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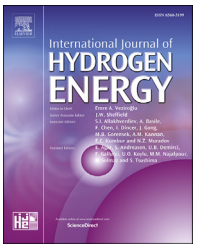

Exploring to direct the reaction pathway for hydrogenation of levulinic acid into γ-valerolactone for future Clean-Energy Vehicles over a magnetic Cu-Ni catalyst

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ABSTRACT

A cheap and magnetic Ni/Cu/Al/Fe catalyst for the selective hydrogenation of LA into GVL catalysts was prepared by sol-gel method. The reaction pathway was systematically studied by examining the reaction conditions, such as reaction pressure, catalyst loadings, water content, and reaction temperature. Higher reaction pressure and catalyst loadings were prior to form HA, then MHV, finally GVL; ML was easily to form with a higher reaction temperature. Water, as a key role, which was in favor to form HA, then MHV, finally GVL; more important, a higher LA conversion could be obtained in methanol as the solvent with some certain content of water. And, it can give a reference for future new clean energy vehicles' application.

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Introduction

With growing concerns about global warming and depletion of fossil-derived carbon resources, the search for sustainable alternative energy sources has increasingly represented a challenge for a sustainable development of the society, for example, Clean-Energy Vehicles. Biomass, one the most abundant renewable carbon resources, is regarded as a promising alternative to non-renewable resources for the production of bio-fuels and platform chemicals [1–7], as shown in Fig. 1. Furthermore, compared with non-renewable

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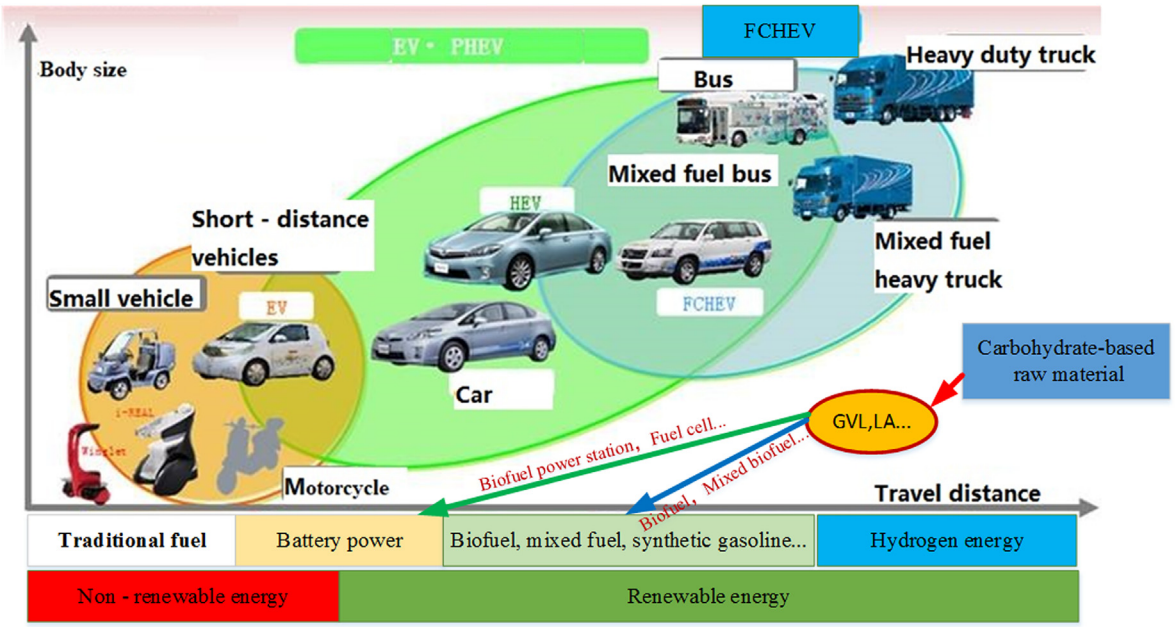

Fig. 1 – Traffic energy structure of post – oil age.

traditional energy such as oil and gas, carbohydrate-based bio-fuels are renewable and stockpile, it is an important raw material for the development of new energy.

