

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry



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Copper(II) imidazolate frameworks as highly efficient photocatalysts for reduction of CO₂ into methanol under visible light irradiation

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ARTICLE INFO

ABSTRACT

Article history: Received 20 November 2012 Received in revised form 11 April 2013 Accepted 14 April 2013 Available online 23 April 2013

Keywords: Photocatalysts MOFs Imidazolate frameworks Visible-light photocatalysis Photocatalytic reduction of CO₂

Three copper(II) imidazolate frameworks were synthesized by a hydrothermal (or precipitation) reaction. The catalysts were characterized by X-ray diffraction (XRD), nitrogen adsorption, transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-vis), Fourier transform infrared spectra (FTIR), thermogravimetry (TG). Meanwhile, the photocatalytic activities of the samples for reduction of CO₂ into methanol and degradation of methylene blue (MB) under visible light irradiation were also investigated. The results show that the as-prepared samples exhibit better photocatalytic activities for the reduction of carbon dioxide into methanol with water and degradation of MB under visible light irradiation. The orthorhombic copper(II) imidazolate frameworks with a band gap of 2.49 eV and green (G) color has the best photocatalytic activity for reduction of CO₂ into methanol, 1712.7 µmol/g over 5 h, which is about three times as large as that of monoclinic copper(II) imidazolate frameworks with a band gap 2.70 eV and blue (I) color. The degradation kinetics of MB over three photocatalysts fitted well to the apparent firstorder rate equation and the apparent rate constants for the degradation of MB over G, J and P (with pink color) are 0.0038, 0.0013 and 0.0016 min⁻¹, respectively. The synergistic effects of smallest band gap and orthorhombic crystal phase structure are the critical factors for the better photocatalytic activities of G. Moreover, three frameworks can also be stable up to 250 °C. The investigation of Cu-based zeolitic imidazolate frameworks maybe provide a design strategy for a new class of photocatalysts applied in degradation of contaminations, reduction of CO₂, and even water splitting into hydrogen and oxygen under visible light.

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1. Introduction

Porous metal-organic frameworks (MOFs) have been extensively investigated since 1990 [1,2]. Zeolitic imidazolate frameworks (ZIFs) are a new class of nanoporous compounds with tetrahedral networks that resemble those of zeolites: transition metals (Co, Cu, Zn, etc.) replace tetrahedrally coordinated atoms (for example, Si), and imidazolate links replace oxygen bridges [3,4]. As a subfamily of MOFs, ZIFs exhibit the tunable pore size and chemical functionality of classical MOFs [5]. Meanwhile, they are chemically and thermally stable, yet have the long-soughtafter design flexibility offered by functionalized organic links and a high density of transition metal ions [3]. Because of these combined features, ZIFs have very promising applications in catalysis [6-8], gas storage [3,9,10], chemical separation [11,12], molecular recognition [13] and optical [14], electronic [15,16], photoluminescence and magnetic materials [17], and consequently have drawn considerable attention from chemists around the

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world nowadays. Recently, Zifs have also been used in the photocatalytic degradation of organic dye, Isimjan et al. [7] loaded Pt/ ZIF-8 nano-crystallites onto the surfaces of TiO₂ nanotubes and observed increase in photocatalytic properties of ZIF-8 loaded TiO₂ nanotubes by photodegradation of phenol. Yang et al. [18] doped copper into ZIF-67 and found that the Cu-doped ZIF-67 showed high gas uptake capacity and highly efficient visible-light-driven photocatalytic property on the degradation of methyl orange.

