Catalysis Today 266 (2016) 136–143

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Photoreactivity of metal-organic frameworks in the decolorization of methylene blue in aqueous solution

Ekaterina A. Kozlova[a,b,c], Valentina N. Panchenko[a,b], Zubair Hasan[d,1], Namzul Abedin Khan[d], Maria N. Timofeeva[a,b,e,*], Sung Hwa Jhung[d,**]

[a] *Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090, Novosibirsk, Russian Federation*
[b] *Novosibirsk State University, Pirogova Str. 2, 630090, Novosibirsk, Russian Federation*
[c] *Research and Educational Center for Energy Efficient Catalysis in Novosibirsk National Research University, Pirogova Str. 2, 630090, Novosibirsk, Russian Federation*
[d] *Department of Chemistry and Green-Nano Materials Research Center, Kyungpook National University, Sankyuck-Dong, Buk-Ku, Daegu 702-701, Republic of Korea*
[e] *Novosibirsk State Technical University, Prospekt K. Marksa 20, 630092, Novosibirsk, Russian Federation*

ARTICLE INFO

Article history:
Received 7 April 2015
Received in revised form 26 June 2015
Accepted 17 July 2015
Available online 14 August 2015

Keywords:
Metal-organic frameworks
Photocatalysis
Band gap
Methylene blue

ABSTRACT

The effect of metal ions and functional groups in organic ligands on the photocatalytic properties of metal-carboxylates, such as isostructural MIL-100(M) (M = Al, Fe, V, and Cr), isoreticular UiO-66-R (R = H, NH_2, and NO_2), MIL-47(V), and MIL-125(Ti), was investigated using the decolorization of methylene blue in aqueous solution at pH 7.0 and 20 °C under UV radiation. The metal-carboxylates were characterized by diffuse reflectance UV/vis measurements. The determination of the band gap (E_g) on the basis of DR-UV/vis measurements showed that E_g values correlate with ionic covalent parameters, i.e., the strength of the interaction between metal and oxygen in the "M^{+n}-O^{2-} pair. According to DR-UV/vis spectroscopic and catalytic investigations, the reactivity of metal-carboxylates correlated with the band-gap value (E_g), which could be adjusted by varying the nature of the metal ions in SBUs or functional groups in the organic ligands.

1. Introduction

Metal-organic frameworks (MOFs) are currently attracting attention from the point of view of their application in adsorption and catalysis. Catalytic applications of MOFs are related to their unique structural, textural, and physicochemical properties, which can be adjusted by changing the nature of the metal clusters and organic ligands in the framework [1,2]. Photocatalytic degradation of organic pollutants represents one of the fields of catalytic application [3–6]. Thus, the photocatalytic decolorization of methylene blue (MB) (Fig. 1) has been studied under solar radiation in the presence of MIL-53(Al, Fe, and Cr) [7]; Fe_3O_4/MIL-100(Fe) core–shell microspheres [8]; MOFs formed by d^{10} metals (Cd and Ag); triangular ligands [6]; 3D framework structures $[Co_2(C_{10}H_8N_2)]\cdot[C_{12}H_8O(COO)_2]_2$, $[Ni_2(C_{10}H_8N_2)_2][C_{12}H_8O(COO)_2]_2\cdot H_2O$, and $[Zn_2(C_{10}H_8N_2)]\cdot[C_{12}H_8O(COO)_2]_2$ [4]; ZIF-8 [9]; $Co_2(dcpcpb)(\mu_3\text{-}OH)(H_2O)_2$ and $Cu_4(dcpcpb)_2(\mu_3\text{-}OH)_2(CH_3OH)_2(H_2O)$ [10,11]; $[Cu_5(H_2tmbtmp)_2(btb)_2(OH)_2]\cdot 3H_2O$ [12]; and a titanium(IV)-based MOF (NTU-9, $Ti_2(Hdhbdc)_2(H_2dhbdc)$, H_4dhbdc-2,5-dihydroxyterephathalic acid) [13].

