Directed aqueous-phase reforming of glycerol through tailored platinum nanoparticles

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ABSTRACT

Sustainable technologies require both renewable feedstocks and catalysts that are able to direct their conversion to specific products. We establish a structure-activity relationship for the aqueous phase reforming of glycerol over 2% Pt/Al$_2$O$_3$ catalysts, whereby the reaction pathway can be controlled to produce either hydrogen or 1,2-propanediol as the main product. Using the colloidal synthesis method, the reduction temperature was altered to produce Pt nanoparticle catalysts supported on Al$_2$O$_3$ with varying Pt particle size. The catalytic activity of the samples for the APR of glycerol resulted in a higher conversion of glycerol (34%) for the larger Pt particle size of ~3.5 nm, producing the liquid 1,2-propanediol as the major product with a yield of 12.5%, whereas smaller particles of ~2.2 nm gave hydrogen as the main product (5.5% yield). This work demonstrates how the APR of glycerol can be tuned to yield both valuable liquid and gas products using tailored Pt nanoparticles.

1. Introduction

1.1. Glycerol as a by-product

The production of crude glycerol has increased significantly in recent years as a consequence of the rapid growth in the production of biodiesel as an alternative for petroleum-based fuels. Finding a commercially viable use for this 'waste' glycerol, the main by-product in the production of biodiesel, is now an active area of research, with many possible applications [1–7]. The production of hydrogen, coupled with liquid-phase products, through aqueous phase reforming (APR) of glycerol, is one possible route. A clean and sustainable supply of hydrogen is required to enable a future hydrogen economy, an example being the development of proton exchange membrane fuel cell technology [1,2]. The current industrial processes used to produce hydrogen involve the reforming of hydrocarbons, resulting in high CO$_x$ emissions and adding to the depletion of fossil fuel reserves [2,8].

1.2. Aqueous phase reforming

Aqueous phase reforming of glycerol, shown in Eq. (1), was highlighted in 2002 by Dumesic [8] as a promising method for the production of hydrogen as it is both kinetically and thermodynamically favourable. It can be carried out at relatively low temperatures, ~227 °C, it minimises undesirable side reactions, and facilitates the water gas shift reaction (WGS) (Eq. (2)), limiting the production of CO, known to poison H$_{2(g)}$ fuel streams [1,3,4,9,10].

$$C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

1.3. Glycerol to hydrogen

Recent studies have shown that Pt based catalysts have high activity and selectivity compared to other monometallic systems for the APR of glycerol [4,8,11–13]. Despite its expense, Pt is a favourable choice as a consequence of its enhanced ability to cleave C−C bonds and promote

the WGS reaction [9,14]. The support material has also shown to affect the catalytic activity; Guo et al. studied a range of supports and found that Pt supported on γ-Al₂O₃ gave a higher rate of production of H₂ compared to SiO₂, TiO₂ and CeO₂, which was ascribed to the higher basicity of the Al₂O₃ support [1].

Thus far the majority of studies on glycerol APR has been on commercial catalysts or those produced via classic synthesis methods such as impregnation and precipitation. However, recent work has shown that an increase in activity can be achieved by using supported nanoparticles prepared using colloidal synthesis methods [15–17]. Bönnemann et al concluded that improvement of catalytic activity from a colloidal system was due to the fact that metal nanoparticles prepared by the this method occupy the most exposed sites of a support, rather than being buried under the surface [15].

Compared to the classic synthesis methods, sol-immobilisation techniques afford the possibility of fine-tuning the properties of supported metal nanoparticles, thereby allowing greater control of the size, shape and dispersion in the final catalyst [18–20]. This is achieved by the use of a stabilizing agent during the synthesis, such as polyvinyl alcohol, (PVA), leading to more well dispersed catalysts with narrow particle size distribution [15,21,22].

Recent studies used variation of the colloidal reduction temperature and solvent systems during synthesis to modify gold and palladium nanoparticles for use in the oxidation of glycerol and hydrogenation of furfural, respectively. These studies proved that the colloidal synthesis technique can be used to control the size of the metal nanoparticles and the proportion of available active surface sites, resulting in changes in selectivity [20,23].

1.4. 1,2-Propanediol production

The main focus in the published literature on the APR of glycerol has been the production of hydrogen. However, a high yield of liquid products are also formed from a complex network of reactions. These products also have significant applications, for instance 1,2-propanediol (1,2-PDO), produced from the hydrogenolysis of glycerol under APR conditions, is used in the food, cosmetic and pharmaceutical industries [24,25].

Currently 1,2-Propanediol is commercially produced via the hydration of propylene oxide derived from propylene. Renewable feedstock can be used to produce 1,2-PDO by hydrogenolysis however this pathway requires high temperatures and pressures. For instance, studies on the conversion of glycerol have required pressures upwards of 100 bar and an external hydrogen source, therefore making this an expensive process to consider commercially viable [26].

