Stability of gold nanocatalysts supported on mesoporous silica for the oxidation of 5-hydroxymethyl furfural to furan-2,5-dicarboxylic acid

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ABSTRACT

The synthesis of furan-2,5-dicarboxylic acid via catalytic oxidation of 5-hydroxymethyl furfural is an important step for the production of bio-sourced polymers. We report on the activity of SiO_2-supported Au catalysts for this reaction. These catalysts reached 74% furan-2,5-dicarboxylic acid yield at 90 °C in 5 h when 5-hydroxymethyl furfural to Au molar ratio was 72. We also investigated the influence of the morphologies of the silica supports on the growth of Au nanoparticles under reaction conditions. Pronounced growth of Au nanoparticles occurred on Aerosil, SiO_2 with a disordered porosity and 50 nm average pore diameter: Au nanoparticles grew from 2.4 to 10.1 nm. However, by using ordered mesoporous supports, the growth of the gold nanoparticles was successfully minimized. Also the reaction conditions influenced the particle growth; for instance using HCO_3^- as a base led to more pronounced particle growth than using NaOH. Particle diffusion in solution, and subsequent coalescence and agglomeration was proposed to be the dominant particle growth mechanism. Our results show the importance of support morphology in mitigation of Au particle growth in liquid phase oxidation reactions.

1. Introduction

Furan-2,5-dicarboxylic acid (FDCA) can be used as a renewable building block for the production of polymers like polyesters, polyamides, and polyurethanes [1–3]. For example, FDCA reacts with ethylene glycol to form polyethylene furanoate which is a bio-based polymer. Production of FDCA via catalytic oxidation of 5-hydroxymethyl furfural (HMF) has been widely studied, using air or O_2 as the oxidant and typically under basic conditions. Commercialization of the FDCA production is planned by BASF and Avantium, based on a process involving Co/Mn/Br homogeneous catalysts [4,5]. The design of a heterogeneous catalyst that fulfills the industrial requirements is however highly desirable.

The quest is for catalysts that allow the oxidation of HMF, which contains an alcohol and an aldehyde group, to FDCA, which contains two acid groups [6]. The reaction occurs in consecutive steps via a 5-hydroxymethyl furan carboxylic acid (HMFCA) intermediate, if Au is used as a catalyst (Scheme 1). Supported metal catalysts, for instance Pt [6–11], Pd [12–17], Ru [18,19], and Au [20–22] have been extensively studied for this reaction. Different reaction conditions and different catalysts lead to different activities. In general, higher metal to HMF ratios [23], more alkaline conditions [20,23], and smaller metal nanoparticles [24,25] lead to higher activities of the supported metal
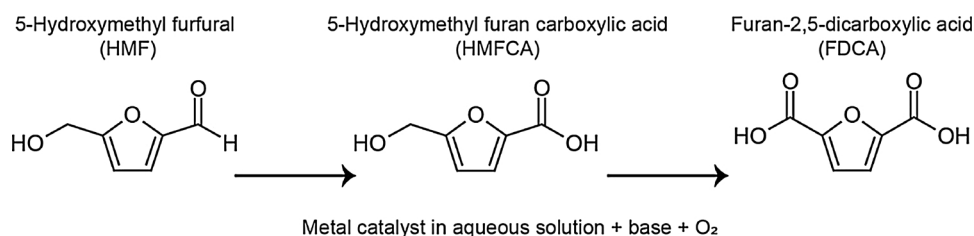
catalysts. It is also reported that the chemical nature of the support can affect the catalytic activity [10,20,22,26–29].

