Conversion of Glycerol into Value Added Products by Catalytic Processing

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ABSTRACT

The conversion of glycerol into value added chemicals have emerged in recent years as a result of glycerol unique structure, properties, bioavailability, and renewability. Glycerol is produced in large amounts during trans-esterification of fatty acids into biodiesel, and as such represents a useful by-product.

In this paper, the liquid phase oxidation of glycerol has been studied over gold nanoparticles supported on TiO_2, and synthesized by using deposition-precipitation method. The catalysts are characterized by XRD, TEM, XPS, and activity towards CO oxidation. Active catalysts comprise particle size distributions (2-5 nm diameters) for gold nanoparticles. The results indicate that the Au/TiO_2 catalyst showed the best performances both for activity and selectivity toward glyceric acid. We have also studied the effect of reaction conditions such as, amount of catalyst and concentration of base in the catalytic activity.

Keywords: Glycerol, Liquid-phase oxidation, Transesterification, Gold nanoparticles, CO oxidation, catalytic activity.

انتاج مركبات ذات فائدة صناعية تطبيقية من مادة الكلسرول باستخدام العوامل المساعدة

الخلاصة

في الآونة الأخيرة يتزايد الأهتمام في انتاج مركبات كيميائية ذات قيمة عالية من مادة الكليسرول وذلك كونه يمتلك صفات استثنائية من ناحية خصائصه وتركيبه بالأضافة الى وفرته وقابليته للتجديد. يتم انتاج الكليسرول بكميات كبيرة خلال عملية استرة الأحماض الدهنية لأنتاج الوقود الحيوي ، وبذلك يمثل ناتج عرضي ذو فائدة .

يتناول البحث اختبار أكسدة الكليسرول في الطور السائل باستخدام دقائق الذهب النانوية محمة على أوكسيد التيتانيوم TiO2 وتم تحضيرها بطريقة الترسيب.

تم تشخيص العامل المساعد باستخدام الأشعة السينية الحيودية XRD , المجهر الألكتروني النافذ TEM , مطياف الأشعة السينية XPS , والفعالية في أكسدة أول أوكسيد الكربون. وأظهرت الفحوصات ان العوامل المساعدة الفعالة تحتوي على الذهب بحجم دقائق يتراوح قطرها (2-5) نانومتر. لقد أظهرت النتائج ان العامل المساعد نوع Au/TiO2 يمتلك فعالية عالية وانتقائية في توليد

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حامض الكليسريك . كذلك تم دراسة ضروف التفاعل كتأثير تركيز القاعدية وكمية العامل المساعد على الفعالية.

INTRODUCTION

With an increase in environmental consciousness throughout the world, there is a challenge for chemists and chemical engineers to develop new products, processes and services that achieve necessary economical and environmental objectives. The green chemistry and green engineering areas, developed in these last years, are the answers of the scientific community to that challenge. As well as using and producing better chemicals with less waste, the challenge also involves reducing other associated environmental impacts including reduction in the amount of energy used in chemical processes [1, 2].