It has been shown that using APR conditions, glycerol can be converted to 1,2-PDO via an acetol pathway, generating hydrogen in situ and has been proposed as a potential alternative to the one step hydrogenolysis [27].

Due to its active nature for the APR of glycerol, Pt nanoparticles supported on γ-Al₂O₃ was chosen for this study as a model catalyst. The colloidal synthesis method was used to generate preformed Pt nanoparticles with specific morphology to obtain structure-activity relationships in an attempt to improve the catalytic activity and control the reaction pathway to favour either hydrogen or 1,2-propanediol, using optimised conditions that we have recently reported [13].

2. Experimental

2.1. Catalyst preparation

Pt/Al₂O₃ catalysts were prepared using the sol-immobilization method based on a previous experimental regime to produce Pt and Au colloidal systems [20,28]. A stock solution containing the precursor, K₂PtCl₄ (99.99%, Aldrich), was added to distilled water (Pt concentration = $1.03–2.05 \times 10^{-4}$ M) that had been heated to the desired

temperature (25–90 °C) using a stirrer/hotplate. For the synthesis at 90 °C a reflux condenser was used to keep the solution in the liquid phase. Poly(vinyl alcohol) (PVA, Aldrich, Mw = 9000–10000 g mol⁻¹, 80% hydrolysed, PVA/Pt (wt/wt) = 0.65) was added in order to stabilise the solution. A freshly prepared solution of the reducing agent, NaBH₄ (0.1 M) (> 96%, Aldrich, NaBH₄/Pt (mol/mol) = 5–10) was added drop wise with stirring to form a black sol. The Al₂O₃ support material (Aeroxide AluC, Degussa) was then added and the solution stirred vigorously. After a period of time the solution was filtered, washed extensively with distilled water to remove any precursor material and dried overnight at room temperature [29].

The colloidal solutions were monitored throughout the synthesis procedure by UV–vis spectroscopy (Shimadzu UV-1800 spectrometer with Quartz cells) to assess the reduction of the Pt precursor.

2.2. Catalyst characterisation

The Pt loading of the samples was determined by both Microwave Plasma - Atomic Emission Spectrometry (MP-AES) and Energy Dispersive X-ray Spectroscopy (EDS). For MP-AES analysis, the solid samples (0.1 g) were digested in aqua regia using an Anton Paar Multiwave 3000 and diluted in deionised water to form a 0.1 wt% solution. The elemental analysis was performed using an Agilent 4100 MP-AES. Pt standards were made up in 10% aqua regia and used to calibrate the instrument before the samples were run. EDS analysis was performed on a JSM-6610LV scanning electron microscope (JEOL) fitted with Oxford Instruments Xmax 80 mm EDS detector running Aztec analysis software. The powder samples were dispersed on conductive carbon tabs placed on aluminium stubs.

Transmission Electron Microscopy (TEM) was used to investigate the particle size and dispersion of the metal nanoparticles on the Al₂O₃ support. Analysis was carried out on a JEM-2100 Plus electron microscope with a 200 kV accelerating voltage. Samples for TEM were prepared by dispersing the supported catalysts in methanol and then dropping the solution on 300 mesh carbon-coated copper grids.

The surface area of the samples was measured using the Brunauer Emmett Teller (BET) method. The samples were first degassed at 140 °C under vacuum using a FloVac Degasser. Analysis was then carried out on a Quadrasorb EVO instrument supplied by Quantachrome.

X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex 600 benchtop powder X-ray diffractometer equipped with a 6-position autosampler and Cu Kα radiation source. The 2θ angles were scanned from 5 to 80° at a rate of 5°/min. The average Pt crystallite sizes were calculated using the Scherrer equation for the Pt (111) diffraction peak at 2θ = 39.9° [30].

X-ray Absorption Fine Structure (XAFS) studies were carried out on the Pt L₃-edge on the B18 beamline at the Diamond Light Source, Didcot, U.K. Measurements were performed in transmission mode using a QEXAFS setup with a fast-scanning Si(111) double crystal monochromator and ion chamber detectors. An average of 6 scans were acquired and merged to help improve the signal-to-noise level of the data. The time resolution of the spectra was 1 min/spectrum (k_max = 18). Fresh catalyst samples were analysed as synthesised and after reduction under hydrogen at room temperature. Used catalyst samples were washed with water and dried at 120 °C in static air overnight before analysis.

The software used to carry out the XAS data processing and the extended X-ray absorption fine structure (EXAFS) analysis was IFEFFIT with the Horae package (Athena and Artemis) [31,32]. The typical fit range for the EXAFS data was 1.1 < R < 6 Å and 3.1 < k < 15.3.

CO adsorption studies were performed on both fresh and used catalyst samples using transmission Fourier Transform Infrared Spectroscopy (FTIR). The used samples were washed with distilled water and dried in an oven overnight at 120 °C to remove as much of the reaction solution as possible. 25–30 mg of sample was pressed into a self-supporting pellet and mounted in a Harrick Dewar transmission/