Gold catalysts are more active than Pt, Ru, and Pd [3,23,26], or according to other reports, at least equally active to the other metal catalysts for this reaction [19,30]. Gold catalysts are more resistant than for instance Pt catalysts to poisoning [3,7,10] and leaching [6]. However, Au catalysts are prone to particle growth especially under oxidative conditions [31–36]. Au nanoparticles supported on carbon with 5 nm open pores grew upon HMF oxidation in the presence of $NaHCO_3$ (initial pH of 8–8.5), and the extent of particle growth depended on the surface properties of the support [37]. Casanova et al. suggested particle growth as a deactivation mechanism for Au/TiO_2 and Au/CeO_2 for HMF oxidation in the presence of NaOH as a base at 45 °C, though a full characterization of the spent catalysts and particle size after catalysis was not given [20]. Gupta et al. reported that Au/hydrotalcite is stable during oxidation of HMF at pH of 10 where the high pH was caused by solid basicity of support [22]. Gupta et al. also reported growth of Au on MgO in a base free condition, suggesting that particle growth depends on the support. Furthermore, Prüße et al. showed a long term stability of the Au on TiO_2 and Al_2O_3 during selective oxidation of glucose at 40 °C and in the presence of KOH or NaOH as a base at pH of 9 [38,39]. It is not clear from the literature which factors affect the particle growth. Hence, a detailed investigation

5-Hydroxymethyl furfural (HMF)

5-Hydroxymethyl furan carboxylic acid (HMFCA)

Furan-2,5-dicarboxylic acid (FDCA)

Metal catalyst in aqueous solution + base + O_2

Scheme 1. Oxidation of 5-hydroxymethyl furfural (HMF) to furan-2,5-dicarboxylic acid (FDCA) via formation of intermediate 5-hydroxymethyl furan carboxylic acid (HMFCA).

of the factors that affect the stability of the Au nanoparticles as well as strategies to alleviate Au particle growth are needed.

Silica supports are widely used in heterogeneous catalysis [40,41]. They can be prepared with different specific surface areas (50–2000 m^2/g) and structures. For example, aggregated spherical particles of Aerosil form a porous material in which the pores are formed by interparticle spaces. Ordered mesoporous structures like SBA16 [42] and mesoporous cellular foam (MCF) [43] have cage like structures with different neck sizes. Like SBA16, silica gel can have small pore sizes (around 9 nm), but it has a disordered structure [44]. The flexibility in having supports with different surface areas and structures allows the design of catalysts with different interparticle distances and a uniform distribution of well-defined nanoparticles. Previously, our group reported for Cu nanoparticles on SiO_2 for methanol synthesis that a uniform distribution of nanoparticles which maximize interparticle distances minimizes particle growth [45,46]. It was also found that the neck size was a crucial factor to limit particle growth for these catalysts [44].

In this study, the activity and stability of Au on SiO_2 for liquid phase oxidation of HMF to FDCA are investigated. This is the first time that the activity of Au/SiO_2 for this reaction is reported. In general, carbon supports are better candidates for this type of reactions due to their higher hydrothermal stability in particular under alkaline conditions. However, diverse structures of the SiO_2 supports allow a detailed investigation of the effect of support morphology on the stability of Au nanoparticles. Our results show that the morphology of the support plays an important role in the stability of the SiO_2-supported Au catalysts.

2. Material and methods

2.1. Catalyst preparation

Aerosil 300 (BET surface area of 270 $m^2 g^{-1}$, mesopore volume of 0.78 mL g^{-1}) was purchased from Evonik. Silica gel 7085 (BET surface area of 500 $m^2 g^{-1}$, mesopore volume of 0.90 mL g^{-1}) was received from Grace Davison. Mesoporous SiO_2 supports (SBA16 and MCF) were prepared in house. MCF [43] was prepared by dissolving Pluronic P123 (2.0 g, $EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Sigma Aldrich) in aqueous HCl solution (75 mL, 1.6 M) at room temperature (RT). Then, 1,3,5-trimethylbenzene (TMB, 2.0 g) was added. After stirring at least 45 min at 35 °C, tetraethoxysilane (4.4 g, TEOS) was added, and the mixture was transferred to a 200 mL Teflon-lined autoclave. After 20 h at 38 °C in static condition, the cloudy suspension was further kept at 100 °C for 24 h in static condition. The precipitate was filtered and washed at RT until no chloride ions were left (verified using an $AgNO_3$ solution to test the washing liquid) and subsequently dried at 120 °C in static air overnight. Finally, the precipitate was calcined at 500 °C in static air for 6 h to yield MCF (BET surface area of 610 $m^2 g^{-1}$, total pore volume of 2.01 mL g^{-1}).