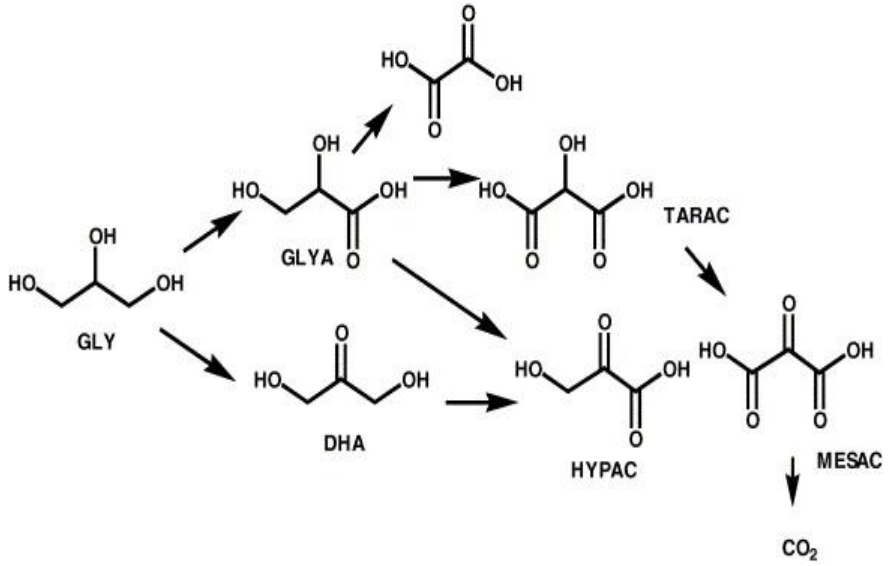
The oxidation of alcohols and pyrols to chemical intermediates represents a demanding target and is of immense importance for the production of chemicals. Glycerol (1, 2, 3-propanetriol) is a highly functionalized molecule that is readily available from bio-sustainable sources; for example it can be obtained as a by-product of the utilisation of rape seed and sunflower crops. It is also a co-product of oils and fats industries which have grown very much in the last years. Moreover, glycerol is also obtained from biodiesel; one ton of biodiesel produces about 100 kg of pure glycerol [3]

The ready bio-availability of glycerol makes it a particularly attractive starting point for the synthesis of intermediates and a large number of products can be obtained from glycerol oxidation [Scheme 1]. The resulting products, aldehydes and ketones are extensively used as precursors and intermediates for the production of flavours, fragrances, and biologically active compounds [4]. The application of these preparations, however, causes severe environmental problems, due to waste from heavy metals or stoichiometric amounts of reagents and the generation of undesirable products [5,6]. From the standpoint of green and sustainable chemistry, there still a need to develop cleaner catalytic oxidation systems. Thus, the heterogeneously catalysed glycerol oxidation is an environmentally friendly alternative to produce these valuable compounds [7]. .

Catalysis represents a key approach to green chemistry in the activation and utilisation of bio-renewable feedstock. Glycerol catalytic oxidation has been studied by using Pd/C and Pt/C under different experimental conditions [8]. In recent years, there has been immense interest in the use of gold catalysts for oxidation reactions.

Prati and co-workers [9, 10] have shown that supported gold nano-particles can be very effective catalysts for the oxidation of alcohols, including diols.

This paper is focused on green and sustainable chemistry in the catalytic activity of supported nanoparticles for organic transformations. The aim of this work is to produce highly interesting chemicals from the environmentally friendly oxidation of bio-sustainable source. We have selected glycerol as a starting point because of its possible availability as a by-product from biofuel industry. Herein, we show that supported gold catalyst can be highly effective for the selective oxidation of glycerol**.**



Scheme (1) Reaction network of the glycerol oxidation

EXPERIMENTAL

Catalyst preparation

The catalysts were prepared by deposition-precipitation via the gold-sol method according to the following procedure: The TiO_2 support (Degussa P25, 2 g) was stirred in deionised water (100 ml) and the pH was adjusted to 7 by dropwise addition of ammonia solution (0.5%). An aqueous 1%Au solution was prepared (3.48 ml $HAuCl_4$ in 100 ml deionised water) and the pH was adjusted to 7.

By the employed precipitation method, the gold solution was added within 30 minutes dropwise to the stirred TiO_2 suspension, the pH was readjusted to 7. The suspension was vigorously stirred and separated by filtration, washed with 200 ml deionised water to remove residual Cl^- ions and dried overnight at 70 ^{0}C. The amount of gold on the catalyst is always given as a weight fraction (wt %).

Catalyst characterization

The gold content of the catalyst was determined by inductively-coupled plasma atom emission spectroscopy (ICP-AES) using a UNICAM PU 700 spectrometer

X-ray diffractometry (XRD) patterns of the catalyst powders were recorded by a Phillips diffractometer (operating at a voltage of 40 kV and a current of 30 mA) using the CuKa radiation and a 2θ scan rate of 1.28^o/min. The crystalline sizes of the samples were determined by Scherrer equation [11].

