Dictating Selectivity in the Catalytic Vapor-Phase Conversion of Glycerol

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Abstract: A viable route for the vapor-phase conversion of glycerol into value-added chemicals is herein presented. This procedure allows to dictate selectivity towards hydroxyacetone (acetol) or methylglyoxal (pyruvaldehyde) by simply tuning the experimental conditions while retaining the same catalytic system. A series of gold- and copper-based catalysts supported on gamma-alumina, including bimetallic formulations, were prepared by incipient wetness impregnation method and tested in a continuous-flow fixed-bed vertical glass reactor at ambient pressure and $T = 250\text{--}300^\circ\text{C}$. The best performance was achieved with 1%wt Au/Al₂O₃. Accordingly, the selectivity could be directed to acetol (sel. 72%) at 87% conversion when performing the reaction at 300°C and adding H₂ to the carrier N₂, or towards pyruvaldehyde (sel. 79%) at 92% conversion when adding O₂ to N₂ at 250°C . These relatively mild conditions not only allow for energy savings with respect to the common procedures so far reported, but also for catalyst stability that can be easily regenerated after use. Furthermore, the low metal loading in the catalyst (1% wt) and its small amount requested for each test (0.1 g catalyst) make this procedure economically sustainable.

Keywords: Gold- and copper- based catalysts, Vapor-phase catalysis, Glycerol, Acetol, Pyruvaldehyde.

1. INTRODUCTION

The necessity to find eco-friendly routes for replacing petroleum derivatives has prompted both academia and industry to search for potential starting materials in biomass. The biodiesel synthesis is likely the most promising answer to such requests, being a fuel comprised of mono-alkyl ester of long chain fatty acids produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol (*transesterification reaction*) [1, 2]. However the growing overproduction of glycerol, the main by-product of biodiesel synthesis, has meanwhile introduced another challenge for scientists now called to find effective ways for converting glycerol into valuable chemicals, as propylene glycol, acetol, acrolein and pyruvaldehyde usually obtained from fossil resources [1-11]. The catalytic route employing transition metals (*i.e.* Au, Pt, Pd, Cu, Ni, Ru) supported on different materials (*i.e.* Al₂O₃, SiO₂, TiO₂, C) in liquid phase seems to meet such expectations, especially for propylene glycol production, but even displays some limits [3-8]. Vapor-phase studies in this field came out later [9-16] but have rapidly gained burgeoning attention since the successful achievement of acrolein by dehydration of glycerol over a variety of catalysts [9-11]. Less effective is the one-step oxidative dehydration of glycerol employing acrolein as an intermediate, due to the low selectivity towards the

corresponding acid. This is because glycerol dehydration to acrolein and its further oxidation to acrylic acid require different catalysts under different reaction conditions. Due to the strategic importance of acrylic acid as a bulk chemical, many efforts are now focused on designing a combined or stacked catalytic system able to perform both the reactions under the same conditions, as well as on optimizing two-step processes [14]. Another key chemical derived from glycerol dehydration is hydroxyacetone (acetol). Acetol is extensively used in food industry to give aroma to foods, as well as in textile industry as a substitute to sodium dithionite usually used as a reducing agent for dyeing processes. Most important, acetol plays a role as an intermediate in organic synthesis because it contains both hydroxyl and carbonyl functional groups [15]. Hence, it is widely employed to promote a variety of reactions including dehydration, hydrogenation, oxidation and polymerization. In particular, propylene glycol via hydrogenation reaction, acrolein through dehydration and methyl glyoxal (pyruvaldehyde) by dehydrogenation. Among these, pyruvaldehyde can serve as an intermediate towards lactic acid. This latter is a high value-added platform molecule in view of its multiple applications, mainly in the production of acrylates and biodegradable/biocompatible polymers [16]. To the best of our knowledge, the selective vapor-phase conversion of glycerol to pyruvaldehyde has been so far rarely investigated [17, 18]. A recent study assessed various metals and carriers identifying 5%wt Ag/Al₂O₃ as the best catalyst for the oxidehydration of glycerol to pyruvaldehyde optimized at 350°C and O₂/glycerol = 0.5 thus leading to 80% yield. The

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authors also demonstrated the superiority of pyruvaldehyde, compared to dihydroxyacetone (DHA), as the intermediate in an alternative two-step glycerol-to-lactic acid process [18].

