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Ru nanoparticles supported graphene oxide catalyst for hydrogenation of bio-based levulinic acid to cyclic ethers

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ABSTRACT

Ruthenium nanoparticles supported on graphene oxide (GO) catalysts have been evaluated for bio-based levulinic acid (LA) hydrogenation to produce vapor-phase cyclic ethers in a fixed-bed reactor. It was found that using the GO supported Ru nanoparticles (Ru/GO) produced additional hydrogenation products – cyclic ethers (54%) and γ-valerolactone (GVL; 41%), while Ru on carbon (Ru/C) catalysts gave only GVL with 100% LA conversion. To improve the yield of cyclic ethers, an additional two-step hydrogenation of LA via GVL was successfully carried out. This provided GVL as a second feedstock from which the Ru/GO catalyst could produce cyclic ethers such as methyltetrahydrofuran (MTHF) and tetrahydrofuran (THF). Ru on GO catalysts showed a 92% selectivity of predominantly cyclic ethers, including a 77% selectivity of MTHF through two steps process. Such a remarkable enhancement in activity and selectivity of LA hydrogenation over Ru/GO can be attributed to the well-dispersion of Ru nanoparticles, as well as favorable interaction with GO in the presence of oxy-functional groups of GO. In order to evaluate the active sites on the catalyst, they were characterized using different characterization techniques such as Raman, XRD, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), temperature-programmed desorption of NH_3 (TPD), electron microscopy (TEM and SEM) and H_2-chemisorption and N_2 adsorption.

1. Introduction

Current world energy needs strongly depend on non-renewable fossil resources, and these resources are in mature stages [1]. There are some crucial issues related to the use of these fossil resources, including global warming, dramatic increase in oil prices, and their storage and transportation [1]. These issues have stimulated the development of alternative and renewable resources to substitute for fossil resources. Biomass is a promising alternative candidate resource with the potential for long-term availability because it is the only renewable source of platform chemicals such as levulinic acid (LA), formic acid (FA), succinic acid (SA), and lactic acid. These could be used for the production of conventional hydrocarbon fuels [2] as well as for non-fuel petrochemical products [3]. Biomass-derived LA is an attractive and versatile platform chemical for value added products such as methyltetrahydrofuran (MTHF), γ-valerolactone (GVL), 1,4-Pentanediol (1,4-PDO), 1-Pentanol, and esters [3–6]. The flexibility of LA is due to the presence of active functional groups, ketones and carboxylic acids, together [6]. The applications of MTHF and GVL are well known, DOE (US Department of Energy) approved MTHF as a P-series fuel and considered it as an alternative for gasoline. Additionally, MTHF has other applications such as solvent for electrolyte formulation, and as adhesives [7]. Tetrahydrofuran (THF) is also a well-known solvent in used in organic and polymer industries [7]. Due to its pleasant herbal scent, there is a large demand for GVL in the perfume and food/fragrance industries [1,2,8,9].

Very few references are reported for the synthesis of MTHF from LA, mostly in batch type reactors using higher hydrogen pressure (>100 bar) [9,10]. However, some reports also exist for the synthesis of MTHF from GVL in liquid phase [11]. We also

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have reported a direct synthesis of MTHF (89%) from LA at low H_2 pressure (25 bar) in vapor phase by Ni-promoted Cu–SiO_2 nanocomposite catalyst [4]. Likewise MTHF synthesis, liquid phase and higher hydrogen pressure were mostly used for the GVL production from LA [1,12,13]. Upare et al. have recently reported the selective production of GVL from LA at lower H_2 pressure [14,15]. In this work, noble metal catalysts like Ru, Pd and Pt supported on carbon were investigated for the synthesis of GVL from LA [15]. Among the catalysts listed, Ru on carbon catalyst was found to be superior in terms of GVL selectivity. Higher dispersion of Ru nanoparticles was observed to be the main reason for its specific activity in the production of GVL from LA. A higher degree of Ru-nanoparticle dispersion in Ru-supported catalysts has been attributed for the active sites with specific hydrogenation activity [13,15–17]. Different reaction parameters were also investigated to improve the activity of Ru/C and to achieve additional hydrogenation products (e.g., MTHF or 1,4-PDO). However, GVL was the main product obtained (>96%) under all the reaction conditions [15]. This means Ru/C has some limitations for the production of MTHF at lower hydrogen pressure (<25 bar). This could be one reason why higher hydrogen pressures were used in previous investigations [9–11].