The energy shortages and the environmental pollution causing by the depletion of fossil fuels and the gradual increase of atmospheric carbon dioxide (CO₂) concentration are two main challenges in today's society. The artificial photosynthesis, converting CO₂ and water into valuable energy-bearing compounds (such as CO, methane, and methanol) by means of solar energy, is one of the most attractive methods to overcome both global warming and energy crisis. Since photocatalytic reducduction of CO₂ to formic acid, formaldehyde, methanol, and methane over TiO₂ under UV light was discovered by Fujishima and Inoue [19], a number of semiconductors such as TiO₂ nanoparticles or nanotubes [20–26], CaFe₂O₄ [27], ZnGa₂O₄ [28], ZnGe₂O₄ [29,30], Bi₂WO₆ [31], HNb₃O₈ [32], InTaO₄ [33], Zn–Cu–Ga photocatalyst [34], and GaP [35] have been reported to be available for CO₂

^{0022-4596/\$-}see front matter © 2013 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.jssc.2013.04.016

conversion under light illumination. However, the efficiency attained by these studies has been very low due to the large band gaps or the photocorrosion process. In order to make full use of solar energy, it is of great importance to develop new visible light photocatalysts with high activities. Moreover, it is well known that copper has good selectivities for photo-reduction CO_2 into methanol [22,36–38] and that the metal free polymer containing C=N band have good photocatalytic activities for hydrogen produced from water [39,40] and photocatalytic reduction of CO_2 [41]. In particular, to our knowledge, the directly photocatalytic reduction of CO_2 on the photocatalysts of copper-based MOFs or imidazo-dlate frameworks containing C=N band under visible light has not been reported yet until now.

Therefore, the synergistic effects of copper and C=N band in imidazodlate frameworks on the photocatalytic activities of semiconductors are very interesting research topics. Herein, we reported for the first time the photocatalytic reduction of CO_2 into methanol on three copper(II) Imidazolate Frameworks, which named green (G), blue (J) and pink (P), respectively. The photocatalytic activities of the photocatalysts were studied in a continuous-flow reactor system under visible light irradiation. The relations between the structures, visible light absorption capabilities and the CO_2 conversion efficiency under visible light irradiation were reported.

2. Experimental

2.1. Preparation of copper(II) imidazolate frameworks

The crystal of P was synthesized according to the procedure reported previously [42], whereas the crystal of G and J were synthesized by a modified procedure reported previously [42]. Briefly, For P, NaOH (0.1 M) was added to a 50 ml of mixture of imidazole (2 g, 29.4 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (2.50 mmol), the obtained reddish-purple powder was washed with ethanol and dried in vacuo at 80 °C for J, after 12.5 ml of CuSO₄ · 5H₂O solution (0.8 M) was added dropwise to a 50 ml of mixture of imidazole and NaHCO₃ at 80 °C, the mixture was left under room temperature for 2 h. Then, the blue compound was filtered off, washed with water, and dried at 80 °C overnight in an oven. For G, after 15 ml of imidazole solution (0.245 M) was added to the 25 ml of mixture of CuSO₄ · 5H₂O and NH₄OH, the mixture was hydrothermally treated at 110 °C in a Teflon-lined stainless steel autoclave for 48 h. After reaction, the product was collected by filtration and then washed 3-4 times with distilled water. Finally, the samples were dried at 80 °C overnight in an oven.

2.2. Characterization

Nitrogen adsorption measurements were carried out at 77 K by using an accelerated surface area and porosimetry system (ASAP 2010, Micromeritics) equipped with commercial software of calculation and analysis for determination of the textural properties of the photocatalyst studied [24,43–45]. The UV–Vis spectroscopy in the 200–800 nm was measured with a Shimadzu UV-2550PC diffuse reflectance spectroscopy. The transmission electron microscopy (TEM) was performed on a JEM-2100HR (200 kV, Japan) operated at 120 kV. The scanning electron microscope (SEM) was done on a LEO 1530VP field emission scanning electron microscope (LEO Electron Microscopy Inc., Germany). The XRD patterns were obtained at room temperature using a MSAL-XD2 diffractometer with CuK α radiation (operated at 36 kV and 30 mA, λ =0.15406 nm). The Fourier transform infrared spectra (FTIR) of the samples were recorded using a Nicolet 510 P spectrometer.