Application of these MOFs in the photocatalytic decolorization of MB clearly revealed their great potential as photocatalysts. In the presence of these materials, the time taken for complete decolorization of MB under visible-light irradiation was 20–60 min. Unfortunately, the comparison of photocatalytic activities of MOFs is practically absent in spite of the large amount of investigations. The high activity has been explained by the photocatalytic reaction. At the same time adsorption of MB on MOFs was not taken into account sometimes, despite the presence of a large amount of MOF in the reaction mixture (0.5–2 g/L) compared with the MB concentration (40 ppm–0.1 mmol/L). We can assume that this does not allow correlations between the catalytic activity of MOFs and their

---

[*] Corresponding author at: Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090, Novosibirsk, Russian Federation. Tel.: +7 383 330 7284; fax: +7 383 330 8056.
[**] Corresponding author. Tel.: +82 53 950 5341; fax: +82 53 950 6330.
E-mail addresses: timofeeva@catalysis.ru (M.N. Timofeeva), sung@knu.ac.kr (S.H. Jhung).
[1] Present address: Department of Environment and Energy, Sejong University, Seoul 143-747, Republic of Korea.

http://dx.doi.org/10.1016/j.cattod.2015.07.026
0920-5861/

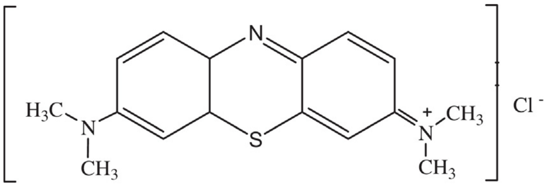

Fig. 1. Structure of methylene blue dye.

physicochemical properties such as band gap value (E_g) and inductive effect of the functional groups in the organic linkers of MOFs. A predictive understanding of the relationship between the activity of MOFs and their corresponding physicochemical properties may be important when choosing MOFs for a particular application. Nowadays, experimental and computational techniques are rarely used to establish structural/physicochemical/photocatalytic property relationships, despite numerous studies on the photocatalytic properties of MOFs.

It is well known that the electronic properties of MOFs depend on their chemical composition and structure [14–17], i.e., the nature of the organic ligands (linkers) and metal ions, or metal-oxide clusters, in the secondary building units (SBUs). The explanation of the electronic properties of MOFs is based on considering the SBUs of a metal-oxide cluster as a discrete quantum dot analogue, stabilized and interconnected by the conjugated organic linkers acting as the photon antenna [18,19]. Thus, the effect of the linker length (one, two, and three aromatic rings) on the E_g value has been demonstrated for UiO-6*x*, which was substituted with dicarboxylate ($x = 6$), biphenyl dicarboxylate ($x = 7$), and terphenyl dicarboxylate ($x = 8$), with a $Zr_6O_4(OH)_4$ cluster as the inorganic fragment [20]. According to theoretical calculations, the E_g value decreases with increasing linker length for the hydroxylated cluster in the following order:

$$2.8\,\text{eV}\,(x = 6) > 2.6\,\text{eV}\,(x = 7) > 2.4\,\text{eV}\,(x = 8)$$

The E_g value can also be tuned by changing the dimensions of the metal cluster in the SBUs. According to Lin et al. [19], the size of SBU clusters of Zn-biphenyl dicarboxylates (Zn-BPDCs) such as IRMOF-9, Zn5-BPDC, and CPO-7 decreases in the following order:

$$\text{CPO} - 7 > \text{Zn}_5 - \text{BPDC} > \text{IRMOF} - 9$$

The E_g values also increase in the same order. This increase in E_g value with decreasing cluster size was attributed to the increasing quantum confinement effect of the SBUs, which was similar to those demonstrated for quantum dots. Effect of the functional groups in linker of MOFs on E_g value was found for UiO-66-R [20] and MIL-125-R (R = H, NH_2, CH_3, OH, or Cl) [21]. However, correlations between E_g values and catalytic properties of MOFs were not demonstrated.