In the last decade, chemically derived GO containing sp^2 carbon arrays have received special interest in various fields. This is because of the potential for functionalization and modification of GO as polymer composites, energy materials, sensors, transistors, and biomedical related applications [18], as well as to the presence of reactive oxygen functional groups (e.g., carboxylic, epoxy, and hydroxide) [19]. Some research groups have also used this material as a catalyst for chemical conversion of organic compounds [19,20] exploiting the active oxy-functional groups presented on the surface of GO. Recently, magnetic nanoparticles (M-NPs) supported on carbonaceous material have attracted great interest in catalysis [21]. The high thermal stability, extensive surface area [22], and the presence of oxy-functional groups on GO facilitate easy dispersion of metallic nanoparticles [23]. The use of GO has been reported in the synthesis of noble-metals (e.g., Pt, Ru, and Pd) supported on GO for different purposes [24]. Among these, Bong et al. [25], and Janiak et al. [20], have successfully investigated the use of Ruthenium-nanoparticle supported on graphene as catalyst for hydrogenation reactions. Recently, Du et al. has researched the catalytic activity of mono-dispersed Ru/graphene material for hydrogen generation from hydrogenolysis of ammonia [26]. However, there was no previous report about found in the literature regarding to the utilization of Ru on multilayered GO for hydrogenation reactions. Such active types of material could be promising catalysts for chemical conversion. Herein, we demonstrate the activity of Ru/GO catalysts for vapor-phase production of cyclic ethers from LA via and GVL hydrogenation. This newly developed catalyst can produce additional hydrogenation products continuously at lower moderate hydrogen pressure.

2. Experimental

2.1. Materials

The substance $RuCl_3{\cdot}xH_2O$ was obtained from Sigma–Aldrich and used in the preparation of the catalyst. Levulinic acid (99.0%, Alfa Aesar), GVL (99.9%, Aldrich), other reference compounds like MTHF, Anjelica-lactone (AL), 1,4-PDO (1,4-Pentanediol), and 1-pentanol were purchased from Sigma–Aldrich. The solvent 1, 4-dioxane (HPLC grade, 99.9%, Samchun Chemical) was used as received.

2.2. Preparation of the Ru/GO catalysts

Ru on GO was prepared by the wetness impregnation method. In a typical procedure, the desired amount of GO (BET 248.0 m^2/g) was soaked in an aqueous solution containing an appropriate amount of $RuCl_3{\cdot}xH_2O$ and 100 ml of double-distilled water. In order to get fine dispersion of Ru particles, the resultant mixture was sonicated for 1 h. Sonication could help in the exploitation of GO, and allow space for easy metallic dispersion. After sonication, the mixture was aged for 12 h at room temperature with constant stirring. Water was removed using a rotary evaporator at 70 °C for 2 h under vacuum. The resultant powder was then dried at 120 °C overnight, and reduced in a fixed bed reactor by a flowing hydrogen stream (in 10% N_2) at 5 cc/min and 450 °C for 2 h. The amount of ruthenium loading on the GO was confirmed using ICP analysis and TEM-EDX. A similar procedure was applied for the preparation of 5% Ru/C, using activated carbon (768.0 m^2/g) as support.

2.3. Catalysts testing for LA hydrogenation

Levulinic acid (LA) hydrogenation was carried out in a conventional fixed-bed down-flow reactor (made of stainless steel tubing 30 cm in length and with 1 cm outer diameter) packed with 1.0 g of reduced catalyst in the center of the flow reactor. The hydrogenation of LA was conducted at 265 °C with hydrogen pressure from 10 to 25 bar. 10 wt% of LA in 1, 4-dioxane solvent was introduced into the reactor using a liquid metering pump (Lab Alliance Series 3) with the desired WHSV (weight hourly space velocity). The samples were collected at different intervals from a cold-water-condensation trap equipped with a reactor, and then subjected to analysis using a gas chromatograph (Donam GC, DS 6200) equipped with FID and a capillary column (Cyclosil B-5). From GC-MS analysis, as well as from the retention times of the authentic samples on the gas chromatogram, we confirmed the presence of LA hydrogenation products including GVL, AL, MTHF, THF, PDO, and 5-hydroxy pentanoic acid (γ-hydroxylvaleric acid). The conversion of LA and selectivity for products were calculated using Eqs. (1) and (2), respectively.

$$\text{Conversion of LA(mol \%)} = \frac{\text{Initial mole of LA} - \text{unreacted mole of LA}}{\text{Initial mole of LA feed}} \times 100 \quad (1)$$

$$\text{Product selectivity(mole \%)} = \frac{\text{Mole of desired product}}{\text{Total moles of all products}} \times 100 \quad (2)$$

$$\text{Carbon ballence(\%)} = \frac{(5\times\text{moles of GVL}) + (5\times\text{moles of MTHF}) + (5\times\text{moles of PDO}) + (4\times\text{moles of MTHF}) + (1\times\text{moles of }CH_4)}{5\times\text{moles of LA converted}} \times 100 \quad (3)$$

2.4. Characterization of the catalysts

The amount of Ru loading was measured using inductively coupled plasma analysis (ICP, Jarrell-Ash, USA). The structural variation of the catalysts before (freshly reduced) and after hydrogenation of LA, was determined using X-ray diffractometer (Rigaku, Japan) with Cu K_α radiation. X-ray photoelectron spectroscopy (XPS) data of the catalysts were recorded using a spectrometer (Model: Kratos