



A comparative study on catalytic properties of solid acid catalysts for glycerol acetylation at low temperatures



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ABSTRACT

The catalytic properties of various types of solid acids, including silica–alumina, HUSY, dodecamolybdophosphoric acids supported on Nb₂O₅ (HPMo/Nb₂O₅) and mesoporous SBA-15 (HPMo/SBA-15), Amberlyst-15, sulfated ceria–zirconia (SCZ), propylsulfonic acid functionalized SBA-15 (PrSO₃H-SBA-15), and sulfonic acid functionalized SBA-15 (SO₃H-SBA-15) and microcrystalline cellulose (SO₃H-Cell) catalysts, are studied for glycerol acetylation with acetic acid at low temperatures. Compared at the same acidity loading and similar glycerol conversion level (~30%) below the equilibrium, the glycerol conversion turnover rate toward di- and triacetin is considerably higher on PrSO₃H-SBA-15 and Amberlyst-15, with the rates shown in order as follows: PrSO₃H-SBA-15 > Amberlyst-15 > HPMo/Nb₂O₅ ≥ HPMo/SBA-15 > HUSY > SCZ > SiO₂–Al₂O₃. The catalytic properties of these solid acids are relatively stable under consecutive batch runs at 353 K, whereas SO₃H-SBA-15 and SO₃H-Cell deactivate with a significant acidity loss due to hydrolysis of the grafted sulfonic acid groups. When similar type of the solid acids is compared, the acid strength affect the rate and selectivity, favoring a higher acid strength for the facilitation of the reactions (PrSO₃H-SBA-15 > Amberlyst-15; HUSY > SiO₂–Al₂O₃; HPMo/Nb₂O₅ ≥ HPMo/SBA-15). However, the proportional correlation between the acid strength and the glycerol conversion turnover rate does not hold when different types of solid acids are compared. The orders of magnitude higher glycerol conversion turnover rates with moderate Brønsted acid strength on the sulfonic acid functionalized catalysts suggest that the configuration of surface acid moieties attribute substantially to their catalytic activity for the reactions. The acid strength on SCZ is the highest, reflecting the super acidic nature of the sites formed on the sulfated metal oxide surface, but its catalytic activity for the reactions is inferior. The glycerol conversion turnover rates on the catalysts follow the Arrhenius type temperature dependence, and the characterization results indicate that the internal mass transfer resistance does not limit the reactions.

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1. Introduction

Glycerol is a byproduct of biodiesel synthesis that forms via the transesterification of natural oils, usually with C₁–C₄ alcohols [1]. The increasing biodiesel production in recent years has resulted in excess production of the glycerol byproduct (stoichiometrically 10 wt% in a biodiesel production basis), but the current market does not cope with the purification cost of crude glycerol for conventional utilizations such as in food additives, cosmetics, and surfactants [2]. The transformation of bio-glycerol into glycerol-ethers and glycerol-esters via etherification and esterification reactions is considered to be a beneficial alternative for

glycerol utilization, because these value-added chemicals have potential uses in versatile industrial applications [3,4]. In particular, acetylation of bio-glycerol with acetic acid into glycerol-esters is of interest, because the mono-, di-, and triacetylated glycerol products, namely mono-, di-, and triacetin, have various uses in cryogenics, and as raw materials for biodegradable polyesters, cosmetics, and fuel additives [3,5]. Special interest has been focused on di- and triacetin because of their potential for vast quantity utilization as valuable biodiesel and petro fuel additives [6–8].

Glycerol acetylation with acetic acid can be conducted at relatively mild temperatures conventionally by using mineral acids [9]; however, the homogeneous acid catalysts are toxic, corrosive, and difficult to remove, so they impose significant drawbacks on the process and environmental aspects. Heterogeneous acid catalysts can be advantageous alternatives for surpassing such critical limitations, and have been investigated extensively in recent studies. Melero et al. studied the catalytic properties of the alkylated