SBA16 [42] was prepared by dissolving Pluronic F127 (4.7 g, $EO_{106}PO_{70}EO_{106}$, M_{av} = 12600, Sigma Aldrich) in a mixture of aqueous HCl solution (75 mL, 1.6 M) and water (210 mL) at RT. Then, 1-butanol (13.2 g) was added, and the mixture was stirred at 35 °C for 1 hour. Then, tetraethoxysilane (20.8 g, TEOS) was added dropwise under fast stirring. The mixture was transferred to a Teflon-lined autoclave, and

after 20 h at 35 °C under static conditions, the cloudy suspension was subsequently kept at 100 °C for 24 h. The precipitate was filtered and washed at RT until no chloride ions were left, as evidenced by silver nitrate test, and subsequently dried at 120 °C in static air overnight. Finally, the precipitate was calcined at 540 °C in static air for 6 h to yield SBA16 (BET surface area of 780 $m^2 g^{-1}$, total pore volume of 1.04 mL g^{-1}).

All supports (3 g for each of them) were functionalized using aminopropyl triethoxysilane (APTES). First, they were dried at 140 °C under vacuum for 24 h. Then, dry toluene (50 mL) and APTES (1 g for Aerosil and 3 g for silica gel, MCF and SB16) were added. We added the amount of APTES needed for covering the support surface based on the BET surface area of the supports, and considering three OH groups per nm^2 of the SiO_2 support [47]. The mixture was refluxed for 24 h at 110 °C in a N_2 atmosphere. The functionalized supports were recovered by centrifugation, washed with ethanol (40 mL) at RT twice, and dried at 60 °C in static air overnight.

All catalysts were prepared following the method of Mou et al. for the deposition of Au on SiO_2 [48]. The functionalized supports (1 g) were dispersed in water (15 mL, doubled distilled). To deposit 1.5 wt% Au on Aerosil and 3 wt% Au on Aerosil, silica gel, MCF, and SBA16, appropriate amount of an aqueous Au solution (0.06 M $HAuCl_4.3H_2O$, Sigma Aldrich) were added. The mixture was stirred at RT for two hours, and the powder was recovered by centrifugation and washed with H_2O (40 mL) at RT twice. Then, the powder was re-dispersed in water (15 mL) and reduced by a rapid addition of an excess of a reducing agent (10 mL, 0.2 M $NaBH_4$) under vigorous stirring at RT. After 20 min, the product was collected by centrifugation, washed with water (40 mL) at RT five times and dried at 60 °C in static air overnight. To eliminate the organic groups, the catalysts were calcined at 500 °C in static air for 4 h. The catalysts are denoted as Au/Aerosil, Au/silica gel, Au/MCF, and Au/SBA16.

2.2. Characterization

Elemental analysis was performed using inductively coupled plasma-optical emission spectrometry in the Faculty of Geosciences at Utrecht University. X-Ray Diffraction (XRD) was carried out with a Bruker D2 phaser with Co K_α source. Crystallite sizes were obtained from the peak broadening at $2\theta = 44°$ using the Scherrer equation. For transmission electron microscopy (TEM) imaging on MCF and SBA16 samples, they were first embedded in epoxy resin (Epofix, EMS), then cut to slides of 70 nm thickness using a Diatome 35° diamond knife mounted on an Ultracut E Reichert-Jung microtome (Leica) and finally collected on TEM grids. TEM imaging was performed on a Tecnai 12 (FEI) microscope operated at 120 kV. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on a Talos F200X microscope operated at 200 kV. Energy-dispersive X-ray (EDX) spectroscopy was performed by four windowless SuperX EDX-detectors with a resolution of 128 eV arranged around the sample. STEM image processing and identification of the EDX signal was carried out using Tecnai Imaging Analysis (TIA) software. Particle sizes were determined from the TEM images by measuring the sizes of typically 300 particles on different places of the sample.

Nitrogen physisorption measurements were performed at −196 °C (Micromeritics, TriStar 3000) to determine the BET surface area of the