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Oxidation of mono- and polyalcohols with gold: Comparison of carbon and ceria supported catalysts

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Abstract

Aim of this work is the investigation of the gold catalysed liquid-phase oxidation of polyalcohols with both, primary and secondary alcohol groups, in order to evaluate the potential of gold catalysts to oxidise a secondary alcohol group in presence of a primary group. For that purpose we investigated the heterogeneously catalysed liquid-phase oxidations of *n*-propanol, as reference for the oxidation of the primary alcohol group only, of propylene glycol, where the competitive reaction can be examined and finally of glycerol, which is the target reaction due to known economic aspects. We report on the performance of ceria supported gold catalysts in these reactions and discuss the results in dependency of the specific surface area of the support, the catalyst and support preparation method and the catalyst activation conditions. Finally, in order to estimate the relative activity and selectivity of the ceria supported catalysts we compared the catalytic results with the performance of carbon and titania supported gold catalysts.

Keywords: Liquid-phase oxidation; Monoalcohol; Polyalcohol; Supported gold catalysts; LSA-ceria; HAS-ceria; *n*-Propanol; Propylene glycol; Glycerol

1. Introduction

Ceria supported catalysts are well known in gas-phase oxidation reactions as reported in abundant communications [1–6]. These catalysts are particularly efficient in exhaust gas catalysis and have achieved much more interest since successfully low-temperature CO oxidations [2,3]. Noble metal supported on ceria are recently also used in liquid-phase oxidation reactions but only a few examples are known [7,8]. Corma et al. have paid more attention to Au/CeO_2 catalysts and investigated their performance in different monoalcohol liquid-phase oxidations. It arises from this study that ceria supported gold catalysts (i) are highly active in the investigated oxidation reactions and (ii) the activities correlate with the specific surface area of the ceria support. They showed that the efficiency of the catalysts can be improved by using ceria supports with high specific surface areas and attributed this behaviour to a cooperative effect between gold and ceria. However, this effect has not been investigated in polyalcohol oxidation reactions. Interesting to examine is the attributed strong cooperative effect in a polyalcohol oxidation reaction, where the competitive reaction between oxidation of the primary and the secondary alcohol group could provide more information about the particularity of this system. To the best of our knowledge, the described cooperative effect in Au/CeO_2 is unknown in polyalcohol oxidation reactions.

In this work we investigated the performance of gold supported on different ceria materials in the oxidation of (i) *n*-propanol, as reference for the monoalcohol oxidation, of (ii) propylene glycol, in order to investigate the competitive reaction and finally of (iii) glycerol, which is the target reaction with a much more complex reaction network. In fact, the revalorisation of glycerol, the over-supplied main by-product of oleochemistry, has significant potential by, amongst others [9–13], its selective oxidation to valuable

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Abbreviations: SSA, specific surface area; LSA, low specific surface area; MSA, middle specific surface area; HAS, high specific surface area; GS, gold-sol method; DPU, deposition-precipitation method with urea; Ox, oxidative activation of the catalyst; Red, reductive activation of the catalyst; THPC, tetrakis(hydroxymethyl)phosphium chloride; t_{ads}, adsorption time of the gold particle on the support; XC72; NSXU; NSX1G, activated carbons; BP, black pearls; CeO_2-*T*, CeO_2 prepared according to Trovarelli et al. [17]; CeO_2-*S*, CeO_2 prepared according to Flytzani-Stephanopoulos and coworkers [18]

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compounds as glyceric acid and dihydroxyacetone [14–16]. We present the gold catalysts properties in these oxidation reactions depending on (i) the used support; (ii) the preparation method of the ceria support; and (iii) the catalyst preparation method. We also investigated the relative performance of the Au/CeO_2 catalysts and compared them for that purpose with carbon and titania supported gold catalysts prepared in our laboratory.

2. Experimental

2.1. Catalyst preparation

2.1.1. Materials

NaOH 0.2 M (>99%), tetrakis-(hydroxymethyl)-phosphonium chloride (THPC, 78 wt.%) from Merck and $HAuCl_4 \cdot 3H_2O$ (99.99% ACS, Au 49.5% min) from Alfa Aesar were used. The carbon black "Black Pearls 2000" (BP) was purchased from Cabot GmbH; glycerol (>99%), $CeCl_3 \cdot 7H_2O$ (99.9%), CeO_2 nanopowder, Cetyltrimethylammonium bromide $CH_3(CH_2)_{15}$-$N(Br)(CH_3)_3$ (98%), *n*-propanol (99.5%) and propylene glycol (99%) from Sigma–Aldrich; urea (99.5%) and $(NH_4)_2Ce(NO_3)_6$ from Roth. The activated carbons (AC) NSX1, NSX1G and NSXU were from Norit.

2.1.2. Preparation procedure

Gold catalysts were prepared on carbon, TiO_2 and different CeO_2 materials. The purchased CeO_2 supports have small (<10 m^2/g) or middle (50 . . . 130 m^2/g) specific surface area. In order to evaluate if the activity of Au/CeO_2 correlates with the specific surface area of the support we also prepared high surface area CeO_2 according to [17,18].

