



Siloxane-based metal–organic frameworks with remarkable catalytic activity in mild environmental photodegradation of azo dyes



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ABSTRACT

Three new metal–organic frameworks (MOFs) were obtained from a siloxane dicarboxylic acid (CX), 4,4'-bipyridyne (BPy) or 1,2-bis(4-pyridyl)ethylene (EBPy) and copper or cobalt acetates. The compounds were characterized by IR spectroscopy, powder X-ray diffraction, energy-dispersive X-ray fluorescence (XRF), thermogravimetric analysis (TGA), dynamic water vapor sorption (DVS), electron microscopy (TEM, SEM), UV–vis diffuse reflectance and fluorescence measurements. These hydrophobic MOFs acted as efficient catalysts in two processes occurring in aqueous media. The best result in alkaline decomposition of hydrogen peroxide was 90% conversion after 30 min. The catalytic activity in photodecomposition of Congo Red (CR) was followed in mild environmental conditions, i.e. under natural sunlight, without additional oxidation agents or pH adjustments. Unprecedented catalytic activity was found, especially for the Co complex with CX and EBPy, with discoloration efficiency of ca. 82% after 80 min of exposure to sunlight. The obtained results, in terms of rate constants and efficiency are comparable with those reported for other catalytic systems in photoreactors or in the presence of H₂O₂. The best catalyst was also tested in a Fenton-like process and it was found that the addition of H₂O₂ doubles the rate constant and increases the efficiency to 97%. On the other hand, the remaining waters after CR photodecomposition were analyzed by mass spectrometry (ESI–MS) and it was concluded that “cleaner” water is obtained when the MOFs are used without addition of H₂O₂.

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1. Introduction

Metal–organic frameworks MOFs (coordination networks or coordination polymers), “the fastest growing class of materials today” [1] consist of metallic nodes linked by polytopic bridging linkers, being in fact hybrid inorganic–organic materials [2–5]. The constant interest in such structures derives from their outstanding potential in gas or solvents sorption [6–17], separation of gases [13,18], sensors [19–21] and catalysis [22–25]. They may also exhibit magnetic properties [26,27] or second order nonlinear optical (NLO) properties [28].

The remarkable properties of MOFs, their rational design according to particular requirements, their distinct architectures, their high specific area and porosity, which allow fast mass transport and/or interactions with substrates, make them

ideal materials used in catalysis [29]. A wide diversity of MOFs have been designed with various homo- and heterometallic ions or clusters and different ligands (carboxylic and N-donor ones), and screened in heterogeneous catalysis [30–33] as eco-friendly alternatives in a variety of organic transformations: oxidation of alcohols, hydrocarbons, sulfides, thioethers or olefins, Friedel–Crafts alkylation, hydrogenation of olefins, Suzuki–Miyaura coupling, cyanosilylation, acetalization and hydroformylation or ring-opening polymerization [34,35]. Of particular importance for environmental remediation is the removal of various contaminants, such as antibiotics or dyes, from wastewaters, where hybrid materials containing MOFs are promising materials, acting as adsorbents and photocatalysts [36,37].

The photodegradation of azo dyes from wastewaters is a very actual environmental topic, since these dyes are toxic and even carcinogenic. Congo Red (CR), extensively used in textile industry due to its affinity for cellulose, is an anionic azo dye with an aromatic structure, containing two azo groups and it is considered a very stable molecule [38]. Besides physical methods, chemical processes

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such as ozonation and chlorination are frequently used for removal of textile dyes [39]. A range of materials have been tested as heterogeneous photocatalysts for azo dyes degradation, the most used being TiO₂ in different forms and combinations [40], to enhance its effect or to ease its removal [39,41,42]. Other materials have also been proposed for azo dyes degradation, in particular for Congo Red, as for example chitosan–CdS nanocomposites [43], Zn oxide [44–46], CuInSe₂–ZnO nanocomposites [38], Zn sulfide [47], rare-earth doped nickel ferrites [48]. Generally, the photodegradation of azo dyes is conducted in photoreactors, under artificial UV irradiation, but the effect of sunlight have also been tested [49,50], as well as other energy sources, such as ultrasounds [42] and gamma irradiation [51], or biochemicals, such as enzymes [52].

In particular, the utility of MOFs as heterogeneous catalysts in photodegradation reactions proved to be very advantageous especially due to their high efficiency, ambient operating temperature, good reproductibility and catalyst reusability, easy handling and simplicity in degradation of persistent, nonbiodegradable and toxic organic dyes, without leaving secondary pollution products [53,54]. Efficient MOF photocatalysts for degradation of organic pollutants have been reported since 2006 [55]. More recently, numerous Ag, Zn, Cd, Fe, Ni, Cu, Mn and Co-based MOFs catalysts active in the decomposition of dyes have been reported, some of them having good photocatalytic performance for the degradation of: methylene blue, methyl orange, rhodamine B, reactive red, methyl red or methyl violet [53].

