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Catalytic conversion of glycerol to lactic acid over graphite-supported nickel nanoparticles and reaction kinetics

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ABSTRACT

Catalytic conversion of biomass glycerol to lactic acid is an alternative to the conventional fermentation process starting from carbohydrate. Graphite-supported metallic Ni^0 nanoparticles effectively catalyzed the hydrothermal conversion of glycerol to lactic acid in NaOH aqueous solution. Ni^0 nanoparticle and NaOH synergistically catalyzed the glycerol conversion to lactic acid. When the reaction was carried out with the initial glycerol and NaOH concentrations of 1.0 and 1.1 mol L^{-1} at 230 °C for 3 h over $Ni_{0.3}$/graphite catalyst, the selectivity of lactic acid was 92.2% at the glycerol conversion of 97.6%. The reaction activation energy, *Ea*, was 69.2 kJ mol L^{-1}.

Introduction

Biodiesel produced from biomass has been used as a sustainable energy source to replace fossil fuel because the utility of biodiesel can avoid natural resource depletion and solve greenhouse gas problem [1–8]. Nowadays, to satisfy the increasing energy demand, the biodiesel production is on a large scale worldwide. Meanwhile, glycerol as a by-product, is largely produced in the biodiesel production *via* the transesterification of vegetable oil or animal fat. In the transesterification process, the production capacity of glycerol is *ca.* 10–20% of raw material in weight [9,10]. In 2016, according to the international market, the production capacity of biodiesel is estimated to be 37 billion liters, 4 billion liters of crude glycerol will be produced [11,12]. However, glycerol is oversupplied in market and unavoidably affects biodiesel market [13]. Recently, catalytic conversion of biomass glycerol into high valued chemicals has attracted researcher's great attention [13,14].

The glycerol derivatives, such as lactic acid, 1,3-propanediol, 1,2-propanediol, and succinic acid, are useful chemicals, which can be synthesized by various catalytic processes [9]. Notably, lactic acid, as an important building block chemical in the chemical platform, has been widely used in food, pharmaceutical, leather, cosmetic, textile, and biodegradable polymer (polylactic acid) fields [9,15]. Moreover, polylactic acid has the potential to replace conventional petroleum-based poly-ethylene terephthalate plastics due to its biocompatibility and biodegradability [14]. The production capacity of polylactic acid is estimated to be 830 kt in 2020 [16].

Commercial lactic acid is mainly produced by the anaerobic fermentation using starch-derived glucose as the raw material [17]. Although the fermentation process gives a high lactic acid yield of 90%, the production cost is at relatively high level due to the specific requirement of bacteria [18] and complex separation steps in downstream [19]. As an alternative to the conventional fermentation process, catalytic conversion of glycerol to lactic acid becomes a hot research topic because biomass glycerol is supplied with a lower price of 0.04–0.11$/kg (crude glycerol) in the United States [1].

Kishida et al. firstly reported that the lactic acid yield of 90% was obtained when the hydrothermal conversion of glycerol (0.33 mol L^{-1}) was carried out at 300 °C using NaOH as the homogeneous catalyst in an aqueous solution [20,21]. Ramírez-López et al. reported that the lactic acid yield of 84.5% was obtained when the hydrothermal conversion of glycerol (2.5 mol L^{-1}) was carried at 280 °C for 2.5 h with a NaOH/glycerol mole ratio of 1.1:1 [22]. Hydrothermal conversion of glycerol using NaOH as the homogeneous catalyst gave high lactic acid yield. However, relatively high reaction temperature probably is the drawback for the homogeneous catalysis method.

When Au-Pt/TiO_2, Au/CeO_2, and Pt-Au/CeO_2 were used as the heterogeneous catalysts to catalyze aerobic oxidation of glycerol (0.17–0.22 mol L^{-1}) at 90–100 °C in a NaOH aqueous solution, the maximum yields of lactic acid were 26%, 81%, and 79%, respectively

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[23–25]. When Pt/ZrO_2 was used as the catalyst for the conversion of glycerol (5%) to lactic acid at 180 °C under anaerobic condition in a NaOH aqueous solution, the highest yield of lactic acid was 84% [26]. The noble metals exhibited high catalytic activities for the conversion of glycerol to lactic acid at a lower reaction temperature under aerobic or anaerobic condition. However, the high cost of noble metal catalyst and low glycerol concentration will cause a high production cost in industrial scale.

Instead of noble metals, copper oxide and metallic copper have been investigated for the catalytically hydrothermal conversion of glycerol to lactic acid. When Cu/SiO_2, CuO/Al_2O_3, and Cu_2O were used as the catalysts for the hydrothermal conversion of glycerol (1 mol L^{-1}) in a NaOH aqueous solution at 240 °C for 6 h, the lactic acid selectivities were 79.7%, 78.6%, and 78.1% at the glycerol conversions of 75.2%, 97.8%, and 93.6%, respectively [27]. The lactic acid selectivity of 90% was obtained at the glycerol conversion of 91% in the hydrothermal conversion of glycerol over Cu(16)/HAP catalyst at 230 °C for 2 h with the initial glycerol and NaOH concentrations of 1.0 and 1.1 mol L^{-1}, respectively [13]. The heterogeneous transition metal catalysts exhibited good catalytic activities for the catalytically hydrothermal conversion of glycerol to lactic acid at a lower reaction temperature than the homogeneous alkaline catalysts.