2.1.2.1. Preparation of high surface area CeO_2. In order to improve the surface area of the ceria support a large number of homogeneous precipitation techniques have been elaborated [19–22]. We prepared CeO_2 by two methods: by the precipitation method developed by Trovarelli and coworkers [17] and the so called "urea gelation" method according to Flytzani-Stephanopoulos and coworkers [18].

In a typical preparation according to [17], a solution containing the ceria precursor (11.2 g $CeCl_3 \cdot 7H_2O$) and the surfactant (9.4 g cetyltrimethyl ammonium bromide) in 550 ml distilled water is stirred at room temperature. In 150 min 250 ml of aqueous ammonia solution (25%) are added to the solution which is then stirred for 1 h at room temperature and then heated to 90 °C. At this temperature the suspension is heated for further 90 h and then filtered, washed with 3 l distilled water and 1 l acetone, dried and finally calcinated with air (180 ml/min) at 350 °C for 3 h.

By the urea gelation method 20 g of the cerium salt $(NH_4)_2Ce(NO_3)_6$ are dissolved in 500 ml distilled water and the stirred solution is then heated to 90 °C. 250 ml of a 3 M urea solution are then added drop wise within 60 min. After 8 h precipitation time, the resulting gel is then filtered with 2 l distilled water, dried under vacuum at 100 °C for 3 h and finally calcinated with air (100 ml/min) at 400 °C for 4 h.

2.1.2.2. Preparation of the supported gold catalysts. The gold catalysts were prepared via two methods: the gold-sol method (GS) with THPC as reducing and stabilising agent and via a deposition-precipitation method using urea as precipitation agent (DPU method). These techniques were employed to prepare 1 wt.% gold catalysts supported on the investigated materials and are described elsewhere [16,23]. In the present study the activation conditions of the catalyst were also investigated so that both activations described in our previous study [16], namely (i) reductive and (ii) oxidative, were tested for each prepared catalyst and discussed in terms of activity and selectivity. Also examined was the influence of the adsorption time (t_{ads}) by the gold-sol method, i.e. the immobilisation time of the gold particle onto the support before filtering the suspension, on the catalyst properties and performance.

2.2. Catalyst characterisation

The gold content of the prepared catalysts was determined with ICP-OES analysis. The morphology of the gold particles was examined by transmission electron microscopy (TEM, Philips CM 20 Ultra Twin 200 kV and HRTEM JEOL, JEM 3010 300 kV) and the mean diameter was calculated by counting at least 300 particles onto the micrographs. N_2 physisorption measurements have been performed with Autosorb 3B (Quantachrome). Characteristic data of the investigated supports are given in Table 1.

2.3. Oxidation experiments

The oxidation experiments were carried out under atmospheric pressure in a 300 ml semi-batch glass reactor equipped with an automated titrator (Metrohm 720-KFS-Titrino) providing continuous pH control during the reaction time and with a four baffle propeller. The reactions were performed, unless otherwise mentioned, with 150 ml of an 1.5 M aqueous alcohol solution at constant pH of 12, with a molar ratio educt/gold of 2460, at an oxygen flow rate of 300 ml/min (checked over a mass flow controller), at 60 °C and a stirring rate of 500 runs per minute (rpm). It is clear that under the experimental conditions not the free acids but the salt of them are produced. Accordingly to the basic conditions, the main products obtained in the oxidation of *n*-propanol, propylene glycol and glycerol are propionate, lactate and glycerate, respectively.

2.4. Analysis of products

The quantitative analyses of the reaction mixtures were performed by high performance liquid chromatography (HPLC) as detailed described elsewhere [23].

Table 1
Specific Surface Area (SSA) of some investigated supports

Support	LSA-CeO_2	MSA-CeO_2	HSA-CeO_2-*T*	HSA-CeO_2-*S*	TiO_2	BP
SSA (m^2/g)	4	60	130	170	55	1300

3. Results and discussion

3.1. Catalyst preparation

3.1.1. Preparation of high surface area CeO_2

By preparing ceria supports according to [17,18] high specific surface areas (HSA) were successfully obtained as the results of physisorption measurements demonstrate (Table 1). The adsorption isotherms of the HSA-CeO_2 are those expected for mesoporous materials. The radial pore size distribution of the CeO_2 supports prepared by the precipitation method according to Trovarelli et al., HSA-CeO_2-*T*, shows the expected pore structure (mean pore diameter = 10.2 nm) in contrary to HSA-CeO_2-*S* (prepared by urea gelation method according to Flytzani-Stephanopoulos et al.) which shows a narrow size pore distribution (mean pore diameter = 5.4 nm). TEM micrographs of CeO_2 materials are shown (Figs. 1 and 2) to point out the difference in the structure depending on the specific surface area. It arises that the structure of HSA-CeO_2, in contrary to LSA supports, is formed by agglomeration of the nanocrystallites. Moreover, by examining the preparation conditions of HSA-CeO_2 it follows that the concentration of the cerium precursor (and consequently the dilution volume) is a factor with important impact on the SSA of the final CeO_2. In fact, by increasing the precursor concentration of 0.48 to 0.96 M, SSA is decreasing from 135 to 82 m^2/g.