In this short communication, we introduce our preliminary results on the possibility to dictate selectivity towards acetol or pyruvaldehyde by vapor-phase conversion of glycerol over the same catalyst (1%wt Au/Al₂O₃) by simply tuning temperature, N₂/H₂/O₂ ratios and gas flow rate thereof. Notably, pyruvaldehyde could be achieved with 79% selectivity at 92% conversion when conducting the reaction at 250°C and adding dioxygen to dinitrogen. The mild experimental conditions, the low metal loading in the catalyst and its small amount required for the tests offer a sustainable route for the glycerol valorisation to value-added chemicals.

2. EXPERIMENTAL

Catalysts Preparation and Characterization

A series of monometallic gold and copper catalysts supported on γ -alumina was prepared by incipient wetness impregnation. Different bimetallic Au-Cu formulations were also synthesized for comparison.

Gold supported on γ -alumina catalysts (0.5, 1 and 2.5 wt% Au nominal loading, γ -Al₂O₃ from BASF, D10-10, particle size 0.4–0.8 mm, A_s = 264 m²/g, V_p = 0.59 mL/g) were prepared using the incipient wetness method. Gold precursor (HAuCl₄ aqueous solution, 50 mg/mL of Au), was prepared dissolving Au of 99.9999 in sponge from Fluka in *aqua regia* and diluted to the appropriate volume with ultrapure deionized water MilliQ®. After thermal pre-treatment of alumina at 300°C in air flow (20 ml/min) for 2h, determined aliquots of chloroauric acid solution (0.10, 0.20 or 0.50 mL according to 0.5, 1 or 2.5 wt% gold loading respectively) were impregnated onto 1 g of γ -Al₂O₃ while mixing with a glass rod for 10 min. The resulting powder was then contacted with a freshly prepared aqueous solution of sodium borohydride to reduce Au³⁺ to Au (NaBH₄ 99.0% purity from Aldrich, 0.1 M NaBH₄ aqueous solution) with Au:NaBH₄ weight ratio = 1. The suspension was kept on stirring at room temperature for 10 min. Due to the reported detrimental effect of chloride to obtaining small and active gold nanoparticles [19], the solid product was thoroughly washed with water until washings contained no chloride. Thereafter, the catalyst was dried in oven at 120°C for 1 h. Copper supported on γ -alumina catalyst (1%wt nominal loading Cu/Al₂O₃) was prepared

following the same incipient wetness impregnation procedure but with some differences. Copper precursor (Cu(NO₃)₂·3H₂O from Sigma-Aldrich, 98–103%) was dissolved in water to achieve a 20 mg/mL aqueous solution. After impregnation of 0.50 mL copper solution onto 1g γ -Al₂O₃, 0.8 mL of ammonia aqueous solution (30% NH₃ from Sigma-Aldrich) was contacted with the powder and stirred for 10 min long. Copper reduction was then performed by H₂ (99.99% from SIAD, 5 mL/min) at 350°C for 1h directly on the continuous-flow fixed-bed reactor used for the catalytic tests. Bimetallic catalysts with two different Au–Cu molar ratios (1:1 and 1:4) were prepared as above. Mixtures of HAuCl₄ and Cu(NO₃)₂ aqueous solutions were used as metal precursors of the catalysts with a nominal total metal loading of 1%wt on γ -alumina. The metal content in the catalysts was confirmed by inductively coupled plasma analyses (ICP), while N₂-adsorption was conducted at -196°C (Brunauer–Emmett–Teller method or BET) using a Micromeritics Tristar analyser for determining the specific surface area of selected samples. X-ray powdered diffraction (XRPD) was performed using a Rigaku Miniflex 600 diffractometer with Cu K α radiation (λ = 0.1541 nm), acquiring data in the 5–80° 2 θ range with a step size of 0.05° and a counting time of 8 s per step.

