



Full Length Article

A novel and highly efficient Zr-containing catalyst based on humic acids for the conversion of biomass-derived ethyl levulinate into gamma-valerolactone



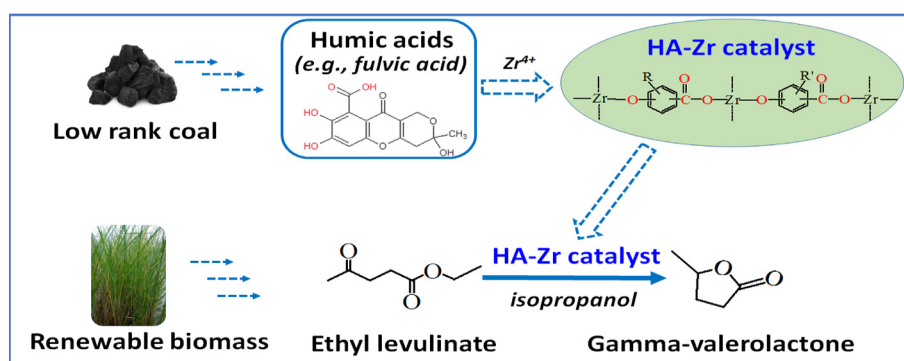
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HIGHLIGHTS

- A novel MPV catalyst based on humic acids and Zr metal (HA-Zr) is prepared.
- HA-Zr is effective for MPV reaction with isopropanol as hydrogen source.
- Ethyl levulinate can be converted efficiently to γ -valerolactone by HA-Zr.
- Both performances and structures of HA-Zr are stable during reuse.

GRAPHICAL ABSTRACT



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ABSTRACT

As the fast depletion of coal resources, exploring the value-added utilization approaches of low rank coals or their components and, in parallel, promoting the conversion of sustainable resources (such as biomass) into useful chemicals are critical issues facing human society. In this work, we used humic acids (HAs), an abundant material in nature (mainly derived from low rank coals), and the transition metal zirconium (Zr) to prepare a novel Zr-containing hydrogen transfer catalyst. The prepared catalyst was applied into the conversion of biomass-derived ethyl levulinate (EL) into gamma-valerolactone (GVL) via hydrogen transfer reaction. Both the preparation conditions of the catalysts and the reaction parameters during the conversion of EL into GVL were systematically investigated. The catalyst was characterized by SEM, TEM, FTIR, powder XRD, and TG analysis. The results demonstrated that the as-prepared catalyst was highly efficient for the conversion of EL into GVL. Under optimized conditions, EL could be completely converted and the GVL yield could reach up to 88.3%. The catalyst could be used at least 11 times without notable changes in both activity and structures, indicating an excellent stability. As far as we know, this is the first work using HAs to prepare Zr-containing catalyst and its application to the conversion of EL into GVL in biomass utilization.

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1. Introduction

Coal, as one of the main fossil resources, plays a key role in promoting the development of global economics and societies, providing human energy and organic chemical sources [1]. However, with the fast exploitation and consumption of the coal resources, the negative effects of the excessive use of coal on the environment are emerging, and the limited reserve of coal on earth, especially the high rank coals, hinders sustainable applications of the coal resource in the long run [2,3]. Therefore, international attentions have been focused on realizing the high efficiency and clean utilization of coal, and special focuses are also paid on exploring value-added utilization approaches of the low rank coals [4–6]. Thus how to improve the utilization efficiency of the low rank coals or their components and realizing their hierarchical utilization is an important issue facing human society [4,5,7,8].

Lignites, as typical representatives in the low rank coal family, have a huge reserve around the world. Compared with the high rank coals, lignites are low-quality fuel for direct combustion due to the high moisture content, poor stability, and low calorific value [4,5]. Humic acids (HAs) are an important component in lignites, accounting for 10–80% of the lignite organic matter depending on the maturity level of lignites [9]. There are amounts of oxygen-containing functional groups (OFGs) in HAs [10]. On one hand, these OFGs may increase the reactivity of HAs and lignites [11], leading to the instability of lignites during applications. On the other hand, OFGs are also potential resources, which can be used as the functional groups and/or are useful in preparing value-added chemicals such as aromatic and phenolic compounds [1], short-chain aliphatic acids [12,13], and benzenepolycarboxylic acids [13–15]. HAs have been found wide applications in various fields, such as agriculture [16,17], adsorption of metal ions [18–20], coal structure analysis via pyrolysis [21], and material sciences [22]. Relatively, the applications of HAs in other fields, such as catalysis, were seldom reported.