3.1.2. Gold catalysts preparation

Gold nanoparticles were successfully prepared on the different investigated supports by both (i) the gold-sol method and (ii) the deposition-precipitation method with urea. The mean diameters of the particles were estimated by TEM and HRTEM (Fig. 3) and were calculated to 2–5 nm.

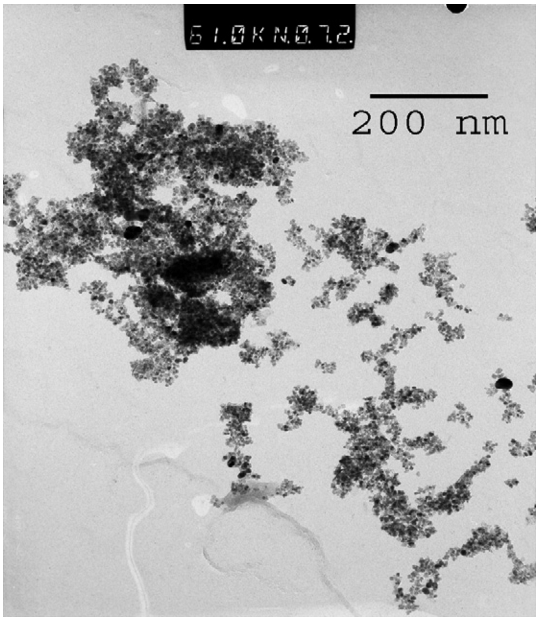

Fig. 1. TEM micrograph of HSA-CeO_2-*T*.

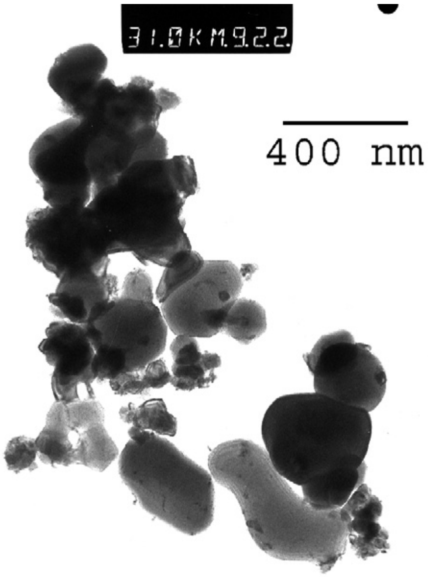

Fig. 2. TEM micrograph of LSA-CeO_2.

Table 2
Selectivities of 1Au/HSA-CeO_2 in dependency of the preparation method of ceria

	$S_{\text{glyceric acid}}$ (%)	$S_{\text{dihydroxyacetone}}$ (%)	$S_{\text{tartronic acid}}$ (%)
1Au/HSA-CeO_2-*S*	38	29	8
1Au/HSA-CeO_2-*T*	43	25	8

Reaction conditions: 150 ml of a 1.5 M glycerol solution, glycerol/Au = 2460 [mol/mol], pH 12, $p_{O_2} = 1$ bar, rpm = 500.

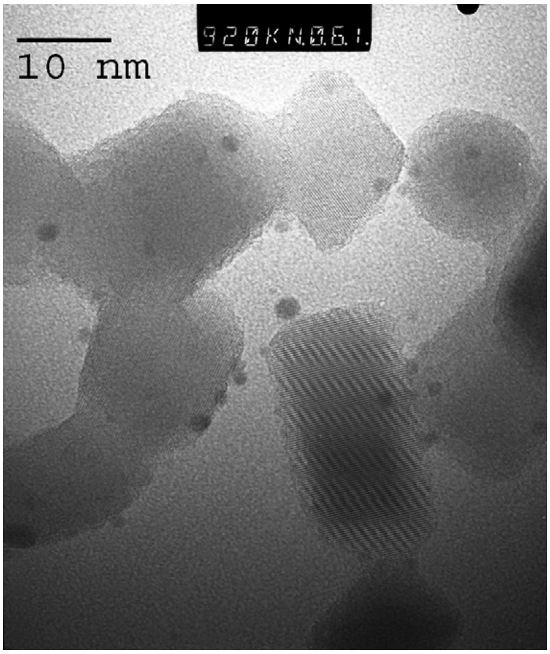

Fig. 3. HRTEM micrograph of 1Au/TiO_2.

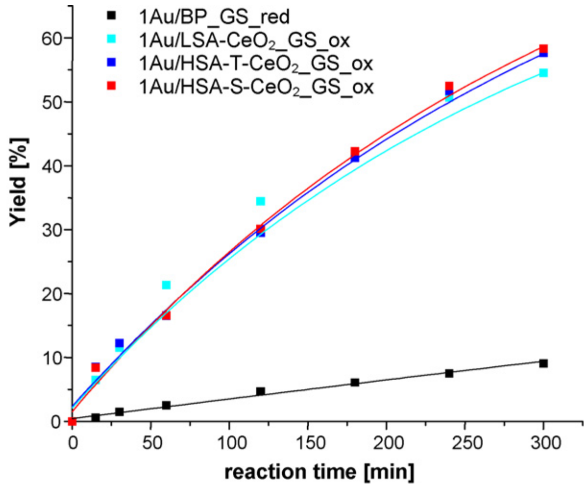

Fig. 4. *n*-Propanol oxidation: yield to propionate depending on the catalyst. Reaction conditions: [*n*-Propanol]$_0$ = 1.5 M, educt/Au [mol/mol] = 2460, pH = const = 12, T = 60 °C, $p_{O_2} = 1$ atm.

