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Incorporation of an asymmetry gadolinium porphyrin into mesoporous SBA-15 and the study of luminescence property

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ABSTRACT

The incorporation of an asymmetry gadolinium porphyrin into the mesoporous molecular sieves SBA-15 by reactions of the surface OH group with an F and OH group of the porphyrin. The resultant material was confirmed that the channels of SBA-15 have been filled with porphyrins by XRD, TEM, solid UV/Vis, nitrogen adsorption, leaving the mesopores unaffected. Luminescent properties were studied by solid fluorescence emission and excitation spectra. Results indicate that the luminescence intensity of SBA-15/porphyrin is stronger than the pure porphyrin. We also provided the FTIR results and study the links between silica wall and gadolinium porphyrin after incorporation porphyrin into SBA-15.

1. Introduction

Metalloporphyrins are the most widely studied catalysts for homogeneous selective oxidation and hydroxylation of hydrocarbons. An important area of research into their catalytic properties is associated with immobilization of the porphyrin onto a solid support, in order to make the catalyst easier to handle and to separate from the reaction medium, as well as possibly stabilize and/or modify the catalytic performance [1].To fulfill these requirements, the metalloporphyrins have been chemically anchored to appropriated substrates and the catalytic properties of the resulting materials compared with the homogeneous counterparts. Furthermore, heterogeneous catalysts have become an important and attractive target (clean technology) since they provide the possibility of replacing the traditional stoichiometric processes in the industry, and therefore help to minimize the problem of industrial waste treatment and disposal [2].

New supports have been used to immobilize these metal complexes with the goal to obtain heterogeneous catalyst with improved activity and selectivity [3–8]. In the recent years, the use of the mesoporous materials, like the SBA-15, as a catalytic support is an important tendency in today's catalysis. SBA-15 has a hexagonal symmetry 2D (ρ6mm) and possesses uniform pore size with high surface area (BET) [9,10], making this a good candidate to be used as a catalytic support [11–13] and host of some other chemical species [14–18].

Incorporation of metal complexes into mesoporous SBA-15 for catalytic purposes has been extensively investigated [19–24]. However, there are no reports on the incorporation of a new meso-substituted unsymmetrical porphyrin, 5-[p-(4-flourobenzoyloxy)-m-ethyloxy] phenyl-10, 15, 20-triphenyl porphyrin Gd metal complexes into SBA-15. In this research, we synthesized the porphyrin according to literature [25] and incorporated the porphyrin molecule with F and OH group into the channels of SBA-15. It is well known that the interior surface of SBA-15 is covered with OH groups, so the F and OH groups on the porphyrin circumference can link to OH groups of the SBA-15 through hydbonding. In this paper, we report the results of our studies on the incorporation of an asymmetry porphyrin into SBA-15 using a combination of techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), UV/Vis spectroscopy, IR spectroscopy and nitrogen adsorption. At the same time, the luminescent properties were studied by emission spectra and excitation spectra.

2. Experimental

2.1. Apparatus and measurements

All reagents and solvents were of commercial reagent grade and used without further purification. SBA-15 was synthesized according to ref [26].

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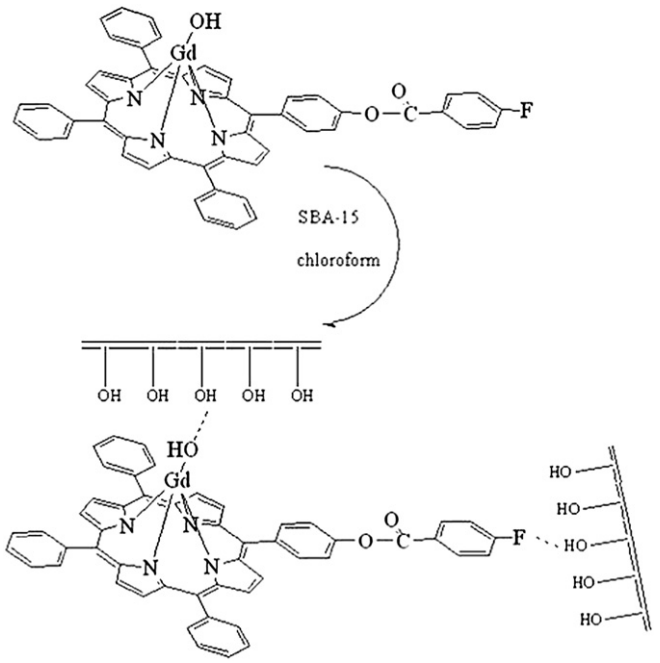

Fig. 1. The incorporation of SBA-15/porphyrin.