One such carbohydrate-based model molecule is γ-valerolactone (GVL), which has been proposed by US Department of Energy to be one of the top 12 platform chemicals [8,9]. When produced economically, GVL can be envisioned to serve as a versatile building block for the production of valuable chemicals and high-grade fuels [10–13]. Typically, GVL production can be achieved through hydrogenation and subsequent cyclization of levulinic acid (LA); the majority of LA hydrogenation processes have used molecular H_2 as a reducing agent [12,14–28]. Over the last several decades, a multitude of catalyst systems have been developed for this reaction, such as homogeneous Ru-based, Pd-based and Ir-based catalysts [29–36], or heterogeneous noble metal catalysts (e.g., Ru, Rh, Pd, Pt and Au) [37–54]and non-noble metal catalysts (e.g., Cu, Ni, Mo) [34,43,55–65]. Water, methanol and ethanol were used as the solvent to carry out this hydrogenation reaction [34,37,38,41–43,55–57,60,63,66–71].

With water as the solvent, the reaction pathway over Ru/C catalyst has been reported by Jesse Q. Bond et al. [37]. The reaction was mainly processed by hydrogenation of LA to HA, and then formed into GVL.

With methanol as the solvent and Ni4.59Cu1Mg1.58Al1.96Fe0.70 as the catalyst, the possible reaction pathways were proposed by Jun Zhang et al. [55] through the products detected during the reaction, shown as Fig. 2.

Chandrashekhar V. Rode et al. [34] also reported a reaction pathway with methanol as the solvent over Cu/ZrO_2 catalyst, the reaction was mainly processed by forming into ML, and then formed into GVL. Although Jun Zhang et al. and Chandrashekhar V. Rode et al. proposed the possible reaction pathway, the evidence for the possible reaction pathway was not clear, more important, whether the reaction pathway could be directed by a certain method or not.

Thus, in this work, a series of experiments were carried out over a broad range of conditions (temperature: 120–200 °C; pressure: 2–5 MPa; catalyst to LA mass ratio: 0.1–0.3; water to LA mass ratio: 0.5–5) for exploring to the possible reaction pathway. The data suggested that the possible reaction pathway were mainly including: a) the hydrogenation of LA into HA followed by esterification with methanol to form MHV, and then further acid-catalyzed into GVL; b) the esterification of LA with methanol into ML followed by hydrogenation into GVL not MHV, which was not in agreement with the previous literatures [55]; the reaction pathway might be different under the various reaction conditions. Higher reaction pressure and catalyst loadings were prior to form HA, then MHV, finally GVL; ML was easily to form with a higher reaction temperature. Water, as a key role, which was in favor to form HA, then MHV, finally GVL; furthermore, a higher LA conversion could be obtained in methanol as the solvent with some certain content of water.

For the Clean-Energy Vehicles, γ-Valerolactone (GVL), produced from biomass-derived carbohydrates, it can be converted to liquid alkenes in the molecular weight range appropriate for transportation bio-fuels. However, GVL suffers from several limitations for widespread use in the bio-fuels, such as high-water solubility, blending limits for use in

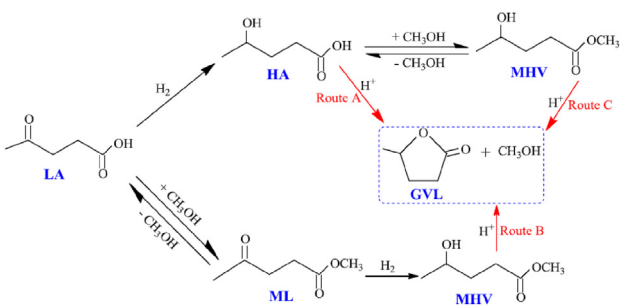

Fig. 2 – The possible reaction pathway.

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