3.2. *n*-Propanol oxidation

In order to firstly check the activity of the prepared catalysts in the monoalcohol oxidation, *n*-propanol was chosen as simple and glycerol corresponding monoalcohol. Under the described experimental conditions the investigated Au/CeO_2 catalysts are highly active in the *n*-propanol oxidation as shown in Fig. 4. Moreover, the conversion of *n*-propanol is almost independent on (i) the preparation method of the ceria support and (ii) the specific surface area of CeO_2 (Fig. 4). In fact, the investigated Au/CeO_2 catalysts all show approximatively the same activity in this reaction.

Furthermore, the main product which was detected is propionate. Considering the mass balance, it arises that, under these experimental conditions, also total oxidation is occurring during the reaction.

Compared to the ceria supported gold catalysts, the carbon supported catalyst is featured by its lower activity. Au/C catalysts are not often used in monoalcohol liquid-phase oxidation reactions due to the strong adsorption of the product, the corresponding acid. This irreversible adsorption of the product might be also here the reason for the observed reduced activity.

3.3. Propylene glycol oxidation

Even though propylene glycol is the simplest polyalcohol with both a primary and a secondary alcohol group, the complex reaction network of its oxidation (Fig. 5) gives an account of the functionality of this molecule.

The propylene glycol oxidation was firstly investigated under the reaction conditions described in Section 2.3. These are the reaction conditions under which the glycerol oxidation have been already investigated in previous studies [23] and have been applied for the present work. But under these mild reaction conditions no conversion could be observed even after 5 h oxidation time. The group of Prati et al. also has reported that the propylene glycol oxidation is, under comparable reaction conditions, slower than the glycerol oxidation [24].

In order to increase the reaction rate, the reaction conditions had to be adapted for the propylene glycol oxidation to the following: [propylene glycol]$_0$ = 0.3 M, educt/base molar ratio = 1, educt/Au molar ratio = 500 and T = 80 °C. In Fig. 6 the conversions of propylene glycol are shown under these experimental conditions depending on the catalyst. The carbon supported gold catalyst is more active than the catalyst supported on high surface area CeO_2. On the other side, the most important detected product, namely lactic acid, is obtained with ceria supported catalysts with higher selectivity (64% yield) than with the gold on carbon catalysts (ca. 54% yield to lactic acid). Thus, after optimising the reaction conditions, the ceria supported catalysts show high activity in the propylene glycol oxidation and the highest yield to lactic acid.

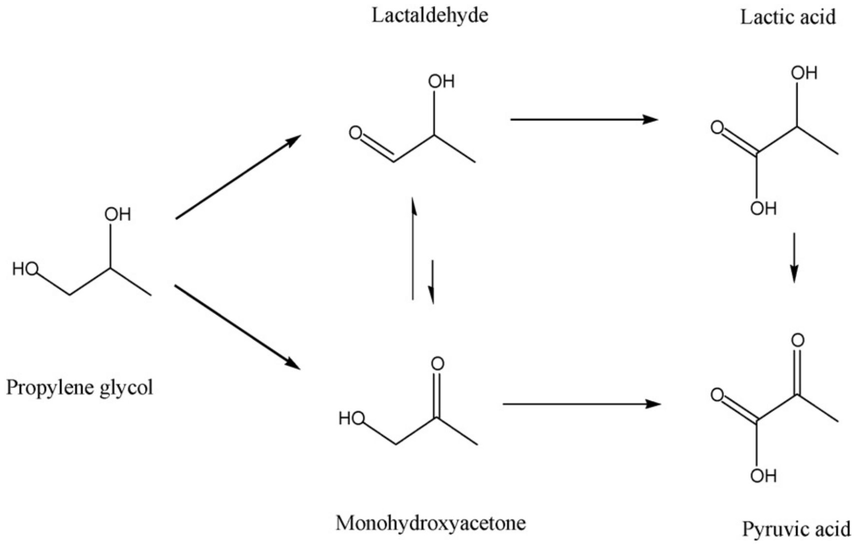

Fig. 5. Reaction network of the propylene glycol oxidation.