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sulfonic acids (propyl-, arene-, and perfluoro-sulfonic acid) functionalized siliceous mesoporous SBA-15, and reported that the formation rates of di- and triacetin increased as the acid strength of the sulfonic acid groups increased, while an enhanced mass transport property was concomitantly offered by mesoporous SBA-15 support [10]. The resin type solid acids, such as commercial Amberlyst and Dowex catalysts consisting of ion-exchanged sulfonic acid groups in the structures, are also extensively applied for the reactions [11–13]. The Keggin type heteropolyacids (HPAs) of molybdo- and tungstophosphoric acids have been investigated as immobilized forms onto high surface area silica [14], zeolites [15], SBA-15 [16], activated carbon [17], niobia [18], and Cs-containing zirconia [19] to provide enhancements in the active surface area and stability of the HPA moieties. Several protonic form zeolites such as HZSM-5 and HUSY [20,21], as well as acidic metal oxides such as niobia [20] and zirconia based multi-metal oxides [22], have also been of interest for the reactions. Various sulfated solid acids that are obtained by impregnation of sulfuric acid on activated carbon [23,24], ZrO_2 [25], and CeO_2 – ZrO_2 and CeO_2 – Al_2O_3 [26] followed by oxidative heat treatments, have been investigated for glycerol acetylation.

Although there have been many studies on various solid acid catalysts for glycerol acetylation, comparative studies that comprehensively assess the catalytic properties of different types of solid acids at similar and controlled reaction conditions based firmly on the types of acid sites, surface acidity, and acid strength of the catalysts has been limited. Herein, we have investigated glycerol acetylation with acetic acid on various solid acids: silica–alumina, HUSY, dodecamolybdophosphoric acids supported on Nb_2O_5 (HPMo/ Nb_2O_5) and mesoporous SBA-15 (HPMo/SBA-15), Amberlyst-15, sulfated ceria–zirconia (SCZ), propylsulfonic acid functionalized SBA-15 (PrSO₃H-SBA-15), and sulfonic acid functionalized SBA-15 (SO₃H-SBA-15) and microcrystalline cellulose (SO₃H-Cell) catalysts. The intrinsic catalytic properties based on glycerol conversion turnover rate and selectivity toward mono-, di-, and triacetin products on these catalysts were extensively compared and characterized under the same reaction condition, and the results were correlated with the physicochemical properties of the catalysts in details.

2. Experimental

2.1. Catalysts synthesis

Silica–alumina (Aldrich, Si/Al atomic ratio=6.2) and HUSY (Alfa, Si/Al=160) were purchased as fine powders and used without further modifications. Amberlyst-15 (Rohm & Haas), which was supplied as beads (surface area=53 m² g⁻¹, average diameter=0.74 mm), was crushed and sieved into fine powders (125–180 μm) to eliminate the effects of internal mass transfer hindrance in the reaction rate assessment. Mesoporous SBA-15 was prepared according to the procedure reported by Zhao et al. [27]. Dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$, referred to as HPMo) immobilized onto SBA-15 (HPMo/SBA-15) was prepared by impregnation with a loading amount of HPMo at 25 wt%. Briefly, 1 g of $H_3PMo_{12}O_{40} \cdot xH_2O$ (Alfa) was dissolved in 30 ml of methanol (Samchun, HPLC grade), and 3 g of SBA-15 was added at room temperature. The mixture was stirred for 7 h, dried at 343 K to evaporate the solvent, and finally calcined at 623 K for 2 h (ramp = 1 K min⁻¹) [28]. The HPMo impregnated Nb_2O_5 (HPMo/ Nb_2O_5) was prepared using a similar procedure with the loading amount of HPMo on the Nb_2O_5 (Junsei Chemical) also at 25 wt%. The resultant was dried at 393 K for 12 h and calcined at 573 K for 2 h [18].

