



A luminescent mesoporous zirconium complex and it as a precursor of environmentally benign catalysts



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ARTICLE INFO

Article history:

Received 19 March 2015

Accepted 12 April 2015

Available online 18 April 2015

Keywords:

Photoluminescence

White-light

Mesopore

Esterification

Isomerization

ABSTRACT

Much attention should be paid to developing new materials for energy saving and environmentally benign catalysis. Herein we report the broad-band direct white-light emission originating from a single-phased and single-doped phosphor, i.e., a luminescent mesoporous zirconium oxy-hydroxy acetate–persulfate complex and the complex doped by Eu^{3+} . The amorphous complexes exhibit the photoluminescence and color properties comparable to or better than those of the crystalline MOFs. The attracting feature of this route to white-light emission comes from the single-phased and single-doped phosphors that can be prepared through a low-cost chemical synthesis approach. In addition to photoluminescence, the complexes show useful textural properties. The pristine complex has been used as a precursor of environmentally benign catalysts in the esterification of lauric acid with methanol and in *n*-hexane isomerization.

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1. Introduction

With the emerging global energy crisis and the concerns of global warming, development of light-emitting diodes (LEDs) with high luminous efficiency will have significant impact on energy conservation. Presently there are two pathways to achieve white-light emission: (1) the combination of two or more phosphors, i.e., either by coating a yellow phosphor or by combining green and red phosphors on a background consisting of a blue-light emitting diode or by employing nanocrystals of three primary colors (red, green, blue) using multilayer structures in LED; (2) a single phosphor with a broad emission spectrum. The main disadvantages for the first method are the necessary for a homogeneous and reproducible phosphor mixture, and the often different thermal behavior of the phosphors. However, the use of single-phased full-color emitting phosphors for near ultraviolet chip-based white-light emitting diode offers many advantages over multiple component systems, for example, greater luminous efficiency and reproducibility, and low cost preparation, due to avoidance of color-aberration and simpler fabrication processes. It is, therefore, an excellent option to develop a single-phased white-light emitting

phosphor using the principle of energy transfer from a sensitizer (energy donor) to an activator (energy acceptor) in a single host lattice, in other words, multidoped luminescent ions in one matrix [1]. Although myriads of new phosphors have been recently reported, it was indicated in a critical review that the number of currently available conversion phosphors fulfilling all the following requirements is still limited [2]. Main requirements for conversion phosphors are 1. good excitability in the near-UV to blue region of the spectrum, namely, the excitation spectrum should be sufficiently broad to cover the wavelength range; 2. a broad emission spectrum that can lead to a white-light emission with a high color rendering and warm color temperature; 3. absence of emission saturation at high fluxes. In addition, the fluorescent materials should exhibit structural, thermal, and photochemical stability in aggressive environments while showing high absorption coefficient and quantum yield with minimal toxicity. Even if a phosphor gets high marks on all these requirements, the actual device development involves several other considerations such as the ease and environmental friendliness of a synthesis method and ultimately also the cost of the material. Research into photoluminescent materials should therefore continue. One of the most exciting advances in the field of multifunctional materials in recent years is the emergence of a fascinating family of organic-inorganic hybrid materials, known as metal-organic frameworks (MOFs).

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Metal-organic-frameworks (MOFs) or porous coordination polymers are crystalline porous materials. In MOFs, metal complexes form vertices of the structure, connected by organic linker. This architecture allow one, through selection of appropriate linkers, to create extremely sparse materials with record low crystal densities and ultrahigh surface areas, which can be applied to gas adsorption and storage, catalysis, and drug delivery. Additionally fuelling interest in MOFs is their luminescence properties. MOFs offer the advantages of the choice of light-emission building block for both the metal clusters as nodes and the functional organic ligands as spokes; furthermore, the spatial regularity of these building blocks prevents the preferential aggregation that causes self-quenching. A combination of porosity and luminescence (MOFs) can be used in everyday life, e.g., solid-state lighting as well as in highly specialized applications such as optoelectronic and photonic devices, chemical and biological sensing, molecular tracing, and cellular imaging.

Direct white-light emission has only been observed in a few coordination compounds [3]. Recently, organic charge–transfer complexes [4], supramolecular gels [5], and organic cations-templated layered perovskites [6] have been developed for white-light emitting, but their photoluminescent quantum yield and thermal stability are major constraints to be overcome for optoelectronic and lighting applications. Herein we report the broadband direct white-light emission originating from a single-phased and single-doped phosphor, i.e., a luminescent mesoporous zirconium oxy-hydroxyl acetate–persulfate complex and the complex doped by Eu^{3+} (10 wt%). The complexes can be synthesized from zirconyl chloride, acetic acid, and ammonium persulfate under structure-directing agents-free at a temperature as low as 210 °C. The amorphous complexes exhibit the photoluminescence and color properties comparable to or better than those of the crystalline MOFs. In addition to photoluminescence, the complexes show useful textural properties. The pristine complex has been used as a precursor of environmentally benign catalysts in the esterification of lauric acid with methanol and in n-hexane isomerization.