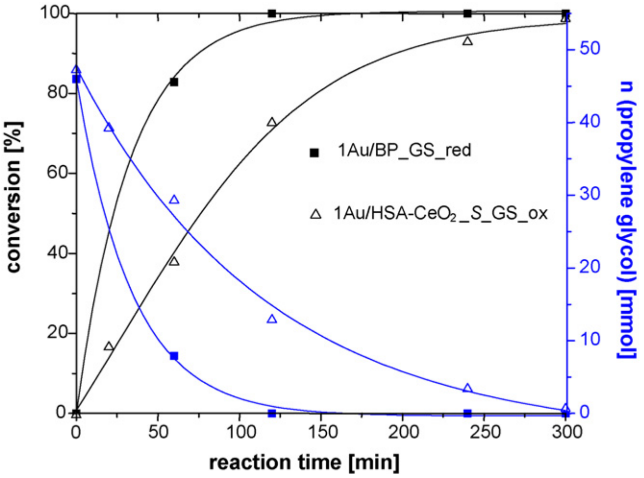

Fig. 6. Propylene glycol conversion depending on the catalyst. Reaction conditions: [propylene glycoll]$_0$ = 0.3 M, educt/Au [mol/mol] = 500, pH = const = 12, T = 80 °C, $p_{O_2} = 1$ atm.

3.4. Glycerol oxidation

3.4.1. Au/CeO$_2$ catalysed glycerol oxidation

The activity of CeO$_2$ supported catalysts is strongly dependent on the SSA of the support as reported for a few reactions [25,26]. We investigated this dependency in the glycerol oxidation (Fig. 7) and prepared, for that purpose, HSA CeO$_2$ supports. As the physisorption measurements confirmed (Table 1), the preparation of high surface area ceria is successfully by both employed methods. The ceria prepared by the urea gelation method has a specific surface area of 170 m^2/g and the preparation by precipitation with surfactant yield to CeO$_2$ with 130 m^2/g SSA. A comparative study of these materials in terms of activity and selectivity in the glycerol oxidation reveals that gold supported on ceria is more active when the support is prepared by the precipitation method according to Trovarelli and coworkers [17] (Fig. 8). This catalyst, 1Au/CeO$_2$-T has a high specific surface area but not the highest achieved by the different preparation methods. Moreover, the selectivity behaviour depending on the preparation method of the ceria support has also been investigated. The prepared gold catalysts show almost the same selectivities independent on the used method to improve the surface area of the oxide support (Table 2).

Ceria supports exhibiting low (4 m^2/g) and middle (60 m^2/g) specific surface areas were purchased and compared to the prepared materials. The ceria supported gold catalysts were tested in the oxidation of glycerol (Fig. 9) and attention has been paid to an eventual correlation between the activity of the different Au/CeO$_2$ catalysts and the corresponding surface area of the supports. It results from this study that the SSA of the ceria support influences the activity of the corresponding gold catalysts, as reported in the literature [7,25,26], but no direct correlation could be found. In fact, the most active catalyst was prepared on ceria providing 60 m^2/g surface area (Fig. 9). Here again, no influence of the specific surface on the selectivity behaviour could be detected. The catalysts all oxidise glycerol to the main products, namely glyceric acid and dihydroxyacetone, with respective selectivities of about 45% and 25% as shown exemplary for the 1Au/HSA-CeO$_2$ catalyst in Fig. 10.

Furthermore, the catalyst preparation method has been investigated in order to optimise the catalyst performance. For that purpose, gold catalysts supported on HSA CeO$_2$ have been prepared by the gold-sol and the precipitation-deposition method. Each catalyst has then been activated in two ways: oxidative (calcination with air,100 ml/h 4 h at 300 °C) and reductive (with H$_2$, 100 ml/h 4 h at 350 °C) and have been tested in the glycerol oxidation (Fig. 11).

First of all, this study confirms the already communicated result [23] that gold catalysts prepared by the gold-sol method are more active in the glycerol oxidation than the gold catalysts obtained by the deposition-precipitation method. As a matter of fact, here again the most active catalysts have been prepared by the gold-sol method. Hereby the adsorption time of the gold particle on the support (t$_{ads}$) has an important impact on the catalytic results. In fact, the longer the adsorption time, the lower is the activity of the corresponding catalysts (Fig. 11). After an immobilisation time of 72 h no activity at all is detected. The morphological investigation of theses catalysts shows that the gold particles grow by agglomeration with the adsorption time and this increase of the particle size correlates with the observed decrease in activity. Furthermore, the examination of the activation conditions shows that the oxidative activation (calcination in air) of the CeO$_2$ based catalyst improves the activity compared to the reduced catalysts (Fig. 11). On the basis of these results the oxidative activation was examined more in details to optimise the calcination conditions. Au/CeO$_2$ catalysts have been calcinated at 300 °C for 2, 4 and 8 h. The calcination time has almost no influence on the activity of the catalyst in the glycerol oxidation. A more interesting result reveals the investigation of the calcination temperature (Fig. 12). The highest activity is achieved with the non-activated catalyst and the activity of the Au/CeO$_2$ catalyst decreases with the calcination temperature. That is a known result for nanocristalline ceria and it has been assumed that the effect is due to a probably agglomeration at high temperature with consequently loss of active surface [27]. Thus, after preparation with the gold-sol method, the gold deposed on ceria is already active and this activity decreases if the catalyst is treated at higher temperature due to probably restructuration of the material for example by agglomeration of the metal.