TEM images were acquired using a FEI Talos instrument operated at 200 kV. Powdered sample was deposited on Mo-grids as such.

Scheme 1: Continuous-flow fixed-bed vertical glass reactor setup.

Scheme 3: Glycerol dehydration pathway.

dehydration product under these conditions. A first preliminary test over 1%wt Au/Al₂O₃ (0.1 g) was performed at 250°C, under N₂ flow (20 mL min⁻¹) and 1 mL h⁻¹ glycerol. The low temperature prevented from reaching adequate conversion (only 26%) but, interestingly, selectivity to pyruvaldehyde (65%) prevailed over acetol (34%). In order to address the selectivity to acetol, H₂ (2 mL min⁻¹) was added to N₂ (18 mL min⁻¹). As evinced from Scheme 2, dihydrogen can shift the acetol/pyruvaldehyde *equilibrium* direction towards acetol. Actually the results confirmed the forecast just at 250°C, but a further beneficial effect in terms of conversion and selectivity to acetol was registered at higher temperatures (Table 1). Worth noting, 71.8 % selectivity to acetol at 87.0 % conversion was yielded at 300°C, together with 12.0 % pyruvaldehyde and 16.2 % of acrolein, acetic acid and glycerol oligomers.

To assess the effect of gold loading, the tests were repeated over 0.5% and 2.5%wt Au/Al₂O₃ catalysts. The results are summarized in Tables 2 and 3.

Comparing the catalysts performance at 300°C, conversion was always above 85% but selectivity to acetol decreased to 64.8% over 0.5%wt Au/Al₂O₃ and to 46.2% over the highest metal loading catalyst. Consequently, 1%wt Au/Al₂O₃ was taken as the catalyst of choice for further assessment, including a comparison with the copper catalyst (1%wt Cu/Al₂O₃) (Table 4) and thereof bimetallic formulations, 1%wt Au-Cu (1:1)/Al₂O₃ and 1%wt Au-Cu (1:4)/Al₂O₃.

Lower selectivity to acetol (51.5%) at lower conversion (80.7%) was achieved over 1%wt Cu/Al₂O₃ with respect to the gold catalyst at the same metal loading and temperature (300°C), as evinced by comparing Tables 1 and 4. Alloying gold with a second

Table 1: Glycerol Dehydration and Product Selectivity over 1%wt Au/Al₂O₃ as a Function of Temperature. Reaction Conditions: *P* = 1 bar, Catalyst = 0.1 g, Glycerol = 1 mL h⁻¹, N₂ = 18 mL min⁻¹, H₂ = 2 mL min⁻¹. 'Others' Refers to Acrolein, Acetic Acid, Glycerol Oligomers

T [°C]	Conversion %	Selectivity to Pyruvaldehyde %	Selectivity to Acetol %	Others %
250	30.2	31.4	41.4	27.2
270	57.1	25.1	52.2	22.7
280	67.0	21.7	57.1	21.2
300	87.0	12.0	71.8	16.2

Table 2: Glycerol Dehydration and Product Selectivity over 0.5%wt Au/Al₂O₃ as a Function of Temperature. Reaction Conditions: *P* = 1 bar, Catalyst = 0.1 g, Glycerol = 1 mL h⁻¹, N₂ = 18 mL min⁻¹, H₂ = 2 mL min⁻¹. 'Others' Refers to Acrolein, Acetic Acid, Glycerol Oligomers

T [°C]	Conversion %	Selectivity to Pyruvaldehyde %	Selectivity to Acetol %	Others %
250	31.5	32.4	37.0	35.9
270	55.1	28.6	39.5	34.0
280	67.5	19.9	52.8	31.9
300	85.4	14.0	64.8	28.1

