



Short communication

Metal-organic frameworks as heterogeneous catalysts for electrocatalytic oxidative carbonylation of methanol to dimethyl carbonate

Gan Jia, Yanfang Gao^{*}, Wen Zhang, Hong Wang, Zhenzhu Cao, Caihong Li, Jinrong Liu

College of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051, China

ARTICLE INFO

Article history:

Received 21 May 2013

Received in revised form 10 June 2013

Accepted 14 June 2013

Available online 22 June 2013

Keywords:

MOFs

Dimethyl carbonate

Electro-synthesis

Oxidative carbonylation

ABSTRACT

The development of heterogeneous catalysts, such as metal-organic frameworks (MOFs), may overcome most of the problems associated with homogeneous catalysts. A Cu-based MOF with mixed ligands was synthesized, and its electrocatalytic activity for the oxidative carbonylation of methanol was studied. This study demonstrates for the first time that a Cu-based MOF can actively electrocatalyze methanol into dimethyl carbonate (DMC). A self-designed electrolytic cell was constructed for electrocatalysis experiments. The as-synthesized Cu-based MOF showed a pair of redox peaks at ca. +0.3 V. This paper utilizes a new approach for synthesizing DMC in a heterogeneous catalytic system.

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1. Introduction

Dimethyl carbonate (DMC) has attracted significant research attention because of its high oxygen content, high solubility, low boiling point, and rapid biodegradability [1]. It is an important building block [2] in the current chemical industry. DMC can also substitute methyl tert-butyl ether as an oxygen-containing fuel additive [3] and exhibits wide application in the synthesis of polycarbonate [4] and polyurethane.

Several catalytic processes have been developed for the synthesis of DMC, including phosgenation [5], oxidative carbonylation of methanol [6], direct synthesis from CO₂ and methanol [7], urea methanolysis [8,9], and transesterification [10]. As green chemistry is currently a major global theme, green catalytic processes, such as the electrochemical synthesis of DMC [11–13], have captured the interest of many researchers.

Previous investigations provided evidences that, noble metal (e.g., Pd [13], Rh [14], Au [15]) and transition metal coordination complexes (e.g., Cu(bipy) [14], Cu(phen) [16], Co(salen) [17]) exhibit activity for electrosynthesis of DMC. However, major problems, including the poor recyclability of the electrocatalysts and undesirable stability of catalytic activity, are frequently encountered in such homo-electrocatalytic systems. We hope to immobilize the electrocatalysts onto the surface of anodes in future research.

Metal-organic frameworks (MOFs) are a specific class of coordination polymers with high crystallinity, high porosity, and a large number of metal sites. MOFs are attractive materials because of their unique

properties, which include large surface areas, tunable pore sizes, and open metal sites [18–20]. The potential applications of MOFs have been explored in gas separation/storage [21], magnet [22], sensing [23], imaging [24], drug delivery [25], and catalysis [26–30]. In this work, we attempt to develop a new catalytic MOF system with Cu as the metal active center. To date, no efforts have been paid on MOFs as electrocatalysts for the electrocatalytic oxidative carbonylation of methanol to DMC.

Previous studies by our group focused on non-noble homogeneous metal catalysts for this electrocatalytic system [31]. The applications of a Cu(II)-based MOF with 2,2'-bipyridine and carboxylate ligands as a heterogeneous electrocatalyst for the electrocatalytic oxidative carbonylation of methanol to DMC are first described in this work.

2. Experimental

2.1. Apparatus & materials

All reagents and solvents were of analytical grade and used without further purification. Cyclic voltammetry and electrocatalytic studies were performed using a CHI 660C electrochemical workstation (CH Instruments, Austin, TX, USA). IR spectra were recorded with a NEXUS 670 FT-IR spectrometer using the KBr pellet technique. X-ray powder diffraction experiments were carried out on a XD8 Advance-Bruker AXS diffractometer using CuK α radiation. The program Mercury 3.0 was used to calculate the X-ray crystallographic powder patterns of Cu(II)-2,2'-bipyridine-BTC (BTC = benzene-1,3,5-tricarboxylate). The analyte obtained was distilled and analyzed

^{*} Corresponding author. Tel.: +86 471 6575722; fax: +86 471 6503298.
E-mail address: yf_gao@imut.edu.cn (Y. Gao).

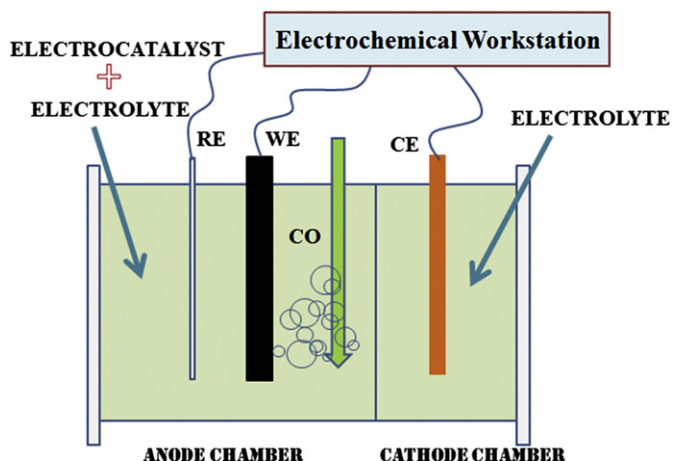


Fig. 1. Schematic illustration of the structure of the electrolytic cell.

by gas chromatograph (GC-17A with a flame ionization detector and 30 m × 0.25 mm capillary column, Shimadzu).