3.4.2. Relative performance of Au/CeO$_2$: comparison with Au/C and Au/TiO$_2$

In a previous study we optimised the preparation conditions of carbon supported gold catalysts [23] for the glycerol oxidation. The most active gold on carbon catalysts were achieved by the gold-sol preparation with THPC as reducing agent and by reductive activation. A few Au/C catalysts have been prepared by this way and tested in the glycerol oxidation in order to estimate the relative activity of the prepared Au/CeO$_2$ catalysts. It results that the ceria supported gold catalysts are less active than the gold on carbons (Figs. 11 and 13).

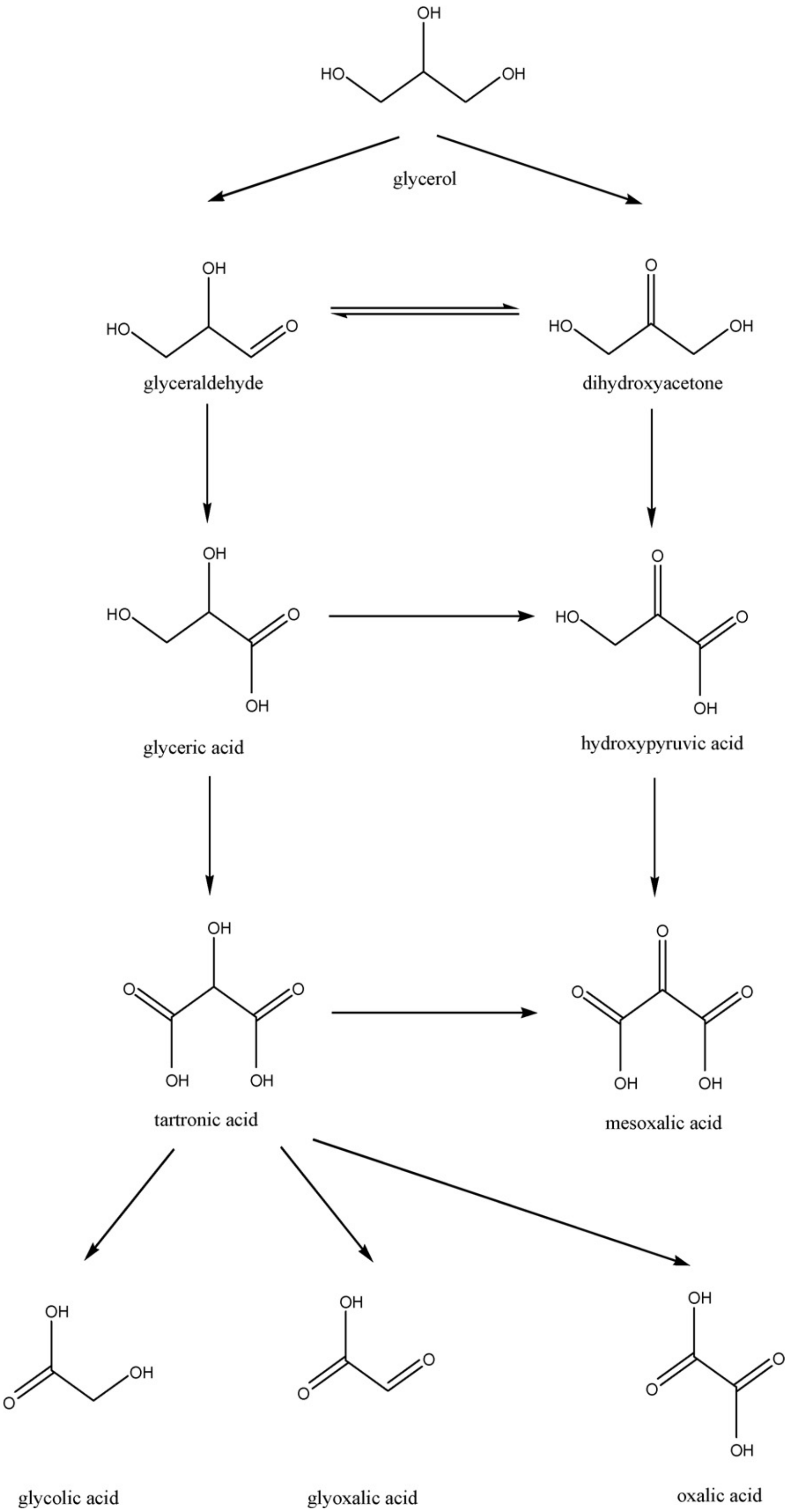

Fig. 7. Reaction network of the glycerol oxidation.

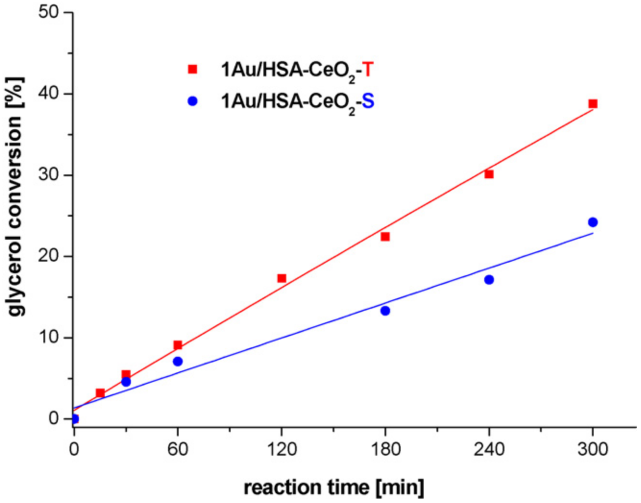

Fig. 8. Gold catalyst activity depending on the preparation method of the CeO_2 support. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\,^{\circ}C$, $p_{O_2} = 1$ atm.