In this investigation, we wanted to estimate the effect of the nature of metal ions and functional groups in organic ligands on the band gap (E_g) and photocatalytic properties of metal-carboxylates, based on experimental DR-UV/vis spectroscopic and catalytic data. The nature of the metal ions and the functional groups in organic ligands was studied using isostructural MIL-100(M) (M = Al, Fe, Cr, and V) and isoreticular UiO-66-R (R = H, NH_2, and NO_2). We predicted that the variation in the chemical composition of MOFs should affect the E_g values, and, in turn, affect their photocatalytic properties. The catalytic properties were investigated in the photocatalytic degradation of MB by oxygen in air in an aqueous solution at pH 7.0 and 20 °C under solar radiation. Note that MB is widely used as an organic dye to examine the photocatalytic activities of MOFs.

2. Experimental

2.1. Materials

Zirconium(IV) chloride and terephthalic acid (TPA, H_2BDC), were purchased from Sigma–Aldrich (St. Louis, MO, USA). 2-amino-terephthalic acid (H_2N-H_2BDC) was procured from Alfa-Aesar (Ward Hill, MA, USA).

UiO-66-R (R = H, NH_2 and NO_2) samples were synthesized following previously reported procedures [22,23], as were MIL-100(Cr, Fe and V) [24,25], MIL-125(Ti) [27], MIL-100(Al) [28], and MIL-47(V) [29]. Textural properties and XRD patterns of MOFs are shown in Table S1 and Fig. S1 (supporting information).

2.2. Instrumental measurements

The porous structure of the materials was determined from the adsorption isotherm of N_2 at −196 °C using Micromeritics ASAP 2400 equipment. The Brunauer–Emmett–Teller specific surface area (S_{BET}) was calculated from adsorption data over the relative pressure range 0.05–0.20. The total pore volume (V_Σ) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The X-ray diffraction patterns were measured with an X-ray diffractometer (ThermoARL) with Cu-K$_\alpha$ ($\lambda = 1.5418$ Å) radiation. The DR-UV/vis spectra were recorded on a UV-2501 PC Shimadzu spectrometer with an IRS-250A accessory in the range 190–900 nm, with a 2 nm resolution. $BaSO_4$ was used as a standard.

2.3. Photocatalytic activity tests

The photocatalytic activity of the MOFs was studied in terms of the degradation of MB by dissolved oxygen in aqueous solution at pH 7.0 and 20 °C, in a batch temperature-controlled photoreactor with a quartz window, under continuous stirring for 3 h. The distance between the light source and the reactor was 10 cm. In a typical experiment, 5 mg of the catalyst was added into 100 mL of MB aqueous solution (0.2 mmol/L) in a 200 mL reactor. The pH value of the suspension was adjusted to neutral (pH 7.0) by addition of NaOH solution (0.1 M). The reaction mixture was stirred in the dark for 60 min to ensure the establishment of an adsorption–desorption equilibrium before the suspension was illuminated by the full irradiation of a high-pressure mercury lamp (1000 W, USSR, main peaks at 310, 365 (maximum), 380, 405, 440, 555, and 585 nm, 21 mV/cm^2, predominantly wavelength 365 nm). The selected radiation wavelength of the lamp (365 nm) accounted for the fact that the width of the photon energy expected is higher than the region of fundamental absorption. The concentration of MB was analyzed by UV/vis spectroscopy at $\lambda = 660$ nm using a UV/vis spectrophotometer (Cary 100 Varian) and a spectrometric quartz cell with a path length of 1 cm. Additionally, an experiment with a 365 nm LED (30 W, China, 25 mV/cm^2) was carried out. The total organic carbon (TOC) content was determined in filtered aliquots of the reaction mixture using TOC/Nb Analyzer (Multi N/C 2100 S, Analytik Jena AG, Germany).

3. Results and discussion

3.1. DR-UV/vis investigation of MOFs

The E_g values of metal-carboxylates were calculated from their DR-UV/vis spectra (Figs. S2–S3, supporting information) according to the well-known energy exponential relationship (Eq. (1)) [30]:

$$(\alpha h\nu)^{1/2} = B \cdot (h\nu - E_g) \tag{1}$$