2.2. Preparation of copper(II)-based MOF

The Cu-based MOF: copper(II)-2,2'-bipyridine-BTC was synthesized as reported previously [28,32].

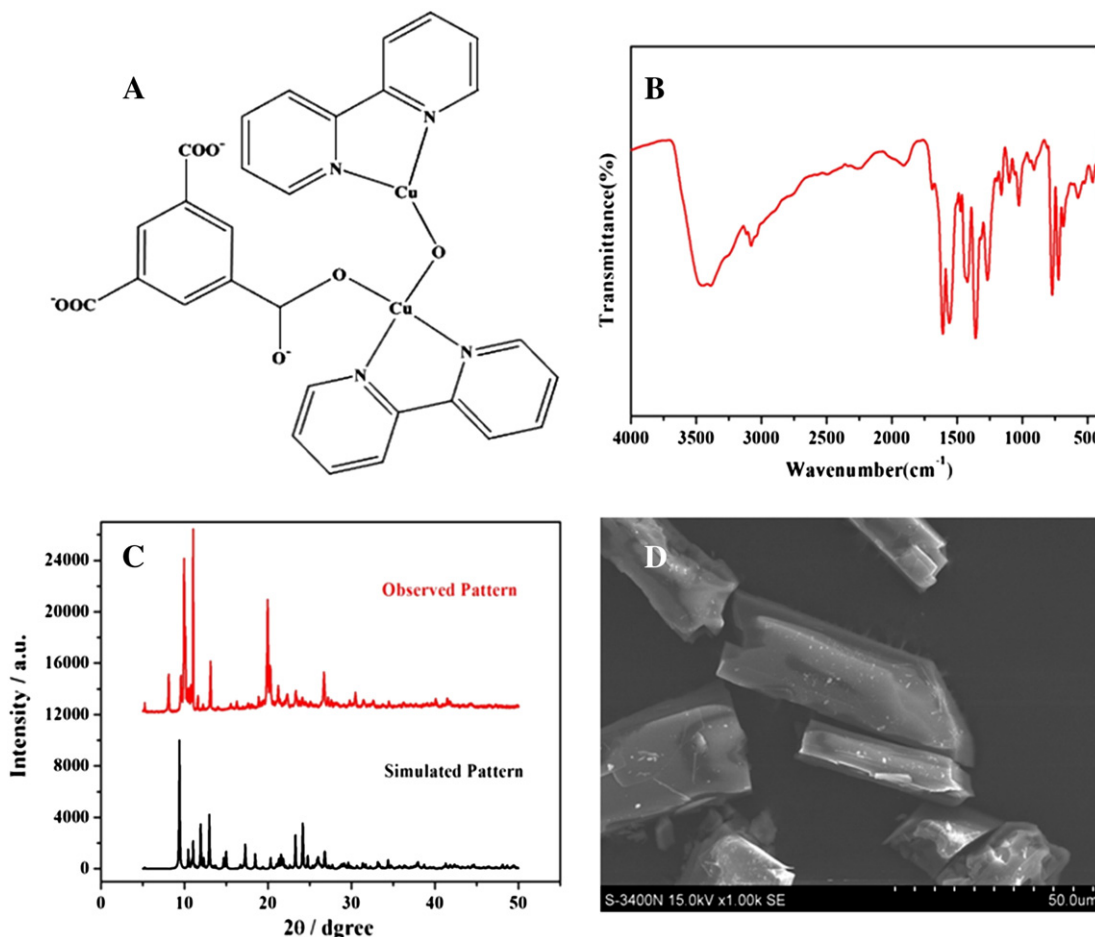


Fig. 2. (A) Coordination geometry of Cu atoms in the Cu(II)-based MOF; (B) FT-IR curves of the as-synthesized Cu(II)-based MOF; (C) Observed and simulated XRD patterns of the Cu(II)-based MOF; (D) Typical SEM image of a fully crystallized Cu(II)-based MOF.

2.3. Electrocatalytic experiments

The electrochemical experiments were performed at room temperature and under normal pressure. Electrosynthesis was performed in a two-compartment, three-electrode cell. Anodic and cathodic compartments were divided by an anion-exchange membrane. Each compartment had a volume of 20 cm³. The anode of the electrolytic cell was equipped with a gas inlet and outlet, a carbon rod (self-made from a waste dry battery, surface area of 1.88 cm²) was used as the working electrode and Ag/Ag₂O electrode was used as the reference electrode. Copper wire was used as the counter electrode and placed in the cathodic compartment of the electrolytic cell. The anolyte consisted of CH₃OH (10 mL) and a supporting electrolyte (KOH, 0.1 mol L⁻¹). The electrocatalyst (Cu-based MOF, 0.4 g) was added to the anolyte, and CO was bubbled into the solution as a reactant. About 10 mL of CH₃OH and the supporting electrolyte were added to the cathode compartment. A schematic illustration of the electrolytic cell structure is shown in Fig. 1, and more details about the structure of the electrolytic cell and working conditions are described in our previous work [31].

3. Results and discussions

To demonstrate that the MOF material can actively catalyze electrochemical reactions, we synthesized a Cu(II)-based MOF and studied its electrocatalytic properties. The coordination geometry of Cu atoms in Fig. 2A shows that each divalent Cu center is coordinated with two carboxyl groups from different BTC ligands, one oxygen atom from water,

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