Table 3: Glycerol Dehydration and Product Selectivity over 2.5%wt Au/Al₂O₃ as a Function of Temperature. Reaction Conditions: *P* = 1 bar, Catalyst = 0.1 g, Glycerol = 1 mL h⁻¹, N₂ = 18 mL min⁻¹, H₂ = 2 mL min⁻¹. 'Others' Refers to Acrolein, Acetic Acid, Glycerol Oligomers

T [°C]	Conversion %	Selectivity to Pyruvaldehyde %	Selectivity to Acetol %	Others %
250	36.8	33.7	50.2	16.1
270	56.3	41.4	40.3	18.3
280	61.7	36.1	49.4	14.5
300	88.3	36.7	46.2	17.1

Table 4: Glycerol Dehydration and Product Selectivity over 1%wt Cu/Al₂O₃ as a Function of Temperature. Reaction Conditions: *P* = 1 bar, Catalyst = 0.1 g, Glycerol = 1 mL h⁻¹, N₂ = 18 mL min⁻¹, H₂ = 2 mL min⁻¹. 'Others' Refers to Acrolein, Acetic Acid, Glycerol Oligomers

T [°C]	Conversion %	Selectivity to Pyruvaldehyde %	Selectivity to Acetol %	Others %
250	36.8	44.9	40.1	15.0
270	49.7	41.7	41.6	16.6
280	73.8	34.4	44.0	21.6
300	80.7	15.8	51.5	32.7

metal (*i.e.* Cu and Pt) has been demonstrated to enhance gold catalytic performance, especially in the selective oxidation of alcohols and aldehydes [20-22]. Moreover, the possibility to decrease gold amount by adding a cheaper metal as copper could be welcome in view of a potential industrial application. Due to our expertise in gold-based bimetallic catalysts, we decided to explore two gold-copper formulations, 1%wt Au-Cu (1:1)/Al₂O₃ and 1%wt Au-Cu (1:4)/Al₂O₃ under the same experimental conditions. Differently from our previous experience, no marked benefit in using bimetallic catalysts was detected and monometallic gold was confirmed to be superior especially in terms of selectivity to acetol. To better visualize the performance at 300°C of all the catalysts, a series of histograms is reported in Figure 1.

Regarding the two bimetallic formulations, 1%wt Au-Cu (1:1)/Al₂O₃ allowed to direct selectivity more to the desired acetol than to a mixture of other dehydration/oxidation/oligomerization products (namely acrolein, acetic acid and glycerol oligomers). Conversely, increasing copper with respect to gold led to a selectivity dispersion in line with what observed employing copper monometallic catalyst (Figure 1 B-D). The reasons might be multiple. Copper and gold exhibit two different redox potentials ($E^\circ_{\text{Au}^+/\text{Au}} = 1.69 \text{ V}$ and $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$) which also impact differently on their catalytic activity and stability.

Copper, in fact, can be more easily oxidized than gold to such an extent that its initial zero oxidation state might not be retained before starting the catalytic tests. Another key point is the role of the supporting material, γ -Al₂O₃. The choice of alumina was suggested by literature reports indicating that glycerol dehydration to acetol is favored by Lewis-acid sites [18]. In principle, the impregnation of the support with metal precursors could alter its Lewis and Brønsted acidity. Regarding this latter, the potential replacement of protons at ion-exchange positions with the metal cations might change Brønsted acidity. Accordingly, the different electronegativity of the metals could slightly alter the acidic nature of H atoms of hydroxyl groups. Such hypotheses should be underpinned by advanced analytical characterization, which is beyond the scope of a brief research communication but planned for a future assessment study. As far as basic characterization is concerned, XRPD diffractograms were collected over the monometallic catalysts (Au and Cu) and the best bimetallic formulation in terms of selectivity (Au:Cu = 1:1), before and after the dehydration reaction at 300°C (Figure 2 A-C). The supporting material γ -Al₂O₃ as such was always included for comparison. The crystalline phases were identified by comparing the diffraction patterns with those present in ICDD database (International Centre for Diffraction Data, www.icdd.com). The diffraction patterns of γ -Al₂O₃ display three major peaks at 2 θ