Transmission Electron Microscopy (TEM) images were obtained using an TEM microscope (Phillips XL30) operating at 25 kV. The sizes of particles were determined by analyzing the images for at least 300 particles. The dispersion (D) is calculated by the fraction of gold atoms which are located at the surface with respect to the total amount of the Au atoms.

X-ray photoelectron spectroscopy (XPS), The surface composition and oxidation states of the Au/TiO_2 catalyst was studied by XPS-PHI system using mono chromatized Al-Kα radiation (1486 eV). The photons are absorbed by the studied samples and induce the ejection of core electrons.

All spectra were recorded with a power of 250 W, an angle of 45^0 and an aperture size of 4 mm. The detail spectra of the elements of interest Au, O, and Ti were recorded with pass energy of 11.75 eV. All measurements were performed under the same conditions (pass energy, power, aperture size, and angle).

The CO oxidation test reaction was carried out in a low-pressure gas flow reactor designed and developed in the University of Manchester. The system consisted of a gas mixing unit, gas flow controller, micro-reactor, pressure control, pumping stage and the MS as gas analyzing system. The micro-reactor consisted of a 6 mm quartz tube with an inner diameter of 4 mm. The catalyst powder was fixed inside the reactor with quartz wool. The reaction gases containing CO, O_2 and He with different stoichiometry ratios were allowed to pass over the catalyst bed.

Oxidation experiments

The glycerol oxidation experiments were carried out using 1 wt% Au/TiO_2 under atmospheric pressure in a 300 ml semi-batch glass reactor. The reactions were performed with 150 ml of an aqueous glycerol solution with and without catalyst and NaOH addition. We tried an oxygen flow rate of 300 ml/min at 60-70 ^{0}C and a stirring rate of 300 rounds per minute (rpm). The reaction courses were controlled by taking samples and analyzing them by High Performance Liquid Chromatography System, Varian HPLC Analytical Instrument with ProStar 330 photodiode array detector equipped with ion exchange column and a UV (220 nm) with light reflectance detectors. Distilled water was employed as elluent.

RESULTS AND DISCUSSIONS

Catalyst Characterization

The influence of the gold loading on the catalytic activity was investigated for catalysts prepared by deposition-precipitation method. For the Au/TiO_2 which had been precipitated at pH 7, the gold content determined by ICP was 0.9-1.0 wt%. The chlorine content was found to be below the detection level (0.1 wt.%}.

The catalyst materials had been dried for 24 hours and calcined at different temperatures, namely 70, 100, 150, 200 ^{0}C, which had a considerable effect on the size of the gold particles and the resulting catalytic activity. The investigations by XRD and TEM revealed that a significant increase in the gold particle size with increasing calcination temperature. Therefore, in the case of the Au/TiO_2 catalysts calcined at >100 ^{0}C, the decreasing catalytic activity might be due to agglomeration which will then lead to a decrease in the catalytic activity [12, 13].

In Fig.(1), the XRD patterns of the Au/TiO_2 show that no reflections of gold could be detected for the uncalcined material and the material calcined at 70, 100 ^{0}C. The appearance of Au (111) and Au (200) reflections can be observed at higher calcination temperatures, and they become more significant after calcination at 200 ^{0}C. This increase in the gold reflections at higher temperature of calcinations could be attributed to the higher gold average particle size [14]. According to the ICP analysis, the catalyst contains less than 1 wt.% gold. At this low gold content, the

determination of gold particle size from X-ray diffraction line broadening become very difficult.

