MCAT

Editor's choice paper

Base-free aerobic oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid in water by hydrotalcite-activated carbon composite supported gold catalyst

CrossMark

Tianqi Gao, Tianyu Gao, Wenhao Fang*, Qiue Cao

School of Chemical Science and Technology, Key Laboratory of Medicinal Chemistry for Natural Resource – Ministry of Education, Yunnan University, 2 North Cuihu Road, 650091 Kunming, China

ARTICLE INFO

ABSTRACT

Selective conversion of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) was studied using molecular oxygen without addition of any soluble base. A new, cheap and robust support (*i.e.* hydrotalcite-activated carbon composite, HT-AC) was prepared by physical milling of home-made HT and commercial AC, which required using less chemical consumption and simpler chemical protocol. Au/HT-AC catalyst showed superior catalytic performance for aerobic oxidation of HMF in water under mild conditions compared to Au/HT and Au/AC catalysts, respectively. It was found that the HT-AC support with the optimal ratio (2:1 in mass ratio) significantly enhanced FDCA yield and catalytic stability. After 12 h at 100 °C, 99.5% FDCA yield was achieved using O_2 at 0.5 MPa. Moreover, 99% FDCA yield was obtained using air as oxidant after 18 h. The catalyst demonstrated remarkable stability during recycling up to six times. The influence of different reaction parameters was studied and optimized. Furthermore, the properties of catalysts were characterized by ICP-MS, N_2 isotherms, XRD, XPS and TEM.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The valorization of renewable lignocellulosic biomass for the sustainable production of fuels and chemicals has attracted much attention due to the depletion of fossil resources and environmental concerns. A very desirable approach is the (bio)chemical transformation of biomass to platform molecules followed by catalytic conversion into high-value-added chemicals, such as polymer precursors, pharmaceuticals and fine chemicals [1]. 5-Hydroxymethylfurfural (HMF) has been identified as a key and versatile platform compound derived from cellulosic C_6 carbohydrates, because HMF can be used for the integrated production of various building-block compounds [2]. Particularly, 2,5-furandicarboxylic acid (FDCA), the symmetrical furanic diacid synthesized *via* oxidation of HMF, is a promising substitute for terephthalic acid that represents a petroleum-based monomer largely used for the manufacture of polyethylene terephthalate (PET) plastic [3].

Previously, stoichiometric oxidant like $KMnO_4$ was used for HMF oxidation, leading to pollutants emission and toxicity issue [4]. Instead, using air as oxidant, homogenous Co/Mn/Br halides in

the presence of corrosive solvent like acetic acid was employed, affording a moderate FDCA yield (*ca.* 60%) but under rather harsh reaction conditions (70 bar) [5]. Obviously, homogeneous catalytic systems inevitably suffer from the problems of low atom efficiency, waste generation and catalyst recycling. In such a context, heterogeneous selective oxidation of HMF to FDCA using molecular oxygen is of great importance and has become a focus of oxidative model reactions for biorefineries [6,7].

Recent progress on the aerobic oxidation of HMF has been achieved by using supported noble metals. Representative active heterogeneous gold [8,9], palladium [10,11], platinum [12,13], and ruthenium [14,15] catalysts were reported. Nevertheless, the above-reported systems cannot work so well without the addition of 1–20 equivalent homogeneous bases (such as NaOH and K_2CO_3) in order to facilitate alkoxide formation and C—H activation in the process. As a result, further acidification and purification are required for subsequent use of FDCA in the polymer industrial, hampering the green footprint of the process. Therefore, the aerobic oxidation of HMF to FDCA under base-free conditions is highly desirable but remains significant challenge.

On the other hand, supported-Au nanoparticles have emerged as promising catalysts for diverse mild and efficient selective aerobic oxidations in liquid phase [16]. As Au-based catalysts can offer better resistance to water and oxygen, it is generally accepted that Au catalyst are more selective and stable for the aerobic oxidation

of organic compounds in water rather than the conventional Pd and Pt oxidation catalysts. To the best of our knowledge, there is very few Au-based catalysts reported for the base-free aerobic oxidation of HMF, even if Pd [17], Pt [18,19] and Ru [20,21] catalysts have been developed.

N.K. Gupta et al. showed that hydrotalcite-supported gold nanoparticle (Au/HT) catalyst can convert HMF to FDCA at 95 °C without addition of homogeneous base. FDCA yield reached 99% and 81% using O_2 or air at ambient pressure, respectively [22]. But it should be mentioned that during recycling FDCA yield decreased quickly to 90% after only two cycles due to the leaching of the basic sites of hydrotalcite in an aqueous solution. Following that, L. Ardemani et al. demonstrated that HT solid base could drive HMF oxidation but only in concert with very high concentrations of surface gold [23]. Apart from the monometallic Au catalysts, X. Wan et al. reported that carbon nanotube (CNT) supported Au-Pd alloy can afford high FDCA yield (>94%) at 100 °C under 0.5 MPa O_2 while maintaining good stability [24]. However, CNT as support is rather expensive. It has to be also noted that CNT must be functionalized previously by HNO_3 or H_2O_2 to enhance the adsorption of HMF and the intermediates, which is essential for realization of the base-free oxidation. Therefore, development of more cost-effective and stable heterogeneous Au catalyst is of still high importance and challenge.

As it is known, Au catalyst may be deactivated more easily by the formed organic products like carboxylic acid in the absence of basic promoter. In light of this, developing inexpensive support materials that combine robust basic sites and sufficient adsorption of substrate/intermediates by using less chemical and facile protocol is becoming the breakthrough to Au catalyst for aerobic oxidation of HMF under base-free conditions.