Figure 1: Comparison among the catalysts in the glycerol dehydration at 300°C over 1%wt Au/Al₂O₃, 1%wt Cu/Al₂O₃, 1%wt Au-Cu (1:1)/Al₂O₃ and 1%wt Au-Cu (1:4)/Al₂O₃ catalysts. **A)** conversion (%); **B)** selectivity to pyruvaldehyde (%); **C)** selectivity to acetol (%) **D)** Others (%) refers to acrolein, acetic acid, glycerol oligomers. Reaction conditions: $T = 300^{\circ}\text{C}$, $P = 1$ bar, catalyst = 0.1 g, glycerol = 1 mL h⁻¹, N₂ = 18 mL min⁻¹, H₂ = 2 mL min⁻¹.

equal to 37.1°, 45.9° and 67.0° (Figure 2 A-C). These correspond to reflections of γ -Al₂O₃ crystal planes (311), (400) and (440), respectively. No peaks for Cu diffraction or cupric oxide were observed in 1% Cu/Al₂O₃ either before or after use, thus suggesting that the metal was in amorphous state or maybe highly dispersed on support (Figure 2B). Regarding gold, its nanocrystals present four distinct peaks at $2\theta = 38.1^{\circ}$, 44.3° , 64.5° and 77.7° corresponding to standard Bragg reflection (111), (200), (220) and (311) of face centered cubic lattice. Despite alumina major peaks overlapping, the first three peaks of gold are able to emerge in 1% Au/Al₂O₃ catalyst (Figure 2A). The fourth typical peak at $2\theta = 77.7^{\circ}$ is particularly evident since alumina presents no reflection in this area. After use, some gold peaks (namely at $2\theta = 38.1^{\circ}$ and 77.7°) look slightly sharper than in the 'fresh' catalyst likely due to nanoparticle size growth as confirmed by TEM image (see later on, Figure 4). The bimetallic catalyst displays distinctly the first and fourth peaks of gold at $2\theta = 38.1^{\circ}$ and 77.7° , whereas the intermediate ones (44.3° and 64.5°) are not detectable as well as copper peaks.

The specific surface area of the supporting material γ -Al₂O₃ is in line with the typical value reported in literature for gamma alumina ($A_s = 264$ m²/g by BET method). The metal impregnation led to only minor

modification in the surface area of all the samples, thus suggesting a good metal dispersion in particular in the case of gold, alone or alloyed with copper (Table 5).

Table 5: Specific Surface area Determined by N₂-Adsorption at -196°C (Brunauer-Emmett-Teller Method) over γ -Al₂O₃ and the Catalysts as-Prepared (1%wt Au/Al₂O₃; 1%wt Cu/Al₂O₃ and 1%wt Au-Cu (1:1)/Al₂O₃)

Sample	A_s (m ² /g)
γ -Al ₂ O ₃	264
1%Au/Al ₂ O ₃	226
1%Cu/Al ₂ O ₃	216
1%Au-Cu (1:1)/Al ₂ O ₃	227

Since 1%wt Au/Al₂O₃ emerged as the catalyst with the best overall performance in glycerol conversion to acetol, it was selected to carry out even the second step towards pyruvaldehyde.

Dehydrogenation to Pyruvaldehyde

A key product derived from glycerol dehydration and subsequent dehydrogenation of acetol is pyruvaldehyde. As a strategy to shift the acetol/pyruvaldehyde equilibrium towards the

Figure 2: XRPD patterns before and after glycerol dehydration at 300°C over: **A)** 1%wt Au/Al₂O₃; **B)** 1%wt Cu/Al₂O₃ and **C)** 1%wt Au-Cu (1:1)/Al₂O₃. The supporting material γ -Al₂O₃ is always included for comparison.

aldehyde, dioxygen was added to the carrier dinitrogen. Accordingly, the formation of H₂O from the reaction between O₂ and the withdrawn H₂ is supposed to push the *equilibrium* to the right (Scheme 4).