2. Experimental

2.1. Synthesis

$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ or its mixture with EuCl_3 aqueous solution followed by aqueous ammonia was dropwise added to a boiled and cooled mixture of water, acetic acid and ammonium persulfate until pH 4.9 for catalyst or pH 5.5 for phosphor. The resultant precipitate was aged in the mother liquor overnight, and then kept in a boiling water bath for 2 h. The precipitate was washed with deionized water, ammonia/absolute alcohol (1:1), and only absolute alcohol, and dried at 100 °C for 48 h for catalyst or at 210 °C for phosphor. The dried precipitate also called phosphor looked yellowish. It was impregnated by an incipient wetness method with 30 g l^{-1} ammonium persulfate solution for 30 min, dried at 100 °C for 15 h, and calcined at 650 °C for 3 h, yielding sulfated zirconia (SZ). The palladium (around 0.5 wt%) was incorporated on the SZ calcined at 650 °C by classical impregnation using an acidic solution of Pd. After drying at 120 °C for 13 h, the catalyst was calcined in air at 450 °C for 3 h.

2.2. Catalytic evaluation

The catalytic properties of samples in an acid-catalyzed reaction (n-hexane isomerization) were studied in a continuous fixed-bed reactor under atmospheric pressure and at 180 °C, with a molar ratio of $\text{H}_2/\text{n-C}_6 = 2.0$ in the feed. n-Hexane was fed into the reactor with a syringe pump with a rate of 2 ml h^{-1} , while hydrogen flowed

at 60 ml min^{-1} 1 g catalyst was taken and placed between two section of sand beads in the reactor tube. Prior to reaction, the catalyst was pretreated at 300 °C for 40 min in H_2 (60 ml min^{-1}). n-Hexane flew first through a trap filled with 4A zeolite to remove impurities then through the catalyst bed at weight hourly space velocity ($\text{WHSV} = 1.0 \text{ h}^{-1}$). The reaction mixture was analyzed by on-line gas chromatograph. Besides iso-hexane, minor amounts of cracking products were formed. The conversions are those measured at 25 min time on stream.

Esterification was performed in a stirred round bottom flask from where samples were withdrawn periodically for analysis on a gas chromatograph equipped with a capillary column and a flame ionization detector. Esterification was carried out at 60 °C using 0.16 g of catalyst, 4.167 g of lauric acid and 10 g of methanol.

2.3. Characterization

For the acidity measurements, the sample was pressed into a disk (ca. 30 mg, 1.5 cm diameter), and treated in an IR cell equipped with CaF_2 windows under vacuum conditions (5×10^{-3} torr) at 200 °C for 4 h and then cooled to room temperature. Pyridine is widely used to identify the concentration and nature of acid sites on the surface of sulfated zirconia. Pyridine-saturated vapor was adsorbed on the sample disk at room temperature for 15 min followed by thermal desorption from room temperature to 300 °C under vacuum.

IR spectra for pyridine adsorption and desorption testes were obtained with a Nicolet-5700 spectrophotometer at 4 cm^{-1} resolution, and were a result of 32 co-added scans. Spectra were presented in the form of absorbance, and difference FTIR spectra were obtained by subtracting the spectrum of the catalyst from that of the sample with adsorbed pyridine.

Surface area, pore size distribution, and total pore volume measurements were performed in an automated nitrogen adsorption-desorption apparatus (Micromeritics ASAP 2010 or ASAP 2020) at liquid nitrogen temperature 77 K using nitrogen as the adsorbate. Prior to measurement, the sample was degassed in vacuo at 200 °C for 2 h. Most important textural parameters were calculated from nitrogen adsorption-desorption isotherms following to a large extent the methodology proposed by IUPAC. Surface area was calculated with the BET equation using a value of 0.162 nm^2 for the cross-sectional area of nitrogen molecule from the adsorption branch of the isotherm in a relative pressure P/P_0 range of 0.07–0.3. Total pore volume was computed based on the amount of N_2 adsorbed at a relative pressure close to unity. Pore size distribution was estimated with the well-known BJH method from the desorption branch.

The diffused reflectance UV-VIS spectra of the sulfated zirconia and phosphors were recorded on a Varian Cary 5000 UV-VIS-NIR spectrophotometer equipped with an integrating sphere attachment. The computer processing of the absorption spectrum was done with Cary I-E software that allowed calculation of the of the Kubelka-Munk function $F(R)$ from the absorbance data. The band gap energy (E_g) for an allowed transition was determined by finding the intercept of the straight line in a plot of $[F(R) \times h\nu]^2$ versus $h\nu$, where $h\nu$ is the incident photon energy. Or, the absorption edge energy was determined for the spectrum by a linear extrapolation to zero absorption.

Photoluminescence (PL) spectra were obtained by mixing the sample with KBr ($\geq 99\%$ purity) in a 1:10 ratio of sample to KBr and pressing into a pellet on a model QM/TM/IM spectrophotometer (Photon Technology International) equipped with a nitrogen laser. The excitation spectra were collected by scanning from 310 to 490 nm under monitoring the emission at 490 nm at a slit width of 2 nm. The emission spectra were scanned from 451 to 535 nm at

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