions with the positively charged surfactants, and the charge density matching will control the resulting mesostructure. This was