



Understanding the role of Keggin type heteropolyacid catalysts for glycerol acetylation using toluene as an entrainer

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ABSTRACT

The heterogeneously catalyzed esterification (acetylation) of glycerol toward triacetin in batch mode in presence of toluene as entrainer was studied. Silicotungstic acid, tungstophosphoric acid and phosphomolybdic acid as heteropolyacids (HPAs) supported on silica, alumina or silica-alumina were used as catalysts. The course of the reaction was found to be very sensitive to the nature of the HPA as well as the support. Solid characterization by Raman spectroscopy, XRD, and pyridine-FTIR revealed that only combinations of tungsten-based HPAs and silica support were able to preserve the structure of active component throughout the preparation process, which was essential to obtain active and selective catalysts. The interaction between HPA and support was decisive for stability and dispersion of the catalytically active species. With the best performing catalyst $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{SiO}_2$, selectivity to triacetin reached 71% at complete conversion within 24 h. The high selectivity to triacetin is attributed the Brønsted acidic sites originated from stabilized Keggin structure and continuous removal of water during course of reaction. Toluene is able to form azeotropic mixtures with water and acetic acid and keeps the reaction temperature below the boiling point of acetic acid. Thus, water-free reaction conditions can be established. The catalyst was reusable; however, the activity and selectivity towards triacetin slightly decreased in a repetition run due to loss of active sites.

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1. Introduction

Glycerol is inevitably produced in the biodiesel production from transesterification of vegetable oil or animal fats and has led to a drastic surplus in chemical market. Global production of biodiesel market is estimated to reach 36.9 million metric tons in 2020, which will give approximately 3.7 million metric tons of crude glycerol [1–3]. The current use of glycerol in pharmaceuticals, food and cosmetics consumes only a small part and hence, demand is somehow limited. To sustain chemical market and industry, it is important to convert glycerol into value added chemicals by several catalytic processes, such as selective oxidation to glyceric acid or hydroxyacetone [4], dehydration to acrolein [5–7], hydrogenolysis to 1,2- or 1,3-propanediol [8], etherification to alkyl ether [9,10], condensation to dimers or higher oligomers [11] and many others [3,12]. Another interesting approach to convert glycerol into monoacetyl glycerol (MAG, monoacetin), diacetyl glycerol (DAG, diacetin) and

triacyl glycerol (TAG, triacetin) by means of esterification with acetic acid (acetylation) as shown in Fig. 1. These products have application in food and leather industry, as plasticizers and also they may serve as solvent and fuel additive [13–15].

Glycerol acetylation is an acid catalyzed reaction with equimolar formation of water as by-product at every consecutive step and the chemical equilibrium limits the extent of the esterification. In addition, Gibbs free energies of the first two acetylation steps (MAG and DAG) are 19.15 and 17.80 kJ/mol, respectively, whereas this value for the third step (TAG) is relatively high (55.58 kJ/mol) and thus, the third step should be the most difficult one [16]. Beyond that, elevated temperatures are necessary to obtain high reaction rates. Generally the reaction is performed using homogeneous catalysts like sulfuric acid and paratoluene sulfonic acid [17] or heterogeneous catalysts such as sulphated mesoporous silica [18], sulphated zirconia [19,20], sulphated activated carbon [21,22], double SO_3H -functionalized ionic liquids [23] and acid ion exchange resins like Amberlyst-15 or Amberlyst-36 [24–26]. On the other side, use of acetic anhydride as acetylation agent instead of acetic acid boosts the selectivity to TAG close to 100% as no water is formed, and the reaction rates are high even in the absence of catalysts. However,

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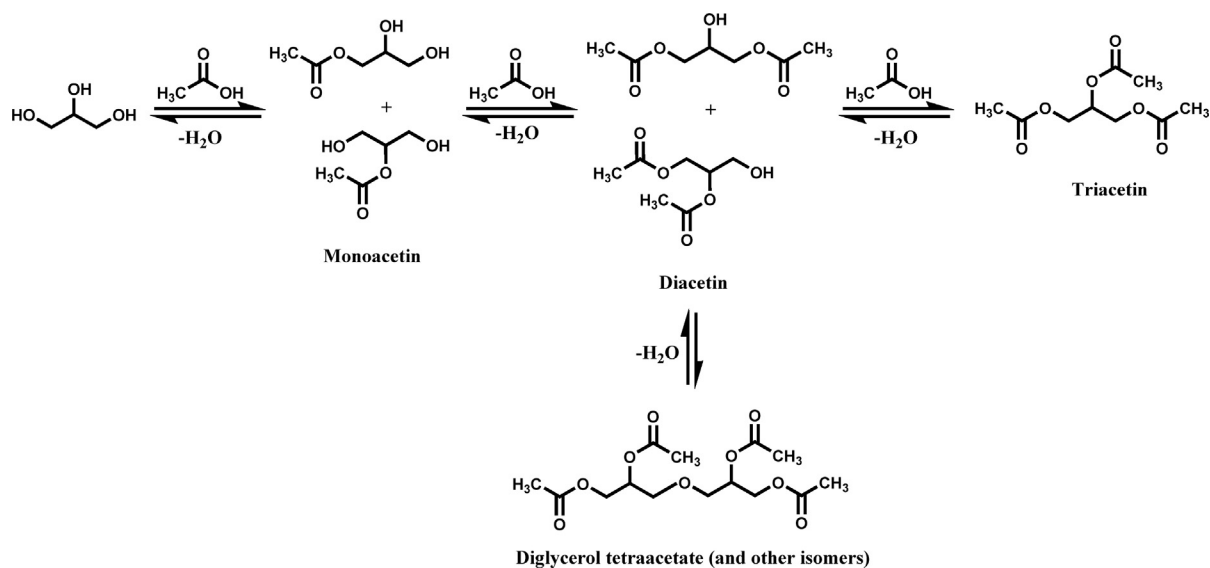


Fig. 1. Reaction scheme for consecutive glycerol acetylation.

acetic anhydride is more expensive and hazardous than acetic acid, and it is not environmentally friendly [27,28].