2.3. Photocatalytic reduction of CO₂

The photocatalytic reduction of CO₂ was performed in a continuous-flow reactor system as shown in our previous study [24]. A 500 W Xe lamp located in the quartz cool trap was the irradiation source and the UV light below 400 nm was removed by a 2.0 M sodium nitrite solution [24,46]. Prior to experiments, sodium hydroxide (0.80 g) and absolute sodium sulfite (2.52 g)were dissolved in 200 ml distilled water. This solution was then put into a photochemical reaction instrument. Before irradiation. ultrapure CO₂ was bubbled through the solution in the reactor for at least 30 min to ensure that all dissolved oxygen was eliminated. then, 200 mg of catalyst powder was added into above solution. and the irradiation lamp was turned on to start the photoreaction. Ultrapure CO₂ was continuously bubbled through the above solution in the reactor during the whole irradiation. The radiation time was 5 h. A needle-type probe was inserted into the solution in the reactor to withdraw a small liquid sample at 1, 2, 2.5, 3, 3.5, 4, 4.5 and 5 h, respectively. The concentration of methanol in the samples was analyzed using a GC9560 gas chromatograph equipped with a flame ionization detector and a stainless steel packed column (Porapak-Q, $2 \text{ mm} \times 3 \text{ m}$). The blank test was performed in the dark with the catalyst and CO₂ or in the light without CO₂ under the same other experimental conditions. The methanol has not been detected.

2.4. Photocatalytic activity for the degradation of methylene blue.

Visible light photocatalytic activities of G, J, and P were also evaluated through the degradation of methylene blue (MB) solution with an initial MB concentration of 10 mg/l. A 500 W Xe lamp located in the quartz cool trap was the irradiation source, and the UV light below 400 nm was removed by a 2.0 M sodium nitrite solution [24,46]. In a typical run, aqueous slurries were prepared by adding 0.2 g photocatalyst to 600 ml methyl orange aqueous solution. After that, the suspension was stirred for 30 min in the dark to ensure adsorption/desorption equilibrium before light illumination. During the irradiation procedure, the reaction sample was collected at 20-min intervals and centrifuged to remove photocatalyst particles. The filtrates were analyzed with a spectrophotometer by measuring its absorbance at 662 nm.

3. Results and discussion

3.1. XRD analysis

All three as-prepared samples were studied by powder XRD to identify the phase structures. Fig. 1 shows the XRD patterns of different samples. As observed in Fig. 1, all the diffraction peaks of G and J matches well with those of G (green) and J (blue) simulated from the single-crystal structure reported in Ref. [42], and no other crystallite phases were observed. Thus, it is easy to find that the G shows orthorhombic structure with distorted square-planar coordination (trans N-Cu-N angles of 154° for Cu₁ and 142° and 138° for Cu₂), and the room temperature lattice parameters are a = 21.139 Å, b = 19.080 Å and c = 9.2843 Å; whereas, the results also revealed that the as-synthesized sample J was monoclinic phase with the unit cell parameters, a = 11.75 Å, b=14.07 Å and c=8.77 Å. Moreover, although P does not match well with any structural model due to its complexity and broad peak features, the XRD patterns of P are consistent with the observed one of the P phase in Ref [42]. In conclusion, the above analyses and XRD patterns evidence further confirm that three different phase structures of G, J and P were successfully prepared.



Fig. 1. XRD patterns of different photocatalysts. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. UV-vis absorption spectra of different photocatalysts.

3.2. UV-vis analysis

The optical properties of three copper(II) imidazolate frameworks were probed by using UV-vis diffuse reflectance spectra. The corresponding optical absorption of three copper(II) imidazolate frameworks is shown in Fig. 2. As can be seen, all three samples display strong absorption in the visible light region above 400 nm and their optical absorbance edges are between 450 and 550 nm. Furthermore, the band gap energy of the synthesized materials can be calculated by the plots of the transformed Kubelka–Munk function versus the wavelength [47–49]. The plots of $(\alpha h\nu)^{2/n}$ as a function of $h\nu$ are in accordance with the theoretical Eq. (1) [24,46,50–52],

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

where a, ν , A, and E_g are the absorption coefficient, light frequency, proportionality constant, and band gap, respectively. In the equation, *n* decides the characteristics of the transition in a semiconductor, i.e., direct transition (n=1) or indirect transition (n=4). For three samples, the band-gap energy in our experiment could be estimated from a plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$. As observed in the inset of Fig. 2, the direct band gaps for G, P and J are estimated to be 2.49, 2.81 and 2.70 eV, respectively. The UV-vis absorption spectra studies clearly indicate that the crystal structures have significant influence on the onset of absorption, of which an obvious shift can be observed due to the change of crystal phases. The results also suggest that G with orthorhombic phase structures can be photoexcited to generate more electron-hole pairs than J with monoclinic phase and P under visible-light irradiation, which could result in higher photocatalytic performance.