In order to confirm such hypothesis, 1%wt Au/Al₂O₃ (0.1 g) was tested in the oxidehydration of glycerol at 250°C, glycerol 1 mL h⁻¹ and tuning O₂/glycerol molar ratio (around 0.5-4) as well as the total gaseous flow (N₂+O₂, from 20 to 100 mL min⁻¹). The best performance was registered with a O₂/glycerol molar ratio around 4, that is markedly higher than the

stoichiometric one, at total gaseous flow of 70 mL min⁻¹. Under these conditions, 78.8% selectivity to pyruvaldehyde and 12.5% to acetol at 91.8% conversion was yielded. Notably, this was achieved at a lower temperature (250°C) and catalyst amount with respect to the presently reported ones [18].

As it is crucial that catalysts can be re-used over many reaction cycles, the stability of 1%wt Au/Al₂O₃ was evaluated at the optimal experimental conditions in a 9h-run (Figure 3).

Scheme 4: Oxidehydration of glycerol to pyruvaldehyde.

Figure 3: Conversion and product selectivity as a function of the time-on-stream in glycerol oxidehydrogenation over 1%wt Au/Al₂O₃ during: **A)** the first 9h-run; **B)** the second 9h-run after catalyst regeneration. Reaction conditions: $T = 250^{\circ}\text{C}$, $P = 1$ bar, catalyst = 0.1 g, glycerol = 1 mL h^{-1} , $\text{N}_2 = 50\text{ mL min}^{-1}$, $\text{O}_2 = 20\text{ mL min}^{-1}$. Others (%) refers to acrolein, acetic acid, glycerol oligomers.

Over the first 9h-run, both conversion and selectivity to pyruvaldehyde retained their initial high values for 4 h long, afterwards conversion slightly decreased whereas selectivity moderately increased up to 8 h. During the last hour, a drop in pyruvaldehyde selectivity was detected, together with an increase in acrolein, acetic acid and glycerol oligomers. This minor loss of conversion could be ascribed to the deposition of carbonaceous species and/or sintering of gold. TEM micrographs of the catalyst before and after the 9h-lifetime test highlighted the robustness of the material since only a negligible sintering could be observed. The average nanoparticles diameter slightly changed from 3.1 to 4.7 nm (Figure 4 A, B).

More likely the catalyst underwent a slight fouling. To confirm this, 1%wt Au/Al₂O₃ was regenerated by keeping it in the flow fixed-bed reactor under dioxygen (20 mL min^{-1}) at 300°C for 1 h long. Afterwards, a second catalytic cycle was repeated under the same experimental conditions. Actually, the initial catalytic

performance was restored and maintained over the second 9h-run similarly as the first run (Figure 3B).

CONCLUSIONS

In this short communication, we have presented our preliminary study aiming to dictate selectivity towards acetol or pyruvaldehyde by vapor-phase oxidehydrogenation of glycerol over the same catalyst by simply tuning temperature, $\text{N}_2/\text{H}_2/\text{O}_2$ ratios and gas flow rate thereof. A series of mono- and bimetallic gold and copper on alumina catalysts was prepared and tested in a continuous-flow fixed-bed vertical glass reactor. Among them, 1%wt Au/Al₂O₃ stood out for directing selectivity to acetol (72%) at 87% conversion when adding dihydrogen to the carrier dinitrogen at 300°C , or towards pyruvaldehyde (sel. 79%) at 92% conversion and 250°C if adding dioxygen to dinitrogen. To the best of our knowledge, only a few studies deal with vapor-phase oxidehydrogenation to pyruvaldehyde and generally require higher temperature and catalyst

Figure 4: TEM micrographs of 1%wt Au/Al₂O₃ A) before the first 9h-run ('fresh catalyst'); B) after the first 9h-run ('used catalyst').

amount. Hence, the present process not only allows for energy savings but also for a good catalyst stability, since it is easily restored after use. Furthermore, the low metal loading in the catalyst and its small amount requested for the tests widely compensate the higher

cost for gold with respect to cheaper metals. In conclusion, the reported results may offer a contribute to glycerol valorisation and can stimulate further insight in future studies.

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