Herein we report for the first time a new and interesting support in the form of composite consisted of hydrotalcite and activated carbon (donated as HT-AC) that was prepared by a simple physical milling of two components. After immobilization of gold nanoparticles, the obtained Au/HT-AC catalyst is efficient and stable for base-free aerobic oxidation of HMF to FDCA in water under mild conditions. We will show the necessary use of HT-AC composite for the enhancement of FDCA yield and catalyst stability. We have investigated and optimized the different reaction parameters, such as reaction time, reaction temperature, and O_2 pressure. And we have also studied the catalyst properties and the reusability.

2. Experimental

2.1. Materials and reagents

$Mg(NO_3)_2 \cdot 6H_2O$ (>99%) and $Al(NO_3)_3 \cdot 9H_2O$ (>98%) from Acros Organics, and $(NH_4)_2CO_3$ and NH_4OH from Sinopharm Chemical Co. Ltd. were used for synthesis of hydrotalcite (HT). Charcoal activated (AC) and polyvinylpyrrolidone (PVP, >98%, MW = 10,000) were purchased from Tokyo Chemical Industry Co. Ltd. $HAuCl_4 \cdot 3H_2O$ (49.0% on Au basis) and $NaBH_4$ (>98%) were purchased from Alfa Aesar. 5-Hydroxymethylfurfural (HMF, 98%), 2,5-diformylfuran (DFF, 98%), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA, 98%), 5-formylfuran-2-carboxylic acid (FFCA, 98%) and 2,5-furandicarboxylic acid (FDCA, 98%) from Ark Pharm were used for catalytic reactions and related quantification. All the chemicals were used as received without further purification or treatment.

2.2. Catalysts preparation

Mg-Al HT was synthesized by an alkali-free co-precipitation method. To an aqueous solution of ammonium carbonate (1 mol L^{-1}), an equivalent mixed solution of metal nitrates (1 mol L^{-1}) with a molar ratio of Mg:Al = 3:1 was slowly added under stirring at 600 rmp. The pH value of the mixture was adjusted to 8 by dropwise addition of 28 wt% solution of ammonium hydroxide. The slurry was kept stirring at 65 °C under condensation reflux for 18 h. The resulting solids were recovered by filtration and washed by excessive deionized water when the filtrate presented a neutral pH value. The solids were afterwards oven-dried at 120 °C for 12 h followed by calcination at 500 °C under an air flow for 4 h. Although the crystalline structure of HT was lost during the calcining, it was regained after the subsequent process of catalyst preparation owing to the memory effect of HT (see Fig. S1 in supplementary material).

HT-AC composites were prepared by manually milling the mixed powder of hydrotalcite and activated carbon. Typically, to an agate mortar (inner diameter: 110 mm) 2 g of HT and AC mixture with various mass ratios (HT:AC = 3:1, 2:1, 1:1, 1:2, 1:3 and 1:4, respectively) was mixed and milled continuously and homogeneously at room temperature for 40 min. The obtained black fine powder was oven-dried at 120 °C for 1 h.

Au/HT-AC catalysts were prepared by immobilization of the PVP-stabilized colloidal Au nanoparticles onto the different HT-AC supports. In a typical protocol, a polyvinyl pyrrolidone (PVP, MW = 10,000) aqueous solution was added into a $HAuCl_4$ solution (PVP/$HAuCl_4$ = 1.2/1, in w/w) under stirring. A freshly made $NaBH_4$ solution ($NaBH_4$/$HAuCl_4$ = 5/1, in mol/mol) was slowly introduced into the mixture to yield a dark-purple colloidal solution. And then a suspension of powdery support was added and the mixture was vigorously stirred at room temperature for 2 h. The solid catalyst was recovered by filtration and washed repeatedly with hot deionized water (95 °C) to remove PVP and with excessive deionized water to remove Na$^+$ and Cl$^-$ ions. Finally, the resultant Au/HT-AC catalyst was freeze-dried at −50 °C for 24 h. This protocol was also applicable to HT and AC as support, respectively.

2.3. Catalytic reaction

The aerobic oxidation of HMF was performed in a batch-type Teflon-lined stainless-steel autoclave (50 mL). Typically, HMF (0.5 mmol) and catalyst (HMF/Au = 100/1, in mol.) were added into the reactor with deionized H_2O (20 mL) as solvent. After the purge and introduction of O_2 at a certain pressure (typically at 0.5 MPa), the reactor was placed in an oil bath pre-heated at 100 °C with magnetic stirring at 600 rpm. After a fixed time (typically 12 h unless otherwise specified), the reactor was quickly transferred to icy water. And then the spent catalyst was carefully separated by high-speed centrifugation (10,000 rmp for 10 min) and washed by ethanol three times followed by freeze-drying before its next use.

The reactant and liquid products were analyzed on an Agilent 1260 Infinity high-performance liquid chromatography (HPLC) with a photodiode array detector (DAD) and a Shodex SH-1011 sugar column (8 mm × 300 mm × 6 μm) using a dilute H_2SO_4 solution (5 mM in water) as mobile phase. The quantification was carried out using the external standard method. Each product (DFF, HMFCA, FFCA and FDCA), as well as reactant (HMF), was calibrated by using its standard at different concentrations at the specific wavelength, i.e. 260 nm for HMFCA and FDCA, 285 nm for HMF, and 290 nm for DFF and FFCA. The conversion of HMF and the selectivity of each product were defined as the molar percentage of HMF converted and the molar percentage of each product formed in HMF converted, respectively. Both the conversion and selectivity were calculated on a carbon basis. Each reaction was repeated twice at least to guarantee a reproducible result.