3.3. Nitrogen sorption

Nitrogen adsorption studies were also conducted to determine the specified surface areas of the samples. Fig. 3 displays nitrogen sorption properties of three copper(II) imidazolate frameworks. According to the Brunauer–Emmett–Teller (BET) equation, the BET surface areas of P, G and J were calculated to be 11.92, 3.99 and 0.68 m²/g, respectively. It is clear to see that J exhibits the smallest BET surface among three samples. The possible reasons may be that J is the one showing the highest density (1.824 g/cm³) [42]. Meanwhile, it is also observed that P has the largest BET surface among three copper(II) imidazolate frameworks.

3.4. TEM analysis

The further morphologic and structural characterization was investigated by a typical transmission electron microscopy (TEM) image. Fig. 4 shows the TEM micrographs of G as an example. As presented in Fig. 4(a), it is found that the irregular particles of G with sizes from 100 to 300 nm were obtained via the hydro-thermal synthesis. Furthermore, it is also seen from Fig. 4(b) that the primary G nanoparticles are inclined to aggregate to form larger secondary particles. The aggregates vary in sizes from less than 1 μ m to as large as 5 μ m with sheet-like or rod-like morphologies.

3.5. FTIR analysis

Fourier transform infrared spectroscopy (FTIR) spectra were measured to identify organic functional-groups in the materials, and the corresponding results were shown in Fig. 5. As presented in Fig. 5, the broad band around 3446 cm⁻¹ is usually assigned to the O–H vibration adsorbed water, H–OH [53–55]. One new peak is distinguished at 3100 cm⁻¹ which is attributed to N–H vibrations [56]. Furthermore, all the peaks for G in the 1700–400 cm⁻¹ region match those reported for copper imidazolate complexes with ancillary ligands [42]. The peaks at 1646 cm⁻¹ result from the stretching vibration of C=N in the imidazole ring, whereas, the peaks at 939 and 1340 cm⁻¹ can be ascribed to the stretching vibration Law cm⁻¹ can be ascribed to the stretching vibration bands due to C–N and C=N groups indicates that the imidazole molecule exists in three copper imidazolate complexes.

3.6. Thermogravimetry (TG) analysis

The thermal stability of the sample was studied by thermogravimetry (TG) analysis, and the corresponding results were shown in Fig. 6. As can be seen in Fig. 6, the sample J shows weight loss from 100 to 140 °C, which may be due to the desorption of surface bound water. Meanwhile, three samples of



Fig. 3. N₂ adsorption isotherms of different photocatalysts.



Fig. 4. TEM images of different photocatalysts.



Fig. 6. Thermogravimetric (TG) curves of different photocatalysts.

G, J and P were also highly thermally stable below 250 °C. The weight loss from 250 to 400 °C could be attributed to the decomposition of the imidazole molecule in the composites. All the results further suggest that three copper imidazolate complexes are highly thermally stable below 250 °C though the sample J contains much water molecular adsorbed in its microporous structure.