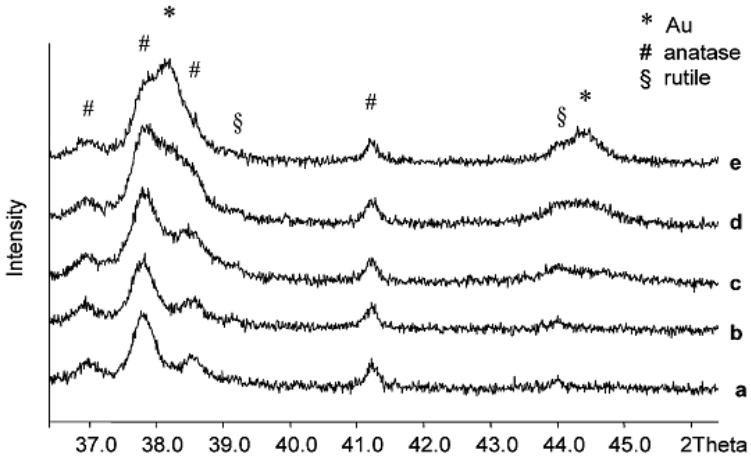


Figure (1). XRD of Au/TiO_2 calcined at different temperatures; (a) uncalcined (b) 70 ^{0}C (c) 100 ^{0}C (d) 150 ^{0}C (e) 200 ^{0}C

All catalyst particle sizes were determined via TEM. In general TEM images show well separated Au particles (dark spots) on the larger TiO_2 substrate particles, fig.(2). The mean particle sizes are about 2-4 nm. Obviously, the Au particle sizes increases with increasing calcination temperatures. The calcined samples exhibit a rather wider particle size distribution with a mean particle size of 3-8 nm. This might be due to the longer pre-treatment conditions and agglomeration of the Au nanoparticles [15, 16]

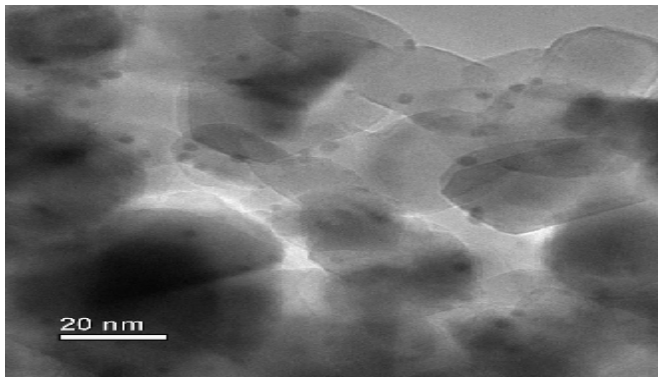


Figure (2) TEM image of the Au/TiO_2 catalyst After calcination at 70 ^{0}C

The surface composition and the oxidation states of the Au species of the Au/TiO_2 catalyst was studied by X-ray Photoelectron Spectroscopy (XPS). A detail spectrum was taken for the Ti 2p, Au 4f and O 1s peaks and partly from the C 1s peak.
Concerning the interaction of gold nanoparticles with the support, it has been proposed that this interaction can lead to the stabilization of positive and negative gold atoms at the interface between gold and the support [17]. Evidence of the presence of gold atoms having positive or negative charge density can be obtained by the Au 4f 7/2 level corresponding to the contribution of three components due to Au (0), Au (I) and Au (III), fig.(3). Normally the population of Au (I) is significantly smaller than that of Au (III).

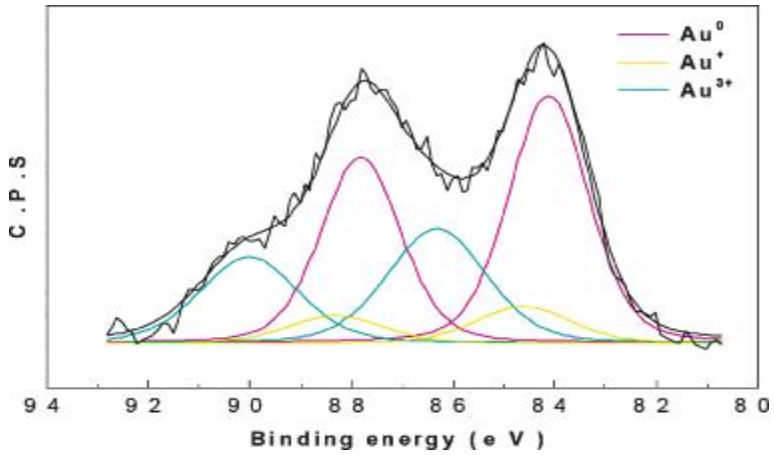


Figure (3) XPS spectra of the Au 4f 7/2 level recorded for Gold nanoparticles supported on TiO_2

ACTIVITY MEASUREMENTS

Catalytic activity in CO oxidation

Catalytic activity in CO oxidation is now being used by many researchers as an oxide. Figure (4) shows CO extension extent as a function of time at room temperature with gas stoichiometric CO/O_2 ratios (1/80). It is clear that as time proceeds, CO conversion increases and the rate of conversion is high initially and slows down until it reaches a steady state, Fig. (4). The CO oxidation extent reaches (80-90) % at room temperature.