Relatively few reports have been published on catalytic efficiency of MOFs in the decomposition of Congo Red. Co, Zn or Cu-based MOFs built on mixed ligands (aromatic polycarboxylic acids and flexible N-donor ligands: pyrazole, imidazole, bezimidazole or pyridyl derivatives) were found as active heterogeneous catalysts for photodecomposition of Congo Red with a degradation efficiency of 55–99% depending on the reaction conditions (temperature, pH, irradiation light source, etc) [56–61]. Most of these reports describe heterogeneous Fenton-like process which uses H₂O₂ and UV lamp and/or high-pressure mercury-vapor lamp to generate hydroxyl radicals that are very effective in degrading such contaminants. The photocatalytic degradation of Congo Red under visible light, with MOFs without oxidation agents like H₂O₂ was rarely studied [59].

One of the most reliable methods for the synthesis of coordination polymers is the mixed-ligand synthetic strategy [62]. In this approach, typical building blocks are bipyridine and polycarboxyl compounds, often as acid-base mixed-ligands. Numerous coordination polymers of different transition metals on the base of ligands containing both COOH and pyridyl groups have been reported [3,4]. In our group, a special attention has been given to the use of siloxane-based ligands, as flexible and hydrophobic bridging elements for a wide range of MOFs [63–66]. The hydrophobicity of these MOFs due to the presence of the tetramethyldisiloxane moieties in their structures (which can protect MOFs from degradation upon contact with water) is a big advantage for their stability and use as heterogeneous catalysts in aqueous medium, because it is well known that the majority of MOFs are usually not stable in water [67,68]. Also, such MOFs can be regarded as amphiphilic compounds, which could support molecular interactions favorable to the catalytic reactions [69]. Some of the siloxane-containing metal complexes have been tested in catalysis applications, for aerobic oxidation of benzyl alcohol to benzaldehyde [70], hydrocarboxylation of linear and cyclic alkanes, oxidation of cyclohexane, and of 1-phenylethanol [71,72].

In a previous paper [73] we reported on Zn coordination polymers (2D MOF structures) obtained by mixed-ligand method, starting from 1,3-bis(3-carboxypropyl)-tetramethyldisiloxane (CX) and 4,4'-bipyridyl or 1,2-bis(4-pyridyl)ethylene as the base component. The Zn MOFs have been tested as catalysts in hydrogen peroxide

decomposition. This is another interesting application, since H₂O₂ is an environmentally friendly oxidation agent, which provides a clean and safe reaction path, being used in the oxidation of alcohols and biopolymers, including cellulose bleaching [74].

Here we report on similar compounds obtained with Co and Cu, their catalytic activity in hydrogen peroxide decomposition and in photodegradation of Congo Red under ambient conditions. The efficiency of Co and Cu catalysts in H₂O₂ decomposition clearly surpassed the Zn homologues reported previously. The decomposition of CR in the absence of additional oxidation agents occurred with similar rate as with core-shell ZnO@ γ -Fe₂O₃ nanocomposites [49], with a remarkable color removal efficiency of 81% after 80 min. A Fenton-like catalytic system was also tested, which showed higher reaction rate and 97% efficiency. The ESI-MS analysis suggested a higher level of the dye decomposition process in reactions catalyzed by MOFs without H₂O₂. Compared to other reports, in this case the proposed decontamination method is overall less energy-consuming. First of all, the synthesis of the metal complexes is facile, occurring at ambient temperature. The dye decomposition (decontamination of wastewaters) involves easily removable solid catalysts, without additional corrosive agents or neutralization steps and it occurs under natural light and ambient temperature, followed by simple filtration for the recovery of the catalyst. Due to the high stability of the MOFs, no trace of metal was detected in purified water. In addition, UV light might negatively affect the living organisms, thus the use of natural light in decontamination processes is of outmost importance. To our knowledge, this is the first report on hydrophobic MOFs acting as efficient catalysts in water decontamination.

2. Experimental

2.1. Materials

1,3-bis(3-carboxypropyl)tetramethyldisiloxane, [HOOC(CH₂)₃(CH₃)₂Si]₂O (CX) was synthesized using a reported method [75]. 4,4'-bipyridine (BPy), 1,2-bis(4-pyridyl)ethylene (EBPy), DMF and THF (from Fluka), cobalt(II) acetate, Co(OCOCH₃)₂·4H₂O and copper(II) acetate Cu(OCOCH₃)₂·H₂O (from Chimopar S.A) were high purity compounds and were used as received.

2.2. Methods

The infrared (IR) spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 400–4000 cm⁻¹ range (resolution 2 cm⁻¹, 32 scans), at ambient temperature. Far IR spectra were recorded using the same spectrometer equipped with a FIR source, CsI beamsplitter and standard DLaTGS detector. Spectra were obtained in the transmission mode in the range 180–700 cm⁻¹ at room temperature with a resolution of 2 cm⁻¹ and accumulation of 64 scans.

Thermogravimetric analyses (TG-DTG-DTA) were performed on an STA 449F1 Jupiter NETZSCH (Germany) equipment. The measurements were made in the temperature range 20–700 °C under a nitrogen flow (50 mL/min) using a heating rate of 10 °C/min. Alumina crucibles were used as sample holders. Qualitative optical observations were done with an Olympus polarized light optical microscope.

The energy-dispersive X-ray fluorescence (XRF) system (EX-2600 X-Calibur SDD) was used to determine the presence and ratio of metal (Co or Cu) and Si in the structure of the coordination polymers. TEM investigations were made with Hitachi High-Tech HT7700 Transmission Electron Microscope, operated in high contrast mode at 100 kV accelerating voltage. Samples were

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