Metallic and oxide nanomaterials have attracted a great attention of researchers because of their excellent performances in catalysis and environmental protection fields [28–36]. Supported metallic Ni^0 and Ni^0 nanoparticles exhibited high catalytic activities for hydrogenation reactions [37–42]. They should also have good catalytic activity for dehydrogenation reaction according to the catalysis principle. As a transition metal catalyst, metallic nickel should have catalytic activity in the hydrothermal conversion of glycerol to lactic acid, in which dehydrogenation reaction is included. To the best of our knowledge, metallic Ni^0 catalyst has not been used for the hydrothermal conversion of glycerol to lactic acid.

Carbon materials have been widely used in catalysis, electrochemistry, heavy metallic ion adsorption, and chemical purification fields. It was reported that activated carbon black-supported Ni/NiO exhibited high capacitance and energy density [43]. Polyacrylonitrile fiber-supported $BiOCl_x/BiOBr_y/BiOI_z$ composites, graphene oxide/BiOCl/PAN nanofibers, and nitrogen-carbon dots/(3D)BiOBr composites exhibited high catalytic activities for the photocatalytic degradation of trichloroethylene and Rhodamine B, respectively [44–46]. The addition of activated carbon in metallic aluminum significantly enhanced the methylation of methyltrichlorosilane [47]. The use of carbon materials as catalyst supports or active components is worth of investigation.

In our present work, catalytically hydrothermal conversion of glycerol to lactic acid over fine graphite-supported nickel nanoparticles was investigated in a batch reactor. The graphite-supported nickel nanoparticle catalysts were prepared by the wet chemical reduction method in an ethanol solution. The effect of reaction parameters, such as reaction time, reaction temperature, glycerol concentration, NaOH/glycerol mole ratio, and catalyst loading, on the catalytic conversion of glycerol to lactic acid was investigated in detail. The roles of metallic Ni^0 nanoparticles and NaOH in the catalytic reaction were discussed. A power-function type reaction kinetic model was used to evaluate the effect of reaction parameters, glycerol and NaOH concentrations and reaction temperature, over the supported nickel nanoparticle catalysts.

Experimental

Materials

Fine graphite slices with the sizes of 1–2.5 μm were supplied by Celtig Co. Ltd. USA. Glycerol, lactic acid, 1,2-propanediol, oxalic acid, formic acid, acetic acid, anhydrous ethanol, isopropyl alcohol, sodium hydroxide (NaOH), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 85%), and nickel acetate ($C_4H_6O_4Ni{\cdot}4H_2O$), were purchased from Sinopharm chemical reagent Co., Ltd. All the chemicals were of reagent grade and were used as received without further purification. Deionized water was used throughout all the experiments.

Preparation of catalysts

The fine graphite-supported nickel nanoparticle catalysts were prepared by the wet chemical reduction method. The metallic Ni^0 nanoparticles were prepared by reducing nickel acetate with hydrazine hydrate in anhydrous ethanol in the presence of fine graphite powder. Firstly, 1.0 g of fine graphite powder was dispersed in 60 mL of anhydrous ethanol by ultrasonic treatment

Table 1
The properties and catalytic activities of Ni/graphite catalysts.[a] Q4

Catalysts	Amount of Ni[b] (mmol g^{-1})	Crystallite sizes of Ni^0 (111)[c] (nm)	Average particle sizes and size distributions[d] (nm)	Specific surface areas (m^2/g)	Glycerol conversions (%)	Selectivities					Carbon balances[e] (%)	TOFs[f] (h^{-1})
						Lactic acid (%)	Oxalic acid (%)	Formic acid (%)	Acetic acid (%)	1,2-propanediol (%)		
$Ni_{0.1}$/graphite	0.97	11.3	22.4, 9.3–45.7	7.7	62.2	83.2	0.3	0.5	0.6	3.1	87.7	59.6
$Ni_{0.2}$/graphite	1.95	12.2	29.5, 12.9–44.6	11.7	77.4	88.9	0.4	1.0	0.9	2.3	93.5	39.2
$Ni_{0.3}$/graphite	2.95	12.7	32.9, 21.3–67.4	13.0	95.1	92.1	0.7	2.0	1.3	1.0	97.1	33.8
(Spent)	2.70											
$Ni_{0.4}$/graphite	3.91	13.2	35.1, 18.9–61.5	13.5	99.3	76.8	1.2	2.8	2.0	0.4	83.2	26.5
graphite	\	\	\	5.9	trace	100	0	0	0	0	100	\

[a] Reaction conditions: glycerol aqueous solution, 100 mL; glycerol concentration, 1.0 mol L^{-1}; NaOH/glycerol mole ratio,1.1:1; catalyst, 0.552 g; reaction temperature 230 °C; reaction time, 2.0 h.
[b] The amount of Ni (mmol) was analyzed by atomic absorption spectrophotometer.
[c] The crystallite sizes of Ni^0 (111) were calculated by XRD.
[d] The particle sizes of Ni^0 nanoparticles were determined by TEM.
[e] Carbon balances were calculated according to both detected products and reacted glycerol.
[f] TOF (h^{-1}) = Converted glycerol (mol) divided by the mole of Ni supported on graphite after reacting for 2.0 h.

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