Furthermore, supported heteropolyacids have been employed for glycerol acetylation reaction. Phosphomolybdic acid encaged in a zeolite catalyst showed 68% glycerol conversion with only 2% selectivity to TAG [29]. Very recently, Patel et al. used MCM-41 and ZrO_2 supported tungstophosphoric acid catalysts but the selectivity to TAG was found to be rather low with 15% and 4%, respectively [30]. The same group also used 30 wt% tungstophosphoric acid impregnated on MCM-48 as catalyst with 30% selectivity to TAG using an acetic acid/glycerol molar ratio of 6 [31]. Silicotungstic acid supported on zirconia showed 32.3% selectivity to TAG with complete conversion of glycerol using acetic acid/glycerol molar ratio of 10 [32]. Huang et al. used tungstophosphoric acid immobilized on ionic liquid as a homogeneous catalyst which showed 98% selectivity to TAG using a high acetic acid/glycerol molar ratio of 10 and toluene as an entrainer under nitrogen flow of 150 ml/h [33].

In general, glycerol acetylation with acetic acid strongly depends on the acidic properties of the catalysts, but it is equilibrium controlled due to formation of water. A recent study from our group has shown that the use of toluene as an entrainer allows to remove formed water immediately by azeotropic distillation and to shift the equilibrium almost completely towards TAG using ion exchange resins Amberlyst-15 or Amberlyst-70 as catalysts [34].

The aim of this present work is to evaluate the catalytic activity of different HPA supported on oxides with large surface area under such water-free conditions with respect to catalyst structure and amount of acid sites. Silica, alumina and silica-alumina supported HPA (STA, TPA and PMA) catalysts were synthesized, characterized in fresh and spent state and evaluated in glycerol acetylation reaction. The results were compared with reference experiments either without catalyst (blank tests) or homogeneously catalyzed (pure HPAs are dissolved in acetic acid) under same reaction conditions and correlated with physicochemical properties of the catalysts.

2. Experimental

2.1. Materials

The organic compounds glycerol (Alfa Aesar, Germany, >99%), acetic acid (Fisher chemicals, Analytical reagent grade), toluene (Acros Organics, analytical reagent grade) and the silico-

tungstic acid (STA, Fluka), tungstophosphoric acid (TPA, Fluka), phosphomolybdic acid (PMA, Merck) and the supports silica-alumina (SIRAL[®] 40; $\text{SiO}_2/\text{Al}_2\text{O}_3 = 40: 60$), dispersible alumina (Disperal[®]/SASOL) as precursor for γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) and silica (SS61138 Chempur/ SiO_2) were used as received. Furthermore, trimethylchlorosilane and hexamethyl disilazane (Aldrich), dodecane (TCI Europe), hexadecane (Aldrich) and pyridine (ACROS) were used for analytical purposes.

2.2. Catalyst preparation

While the silica and silica-alumina supports were not treated before use, dispersible alumina Disperal P2[®] was used as a precursor to prepare mesoporous $\gamma\text{-Al}_2\text{O}_3$ with tailor-made properties. In a typical procedure, 70 g Disperal P2[®] was added to 350 g distilled water and stirred for 1 h; to this solution, 78 g Triton X-100 template and 30 g aqueous ammonium acetate solution (33 wt%) were added to form a white gel. This gel was further dried in air at 110 °C and calcined in air at 600 °C for 4 h. The other supports SiO_2 and $\text{SiO}_2\text{-Al}_2\text{O}_3$ were calcined in air at 500 °C for 5 h before impregnation.

The heteropolyacids STA, TPA, and PMA were supported onto the three supports by wet impregnation method with a nominal HPA loading of 20 wt%. In the typical procedure for STA/ SiO_2 , an aqueous solution (10 ml) of STA (2 g) and some rinsing water (8 ml) was added to the silica (8 g) under constant stirring overnight. In total 18 ml of water was used for synthesis. Excess water was removed using a rotary evaporator. The obtained solid was dried at 120 °C for 2 h and then calcined at 300 °C with air in a muffle for 4 h to obtain the powdery catalyst.

2.3. Characterization of catalysts

BET surface area, pore volume and pore diameter of the catalysts were determined from the nitrogen adsorption/desorption isotherms at -196°C on a Micromeritics ASAP 2010 instrument. Before the measurement, each sample was evacuated at 200 °C for 4 h. The average pore diameters were calculated according to the BJH method.

Powder X-ray diffraction (XRD) patterns were measured on a theta/theta diffractometer (X'Pert Pro from Panalytical, Almelo, Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda = 0.015418$ nm, 40 kV, 40 mA) and an X'Celerator RTMS detector. The alignment was checked by

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