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Editor's choice paper

Cleaner hydrothermal hydrogenolysis of glycerol to 1,2-propanediol over Cu/oxide catalysts without addition of external hydrogen

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ABSTRACT

The hydrogenolysis of glycerol is considered a sustainable process to produce 1,2-propanediol (1,2-PDO). However, the development of a cost-effective solid catalyst and a cleaner process minus the addition of external hydrogen remains a challenge. In the present work, a series of Cu/oxide (SiO_2, MgO, Al_2O_3, and ZnO) catalysts were prepared and evaluated for the hydrothermal hydrogenolysis of glycerol. The relationships of structure-catalytic properties were probed by thermogravimetric analysis (TG), powder X-ray diffraction (XRD), nitrogen adsorption-desorption, temperature-programmed desorption of carbon dioxide (CO_2-TPD), transmission electron microscopy (TEM), and X-ray photoelectron spectra (XPS). The catalytic activity of Cu/oxide catalysts was in the order of $Cu/Al_2O_3 < Cu/SiO_2 \approx Cu/ZnO < Cu/MgO$. The Cu/MgO catalysts were identified as highly active catalysts for the hydrothermal hydrogenolysis of glycerol under autogenic pressure without the addition of external hydrogen. When 1.0 g Cu/MgO (Cu/MgO = 0.5, molar ratio) catalyst and 50 g 20 wt% aqueous glycerol solution as the feedstock was loaded in a batch autoclave reactor, the conversion of glycerol reached 55% with a selectivity of 68% to 1,2-propanediol at 473 K after 6 h. Cu^0 was identified as the active species both for the catalytic *in situ* aqueous-phase reforming of glycerol and for the hydrothermal hydrogenolysis of glycerol. The support basicity played a role in stabilizing the Cu nanoparticles on the support surface. During the catalytic reaction, part of Cu species leached from the MgO support into solvent and meanwhile part of Cu species on the support surface aggregated. The basicity and acidity of the solvent affected the behavior of the Cu/MgO catalysts. This work shows that hydrothermal hydrogenolysis process of glycerol is a facile process and the cost-effective Cu/MgO is worth further development for future industrial practice.

1. Introduction

Glycerol(1,2,3-propanetriol) is produced as an unavoidable by-product in the saponification process in the soap industry [1,2] and in the transesterification process in the biodiesel (fatty acid methyl esters, FAME) industry [3–5]. Both processes are based primarily on bio-based triglycerides as a main feedstock. In addition, it is also possible to produce glycerol from microbial fermentation or the enzyme catalysis of starch, from catalytic hydrogenolysis of sorbitol and from catalytic decomposition of lignocellulose [2]. These bioresources all originate in nature from water and carbon dioxide through photosynthesis. Due to such bioavailability of these feedstocks, glycerol, with non-toxicity, good reactivity and applicability, is now considered as one of renewable platform chemicals and has therefore captured attention from both academia and industry [6,7].

The last decade has witnessed an upsurge in scientific research on the catalytic conversion of glycerol. A broad spectrum of valuable derivatives, such as fuels, fuel additives, fine chemicals, and polymers, can be practically or potentially produced from glycerol through properly-chosen catalytic reactions. The reactions include

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catalytic reforming of glycerol, catalytic hydrogenolysis of glycerol, catalytic oxidation of glycerol, catalytic dehydration of glycerol, catalytic esterification of glycerol, catalytic etherification of glycerol, catalytic acetalization of glycerol, catalytic carboxylation of glycerol, and catalytic chlorination of glycerol [1,2,6,7]. Among them, one of the most attractive processes is the selectively catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) [8,9]. One major reason is that 1,2-PDO can be used as a building block to produce polyesters of high performance. However, the present process to produce 1,2-PDO is still based on multi-step reactions using petroleum-derived propylene as the feedstock. It typically involves the selective oxidation of propylene to propylene oxide and subsequent hydrolysis of propylene oxide to 1,2-PDO [10]. Such a process is time-consuming, energy-intensive and costly. Moreover, in the long term, the petroleum-based process cannot be sustained with the dwindling fossil crude oil resources. In contrast, the catalytic hydrogenolysis of glycerol to 1,2-PDO provides an alternative route to the production of 1,2-PDO in a simpler and more sustainable way [13,25]. Such a new process is expected to become increasingly competitive and lucrative on the condition that an effective heterogeneous catalytic process is developed. In this context, seeking a catalyst of high performance is a major priority.

Currently, catalysts for the hydrogenolysis of glycerol with hydrogen include supported Pt, Ru, Rh or Ir catalysts [11,12] and supported Cu and Ni catalysts [13–17]. The bimetallic catalysts, such as Cu with noble metals, have also been reported [18,19]. Undoubtedly, Cu and Ni-based catalysts are significantly more economical than the noble metal-based catalysts [20–23]. Nevertheless, in most cases, the catalytic hydrogenolysis reactions in the presence of these catalysts are usually carried out at high temperatures with the addition of external hydrogen under high pressure. Many studies suggested that high pressure appeared to be essential for a good conversion and a high selectivity to 1,2-PDO, due primarily to the low solubility of hydrogen in aqueous glycerol solution [2,6]. Initial H_2 pressure of 0.5–10.0 MPa and heating temperatures of 393–513 K are usually employed [2,24,25]. To ensure operational safety and reduce energy consumption, the use of low pressure for the hydrogenolysis of glycerol is desired [26]. Likewise, to facilitate an environmental-friendly and sustainable process, the use of external hydrogen is not recommended as industrial hydrogen is currently derived from non-renewable natural gas, coal or petroleum [27].