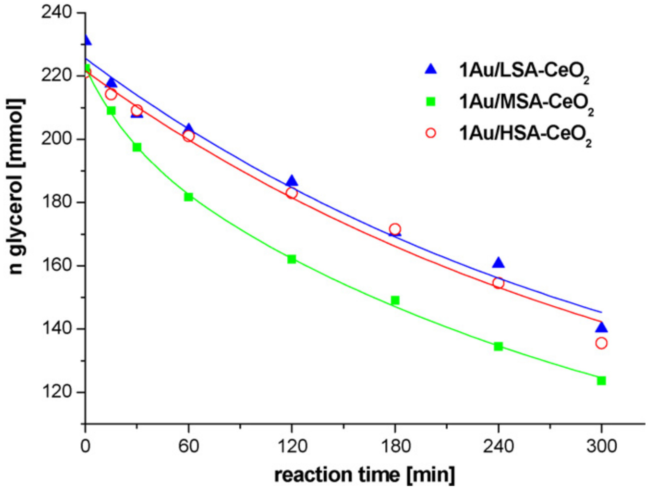

Fig. 9. Gold catalysts activity depending on the SSA of the CeO_2 support. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\,^{\circ}C$, $p_{O_2} = 1$ atm.

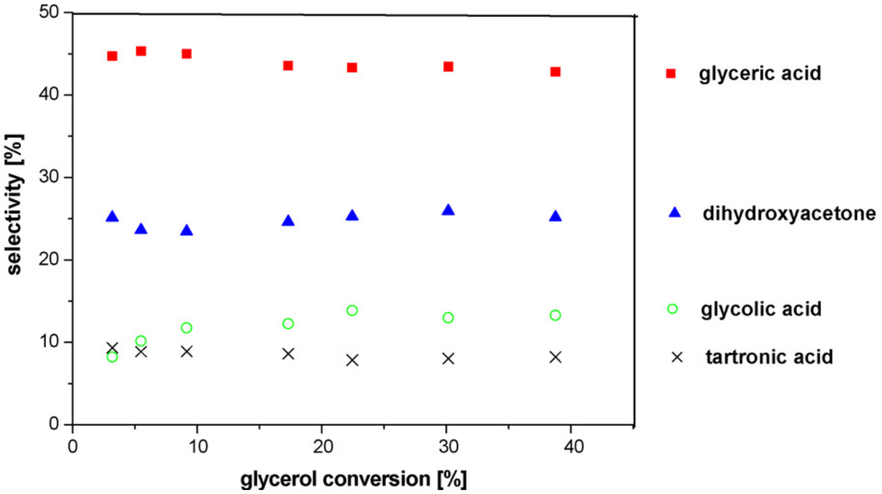

Fig. 10. Selectivity of 1Au/HSA-CeO_2-*T* catalyst depending on the conversion of glycerol. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\,^{\circ}C$, $p_{O_2} = 1$ atm.

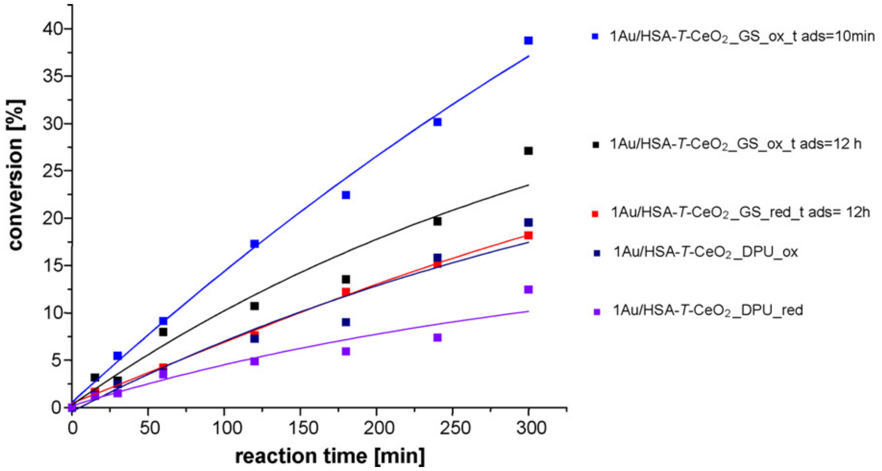

Fig. 11. Activity of 1Au/HSA-CeO_2 depending on the catalyst preparation and activation. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\,^{\circ}C$, $p_{O_2} = 1$ atm.