Catalytic activity in glycerol oxidation

The oxidation of alcohols and pyrols to chemical intermediates represents a demanding target and is of immense importance for the production of fine chemicals. The oxidation of glycerol with oxygen was investigated using 1% Au/TiO_2 under atmospheric pressure and the results are given in Table 1.
In the absence of NaOH, no glycerol conversion was observed, as shown in NMR analysis of the reaction products, Fig. (5). In addition, the TiO_2 support in the absence of gold was also found to be inactive for glycerol oxidation, under these conditions even when NaOH is present.

The reaction products were analysed using HPLC. From the data presented in table 1, it is apparent that the selectivity to glyceric acid and the conversion of glycerol are very dependent upon the glycerol/NaOH ratio. With high concentration of NaOH, high selectivity to glyceric acid can be observed. However, decreasing the concentration of glycerol, and increasing the mass of the catalyst leads to the formation of small amount of tartronic acid.

It is proposed that in the absence of base, the initial dehydrogenation via H-abstraction is not possible. In the presence of the base, the H is readily abstracted from one of the primary hydroxyl groups of glycerol and this promotes the rate for the oxidation process. Hence, it is proposed that the oxidation mechanism proceeds via an initial dehydrogenation pathway. This has been previously observed for other metal oxidation catalysts [20]. We consider that the oxidation of glycerol to glyceric acid probably proceeds via initial formation of glyceraldehyde, which might be

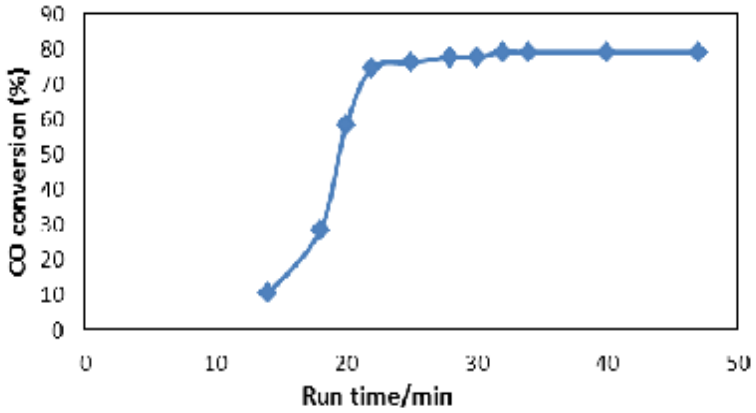


Figure (4). CO conversion over 1% Au/TiO_2 catalyst as a function of time.

readily oxidised to glyceric acid and typically not observed as a product.

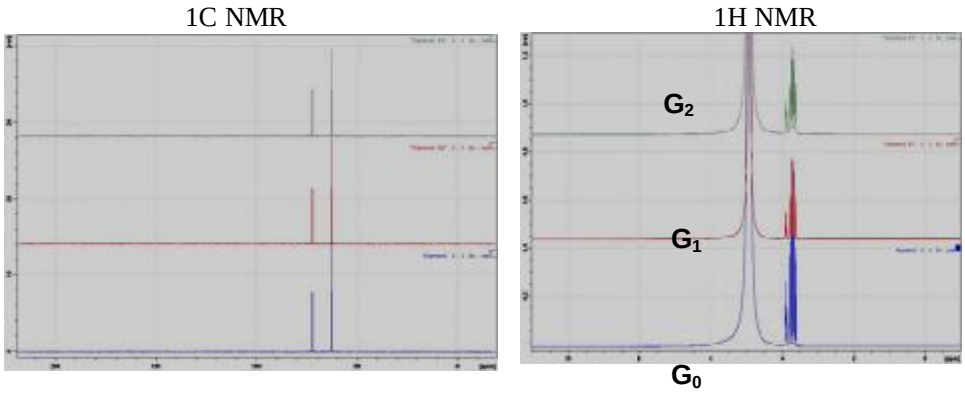


Figure (5) NMR 1H and 1C spectrum for glycerol (G_0), glycerol with catalyst (G_1),glycerol with NaOH; without catalyst(G_2), reaction time 25 hrs. at 60-70 ^{0}C.