In parallel with improving the utilization efficiency of the low rank coal, searching sustainable and renewable resources is the inevitable choice for human beings to meet the energy and material demands in the long run [23–25]. Biomass is believed to be green and renewable carbon resources with the advantages of large reserves, broad distribution, and abundance in varieties [26,27]. Catalytic conversion is an important way for the transformation and utilization of biomass resources [28–31]. Through the rational design of the catalysts and reaction systems, biomass can be transformed into a variety of value-added chemicals, such as various alcohols, short chain hydrocarbons, 5-hydroxymethylfurfural (HMF), levulinic acid and its esters, and gamma-valerolactone (GVL) [26,28,32,33]. Among the chemicals derived from biomass, GVL is an important chemical with unique properties and broad applications [34]. With obvious advantages of high boiling point, good stability at moderate conditions, and low toxicity, GVL can be used in various ways ranging from direct use as a fuel additive or solvent to be upgraded for the production of fuels and chemicals [30,34].

Different approaches and catalysts have been developed to synthesize GVL from biomass or its derivatives. Two routes were commonly reported to produce GVL from biomass, with cellulose-derived levulinic acid or its esters and hemicellulose-derived furfural as the starting materials or key intermediates, respectively [34–36]. Both of the two routes require the step of hydrogenation reaction and the participation of hydrogenation catalysts. Various metal catalysts, including precious metals (Pd, Ru, Rh, Pt, etc.) and transition metals (Ni, Co, Cu, Re, etc.), were reported and proved to be efficient for the conversion of biomass derived platforms into GVL [37]. For these catalysts, H₂ was often used as the

hydrogen source, and mediate to high H₂ pressures and temperatures were often adopted during the hydrogenation reaction, especially for the transition metal catalysts. More mild reaction conditions could be achieved via the Meerwein-Ponndorf-Verley (MPV) reaction under the catalysis of hydrogen transfer catalysts. The MPV reaction, also called catalytic transfer hydrogenation (CTH), was reported to be an efficient approach for the chemoselective reduction of carbonyl compounds using secondary alcohols as the hydrogen source [38,39]. MPV reaction can be catalyzed by various catalysts, including metal alkoxides [40,41], metal oxides or hydroxides [42–45], metal complexes [46,47], and various zeolites [48,49], etc. Among these catalysts, Zr-based catalysts, such as ZrO₂ [43], zirconium alkoxides [41], Zr-containing zeolites [48], and Zr(OH)₄ [44] are commonly used. In the recent work of our group, Song et al. reported a novel hydrogen transfer catalyst prepared by a functional chemical with two acidic groups, 4-hydroxybenzoic acid dipotassium salt, and the prepared catalysts was proved to be highly efficient for the conversion of EL into GVL [50]. Subsequently, a more abundant and cheap chemical, natural phytic acid, was used as building block in our group to prepare catalysts and it was found that the prepared catalysts were highly efficient for MPV reactions of various carbonyl compounds with different structures [51]. Using chemicals from natural sources to construct catalysts or other functional materials is of great importance because the source of the raw materials is abundant and thus make it possible to cut the costs of the materials. Most recently, some Zr-containing MPV catalysts using novel chemicals as the raw materials were reported for the conversion of EL into GVL [52,53], indicating that it is still highly desirable to explore more raw materials, especially the natural, abundant, and low-cost ones, to prepare efficient MPV catalysts. To the best of our knowledge, there are few reports on the application of HAs in the preparation of Zr-containing MPV catalyst.

In this work, we developed a novel strategy to prepare MPV catalysts using the natural HAs and the transition metal Zr salts as the materials. The prepared catalysts were applied into the conversion of EL to GVL, an important reaction synthesizing GVL from biomass (Scheme 1). The experimental factors in both catalyst preparation and reaction process were systematically investigated, and the catalysts were characterized in detail. The results showed that the novel catalyst possessed high activity and excellent stability for the conversion of EL to GVL. The Zr-HA catalyst constructed in this work has several advantages, including using the abundant and low-cost HAs as raw materials, simple preparing procedure, and excellent performances. As far as we know, this is the first report on the synthesis of Zr-containing catalyst using HAs as the raw material and the application of Zr-HA catalyst in the conversion of EL to produce GVL.

2. Experimental

2.1. Materials

Ethyl levulinate (98%), gamma-valerolactone (98%), and ZrOCl₂·8H₂O (AR) were provided by J&K Scientific Ltd. Humic acids (with fulvic acid content of 90%) was purchased from Aladdin Industrial Corporation. Isopropanol (AR), ethanol (AR), KOH (AR), decane (AR) and other chemicals were obtained from Beijing Institute of Chemical Reagent.

2.2. Preparation of catalysts

The catalysts developed in this work were prepared as follows. In a typical procedure, 1 g HAs and 0.17 g KOH were dissolved in 50 mL distilled water, respectively, and then HAs solution was neu-

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