X-ray diffraction (XRD) patterns were performed on a Tokyo X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.15405$ nm). Transmission electron microscopic (TEM) images were performed with a JEOL-2010 electron microscope operating at 200 kV. UV/Vis spectra of solutions were collected with a Perkin–Elmer Lambda 2 spectrometer. Diffuse reflectance UV/Vis spectra of solids were recorded with a Perkin–Elmer Lambda 9 spectrometer. Infrared spectroscopic characterization was carried by a Perkin–Elmer Spectrum One spectrometer. Nitrogen adsorption measurements at 77 K were performed with a Quantacerome AUTOSORB-1C automated chemisorption/physisorption surface area and pore size analyzer samples were outgassed for 6 h in the degas port of the adsorption apparatus. TGA were carried out by DTG-60 Simultaneous DTA-TGA Apparatus (Sample: 3–4 mg; heating rate: 10 °C min^{-1}; atmosphere: Air; Flow rate: 20 ml min^{-1}; Range of temperature: 20 °C–550 °C.). Fluorescence spectra were recorded at room temperature with a Shimadzu RF-5301PC spectrofluorometer using dichloromethane as solvent in the region of 300–600 nm.

2.2. Synthesis of the asymmetry porphyrin

The porphyrin was synthesized according to Ref. [27] The molecular configuration is seen in Fig. 1.

2.3. Incorporation of an asymmetry porphyrin into SBA-15

SBA-15 (100 mg) was mixed with porphyrin 3 (10 mg) in a round-bottomed flask (20 mL), and then chloroform (10 mL) was added and stirred for 48 h at room temperature. The solid was filtered and washed with chloroform until no absorption of porphyrin in the UV/Vis spectrum was seen from the solution. The solid was dried at room temperature. The original white powders of SBA-15 turned jade-green after adding the lanthanide porphyrin, which indicated inclusion of the porphyrins into the SBA-15 frameworks (seen in Fig. 1).

For quantitative determination of the porphyrin incorporated into the SBA-15, a mesoporous composite SBA-15/porphyrin sample (10 mg) was dissolved in aqueous sodium hydroxide solution (8 M) to destroy the framework. Thus the porphyrin in the mesoporous composite was released. The porphyrin was extracted with chloroform (10 mL), and the solution was diluted to 1/5 its concentration with chloroform. The OD value of the porphyrin at 425 nm is 0.1042. A reference solution was made with chiral porphyrin (0.5 mg) dissolved in chloroform (100 mL) and its OD value at 425 nm was measured to be 1.4306 mg. By comparing this with the reference, the amount of porphyrin encapsulated in SBA-15 was determined to be 5.2 mg g^{-1} using Beer's law.

3. Results and discussion

3.1. Materials characterization

The X-ray powder diffraction (XRD) patterns of SBA-15 before (Fig. 2a) and after (Fig. 2b) the incorporation of the porphyrin are given in Fig. 2(1 and 2). The XRD patterns of pure SBA-15 and SBA-15/porphyrin show that the composite of the SBA-15/porphyrin has a strong peak at $2\theta = 18°$, but the pure SBA-15 have no peak at the degree. The change is interpreted as indicating that the porphyrins are dispersed in the mesoporous channels (seen in Fig. 2-2). At the same time, The XRD patterns of pure SBA-15 and SBA-15/porphyrin show the same peaks, suggesting that framework stability of the mesoporous material is well maintained when the porphyrin is incorporated into the channels of SBA-15 (seen in Fig. 2-1).

TEM measurements were used from the on-top view and a cross-section of the pore system (Figs. 3 and 4) to analyze the

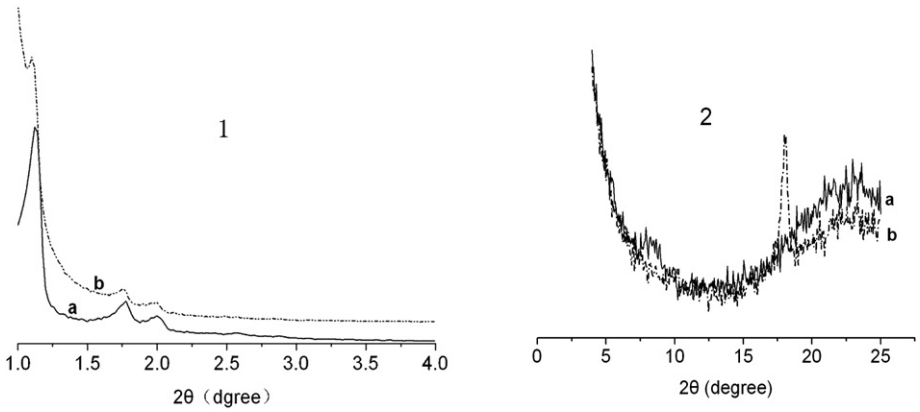

Fig. 2. XRD patterns of SBA-15 samples without (a) and with (b) the incorporated porphyrin (1: small angle, 2: wide angle).