Table (1) Oxidation of glycerol using 1%Au/TiO_2 catalyst.

					Selectivity (%)		
Catalyst	glycerol/catalyst mole ratio	NaOH mmole	Reaction time (h)	glycerol Conversion (%)	Glyceric acid	Glyceraldehyde	tartronic acid
----	Glycerol (100%)	24	25	0	0	0	0
1% Au/TiO_2	500	24	4	10	62	0	0
			10	18	64	0	0
			17	32	64	0	3
			25	58	64	0	5
1% Au/TiO_2	500	12	25	44	52	0	2
1% Au/TiO_2	1000	24	25	32	48	0	1
1% Au/TiO_2	2000	24	25	22	35	0	1

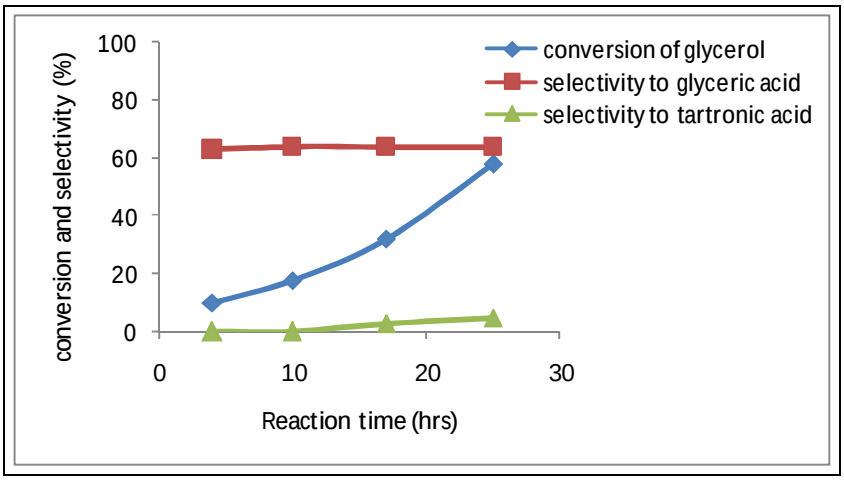


Figure (6) Oxidation of glycerol over 1% Au/TiO_2 catalyst. Experiment performed at a glycerol/catalyst mole Ratio of 500:1, temperature 60 ^{0}C.

CONCLUSIONS

Selective oxidation of glycerol using oxygen in the presence of a catalyst system is one of the challenging reactions; its low environmental impact, especially if compared to stoichiometric oxidation makes this reaction very attractive.

The most important conclusion following from this study is that Au/TiO_2 nano catalyst is highly active and selective for the liquid phase oxidation of glycerol producing glyceric acid as a major constituent. We have observed that glycerol conversion of up to 56% and high selectivity to glyceric acid of ca.64% can be achieved using supported gold nanoparticles as catalysts under mild reaction conditions (atmospheric pressure with molecular oxygen). It indicates that many parameters determine the effectiveness of glycerol oxidation such as, amount of catalyst and concentration of NaOH in the catalytic activity. In terms of selectivity, a decrease in the selectivity to glyceric acid was observed by increasing the glycerol/catalyst molar ratio. The effect of base was also studied and it was found that the catalytic activity is influenced by the concentration of NaOH. For gold as an oxidation catalyst, it has been shown that the activity is highly dependent upon the particle size and, the optimum size is ca.2-5 nm. However, the gold oxidation state has also been found to be important in some cases.

It is apparent by careful control of the reaction conditions; higher selectivity to glyceric acid can be achieved.

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