Recently, several studies [28–32] proved that in the hydrogenolysis of glycerol the hydrogen could be formed and used *in situ* for when a multifunctional catalyst was judiciously designed and employed. Such a creative methodology opens a cost-effective, energy-saving, and simpler route to produce 1,2-PDO from the hydrogenolysis of glycerol. In a pioneering work, D' Hondt et al. reported that a bifunctional Pt /NaY zeolite catalyst was able to catalyze the hydrogenolysis of glycerol without any addition of external hydrogen and convincingly proposed that the hydrogen was generated *in situ* by aqueous phase reforming (APR) of glycerol [30]. Following this work, several other bimetallic catalysts including Pd/Fe_2O_3 [28,31,32], Raney® Ni [32], Pt/Al_2O_3 [29] and Pt-Sn [33] have also been reported to catalyze the hydrogenolysis of glycerol without any use of external hydrogen. Others have reported that without the external addition of hydrogen, the use of a mixed catalyst consisting of 5 wt% Ru /Al_2O_3 and 5 wt% Pt /Al_2O_3 for the hydrogenolysis of glycerol at 493 K resulted in a 50% conversion of glycerol with a 47% selectivity to 1,2-PDO [29]. More recently, Soares et al. [34] revealed that PtFe/Al_2O_3 catalyzed both the APR of glycerol and the hydrogenolysis of glycerol. The hydrogen for the glycerol hydrogenolysis came from *in situ* glycerol reforming and thus the catalysts resulted in better selectivity towards 1,2-PDO than Pt/Al_2O_3. Because hydrogen is inherently generated from the *in situ* catalytic APR of glycerol, it is also possible to add methanol [35], ethanol [28], and formic acid [36] into the reactor for the APR to yield hydrogen.

However, in the hydrogenolysis of glycerol minus the addition of external hydrogen one issue remains: namely thus far catalysts have been mostly based on a noble metal as the active component and acidic oxides as the support [37,38]. In this context, it is worth noting that cheaper Cu-based catalysts are also active in APR and it is therefore possible to use it for the hydrogenolysis of glycerol without external hydrogen [39]. However, the effects of the acidic and alkaline supports, reaction conditions, the deactivation, and the solvent on the *in situ* hydrogenolysis of glycerol remain elusive [40,41]. Here we explored a simple hydrothermal catalytic hydrogenolysis of glycerol without the addition of external hydrogen into the reactor. By comparing Cu/SiO_2, Cu/Al_2O_3, Cu/ZnO, and Cu/MgO catalysts, the effects of the acidity and basicity of the supports on the catalytic performance and the interactions therein were investigated. Meanwhile, the active species on the Cu/MgO, the effects of reaction conditions, the deactivation, and the choice of solvent were explored.

2. Experimental

2.1. Preparation of Catalysts

The typical procedures for the preparation of Cu/Al_2O_3, Cu/ZnO, and Cu/MgO catalysts primarily by coprecipitation and reduction reactions are described as follows:

Cu/Al_2O_3 catalyst – 6.07 g of $Cu(NO_3)_2{\cdot}3H_2O$ (99.5%) and 9.47 g of $Al(NO_3)_3{\cdot}9H_2O$ (99.0%) at a molar ratio of Cu/Al = 1.0 were dissolved in 500 mL of distilled water. Next, 500 mL of an aqueous K_2CO_3 solution (0.2 M) was dripped at a constant rate into the $Cu(NO_3)_2/Al(NO_3)_3$ solution under magnetic stirring at room temperature. This led to a slurry of co-precipitated Cu/Al hydroxide. The slurry was kept stirring for 30 min and then aged for 4 h. Subsequently, the solid was separated by centrifugation and washed three times using 250 mL distilled water each time. After being dried overnight at 383 K, the solid was crushed and ground into powder. The powder was then calcined at 673 K for 3 h. Prior to the use as catalyst, the powder was reduced under a H_2 flow in a tubular oven at 573 K for 3 h.

Following the similar procedure, Cu/MgO, Cu/ZnO catalysts were prepared using $Mg(NO_3)_2{\cdot}6H_2O$ (99%) and $Zn(NO_3)_2{\cdot}6H_2O$ (99%) as the staring materials for MgO and ZnO, respectively.

The Cu/SiO_2 catalyst was prepared by a precipitation-gel method following a process reported in the literature [42]. First, at room temperature, 500 mL of aqueous K_2CO_3 (0.2 M) solution was dripped into aqueous $Cu(NO_3)_2{\cdot}3H_2O$ (0.05 M) solution under magnetic stirring. Then, 1.50 g fumed nano-silica (99.8%, 380m^2/g) was added, forming a mixed gel. The gel was stirred continuously for 30 min and aged for 4 h. Thereafter, the gel slurry was centrifuged, washed, dried, calcined in air and reduced in a hydrogen flow under the same conditions as described above.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a PANalytical X'Pert PRO powder diffractometer in the 2θ range of 5–80° using Cu Kα1 radiation (λ = 1.54056 Å) operated at 40 kV 30 mA. The crystallite size D of each catalyst was estimated according to the Scherrer equation [43] as follows

$$D = \frac{K\lambda}{\beta cos\theta}$$