3.7. Photocatalytic activity for reducing CO₂

The photocatalytic activities of three samples for reducing CO_2 to CH_3OH under visible light irradiation were evaluated in a continuous-flow reactor system under visible light irradiation (> 400 nm) [24]. The concentration of methanol in the liquid



Fig. 7. Methanol yields of different photocatalysts.

was analyzed using a gas chromatography (GC). Fig. 7 shows the methanol yields over various samples under visible light irradiation. As seen in Fig.7, the largest yields of methanol on G, P and J photocatalysts under visible light irradiation for 5 h were 1712.7, 745.1, 581 µmol/g, respectively. The results clearly indicate that the sample G with orthorhombic phase exhibits the best photocatalytic performance though the surface area of G is smaller than that of P. The methanol yield over the sample G is also higher than that of P25 (91 µmol/g) [24],CdS/Bi₂S₃ heterostructure (613 µmol/g) [57] and Bi_2S_3/TiO_2 nanotubes (224.6 μ mol/g) [24] under the same conditions. There are possible several reasons for the highly efficient photocatalytic activities. The main reason may be that G has the smallest band gap, which means that the responding performance towards visible light of G is the best in the three samples. Furthermore, the orthorhombic phase structure of G maybe play an important role for the high photocatalytic activity. In addition, the Cu₄N cluster in the core of MOFs is similar with the inorganic semiconductor, Cu₃N, which has been proven to have good photocatalytic activity for the reduction of CO₂ [58]. What is more, the C=N band in the imidazole ring may have the same function like the C=N band in the C_3N_4 polymer [39,40]. Therefore, the synergistic effects of smallest band gap and orthorhombic crystal phase structure are the critical factors for the better photocatalytic activities of G. Meanwhile, the Cu₄N cluster and C=N band in the imidazole also play important roles for the enhanced photocatalytic activities of three Cu-based zeolitic imidazolate frameworks.

3.8. Photocatalytic performance for degradation of MB

To further test the photocatalytic activities of as-prepared photocatalysts for degradation of pollutants in the liquid phase, the performance of three photocatalysts for degradation of MB has



Fig. 8. (a) Photocatalytic activities of the G, J and P samples for the degradation of MB under visible-light irradiation. (b) ln(C⁰/C) vs. time for the G, J and P samples.

also been investigated. Fig. 8(A) shows photocatalytic activities of the G, J and P samples for the degradation of MB under visiblelight irradiation. It is clearly observed that the sample G exhibited the best visible-light-driven catalytic performance for degradation of MB. For comparison purposes, the rate constants have also been calculated according to an apparent first order in agreement with a generally observed Langmuir-Hinshelwood model [59-61]:

$$\ln(C^0/C) = k_a t \tag{2}$$

where C^0 is the initial concentration of dye, k_a is the apparent first-order rate constant, *C* is the concentration of the dye and *t* is the illumination time. The apparent first order linear transforms are given in Fig. 8(B). It is clear that all degradation reactions over different photocatalysts followed apparent first-order kinetics. The slopes of three lines show that the apparent rate constants for the degradation of MB over G, J and P are 0.0038, 0.0013 and 0.0016 min⁻¹, respectively. It is obvious that the degradation rate constant of MB over G is almost two to three times as large as those over J and P. These results further confirm that the sample G with the smallest band gap and the orthorhombic phase structure also has the best photocatalytic activities for the degradation of MB under visible light.

4. Conclusion

In summary, three copper(II) imidazolate frameworks were synthesized by a hydrothermal (or precipitation) reaction. The as-prepared samples exhibit better photocatalytic activities for the reduction of carbon dioxide with water and degradation of methylene blue under visible light irradiation. The largest yield of methanol on the orthorhombic copper(II) imidazolate frameworks under visible light irradiation over 5 h is 1712.7 µmol/g. The degradation kinetics of MB on three photocatalysts followed well the apparent first-order rate equation and the apparent rate constants for the degradation of MB over G, J and P are 0.0038, 0.0013 and 0.0016 min⁻¹, respectively. Our results and data demonstrate that the Cu-based zeolitic imidazolate frameworks can be directly used as visible-light driven photocatalysts. At this point, the investigation of Cu-based zeolitic imidazolate frameworks may be very interesting and provide a design strategy for new class of photocatalysts applied in degradation of contaminations, reduction of CO₂, and even water splitting into hydrogen and oxygen under visible light.

Acknowledgments

The work is supported by the National Natural Science Foundation of China (Grant No.20906034) and the key Academic Program of the 3rd phase "211 Project" of South China Agricultural University(Grant No.2009B010100001).

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