Sulfonic acid functionalized SBA-15 (SO₃H-SBA-15) was prepared by immobilization of sulfonic acid groups on SBA-15 by

using chlorosulfonic acid (ClSO₃H, Aldrich, 99%) as a precursor. 5.0 g of SBA-15 was dispersed in 40 ml of n-hexane (Aldrich, HPLC grade) with vigorous stirring in a beaker placed in an ice bath, and 9.0 mmol of chlorosulfonic acid was slowly added in a dropwise manner for 2 h. The resultant was filtered, washed with acetonitrile (Aldrich, 99.9%), and dried in air at room temperature for 12 h. Sulfonic acid grafted cellulose catalyst (SO₃H-Cell) was prepared using the same procedure that was used for the SO₃H-SBA-15. The cellulose used for the support was microcrystalline powders (Alfa, particle size < 220 μm), and the final form of SO₃H-Cell was obtained after drying the sample at room temperature for 12 h [29]. Propylsulfonic acid functionalized SBA-15 (PrSO₃H-SBA-15) was prepared according to the method reported by Melero et al. [30]. An aqueous solution containing 4 g of Pluronic P123, 125 g of 1.9 M HCl, and 7.7 g of TEOS was prepared at 313 K, and 0.8 g of 3-mercaptopropyltrimethoxysilane (MPTMS, Alfa, 95%) and 1.3 g of hydrogen peroxide (Alfa, 29–32%) were added subsequently. The resultant was stirred for an additional 20 h, and the hydrothermal synthesis was conducted in a static condition at 373 K for 24 h. The resultant was centrifuged, washed with a copious amount of ethanol under reflux for 24 h, and dried at 373 K for 12 h.

Sulfated CeO_2 – ZrO_2 catalyst (SCZ) was prepared using the procedure reported by Reddy et al. [26]. The CeO_2 – ZrO_2 support was obtained via co-precipitation of the mixed metal hydroxide from an aqueous mixture solution of zirconium nitrate hydrate ($ZrO(NO_3)_2 \cdot xH_2O$, Alfa) and ammonium cerium nitrate ($(NH_4)_2Ce(NO_3)_6$, Deajung) at a Ce/Zr atomic ratio of 1.0 by adjusting the pH of the solution at 9.0 with an ammonium hydroxide titration solution (Alfa, 28 wt%) [31]. The precipitates were centrifuged, washed with distilled water, and dried in a convection oven at 383 K for 12 h. The resultant was impregnated with a 0.5 M H₂SO₄ aqueous solution (H₂SO₄/CeO₂–ZrO₂ hydroxide ratio = 5 ml g⁻¹) with stirring for 1 h at room temperature. The excess water was evaporated, and the resultant was dried at 393 K for 3 h and calcined at 873 K for 5 h (ramp = 10 K min⁻¹).

2.2. Catalyst characterization

Surface area and pore size distribution of the catalysts were characterized using N₂ adsorption–desorption isotherms obtained in a volumetric unit (Autosorb iQ, Quantachrome). The surface area was estimated applying Brunauer–Emmett–Teller (BET) theory. The micropore and mesopore size distributions were obtained with density functional theory (DFT) and Barrett–Joyner–Halenda (BJH) theory, respectively. Powder X-ray diffraction (XRD) patterns of the samples were obtained using monochromic Cu-K_α radiation operating at 40 kV and 40 mA with a step size of 0.05° and a scan rate of 1 step s⁻¹ (AXS diffractometer D8, Bruker). The acidity on the catalysts was characterized by three different methods: neutralization titration [32] for Brønsted acidity, temperature programmed desorption (TPD) of ammonia (NH₃-TPD) for total acidity, and TPD of acetonitrile (CH₃CN-TPD) for Lewis acidity [33,34]. In the neutralization titration method, 0.05 g of catalyst powder was treated with 20 ml of a 1.0 M aqueous NaCl solution for 1 h at room temperature under sonication. After the centrifugal separation, the supernatant solution was titrated with a 0.01 M aqueous NaOH solution using phenolphthalein as the neutralization indicator. The TPD of NH₃ and CH₃CN was carried out in an automatic chemisorption unit (AutoChem 2910, Micromeritics). In the NH₃-TPD, the samples were pre-treated under a He flow (50 ml min⁻¹) at 423 K for 2 h followed by a diluted NH₃ flow (10 mol% NH₃/He-balance, 50 ml min⁻¹) at room temperature for 0.5 h, and finally held at 373 K under a He flow (50 ml min⁻¹) for 1 h to purge the weakly adsorbed NH₃ species. In the CH₃CN-TPD, the samples were pretreated at the same condition except that acetonitrile was introduced onto the sample by pulse injections using a micro-syringe under a He

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