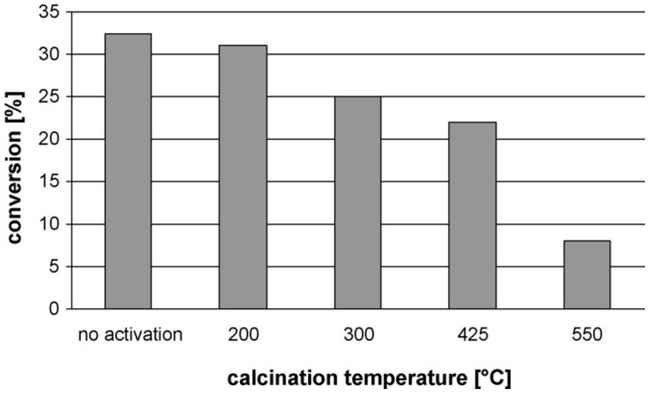

Fig. 12. Influence of the calcination temperature on the activity of 1Au/HSA-CeO_2. Reaction conditions: $[glycerol]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\ ^\circ C$, $p_{O_2} = 1$ atm.

Moreover, the recycling experiments of Au/CeO_2 have shown that gold on ceria deactivates significantly already after one reaction in contrary to the carbon supported gold catalysts. Furthermore, a comparison of the gold contain of the Au/CeO_2 catalyst on the basis of ICP analysis for and after one oxidation experiment indicates that metal leaching is occurring. On the other side, gold on TiO_2 has been prepared by the same way as ceria supported gold catalysts, i.e. by using both methods (GS and DPU) and activating the catalysts oxidative as well as reductive (Fig. 14). The results of this study confirms that gold supported on oxides is more active in the liquid-phase oxidation of glycerol if the nanoparticles are deposed on the support by the gold-sol method and then activated by calcination.

A comparative examination of the prepared catalysts (Fig. 15) finally shows that no investigated catalyst is more

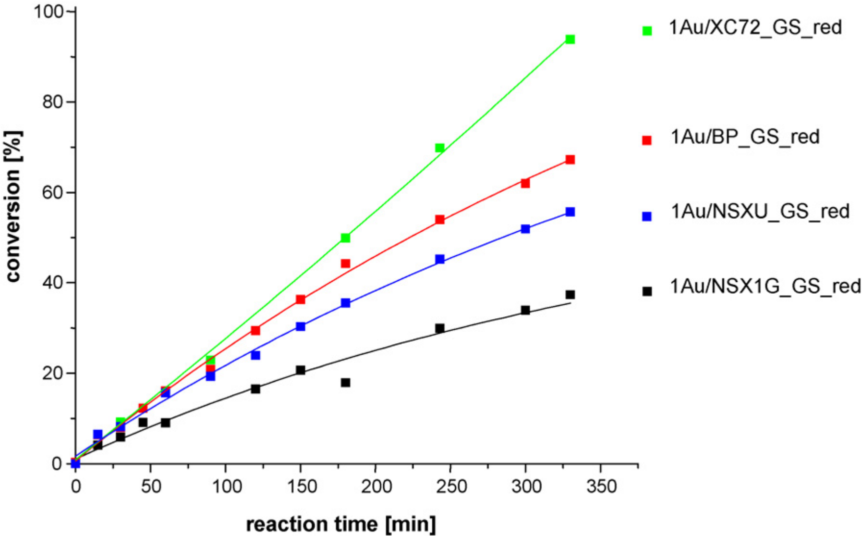

Fig. 13. Activity of Au/C in the glycerol oxidation depending on the carbon support. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\ ^\circ C$, $p_{O_2} = 1$ atm.

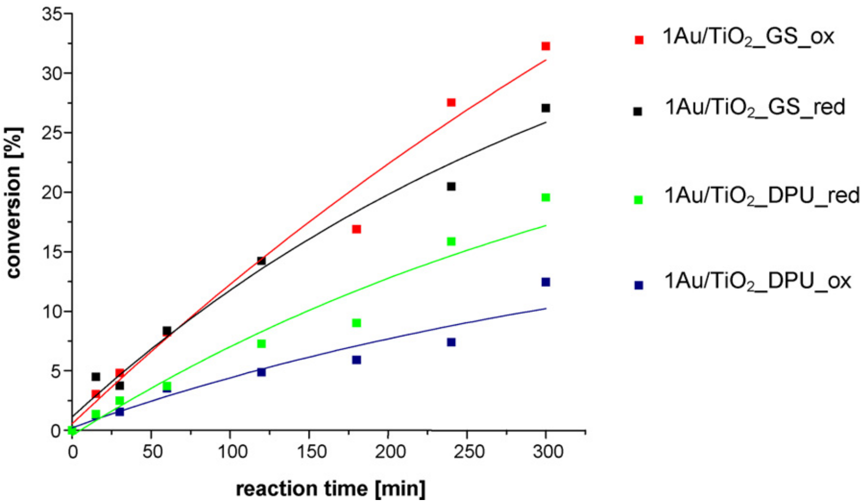

Fig. 14. Activity of 1Au/TiO_2 in the glycerol oxidation depending on the preparation method. Reaction conditions: $[glyceroll]_0 = 1.5$ M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\ ^\circ C$, $p_{O_2} = 1$ atm.

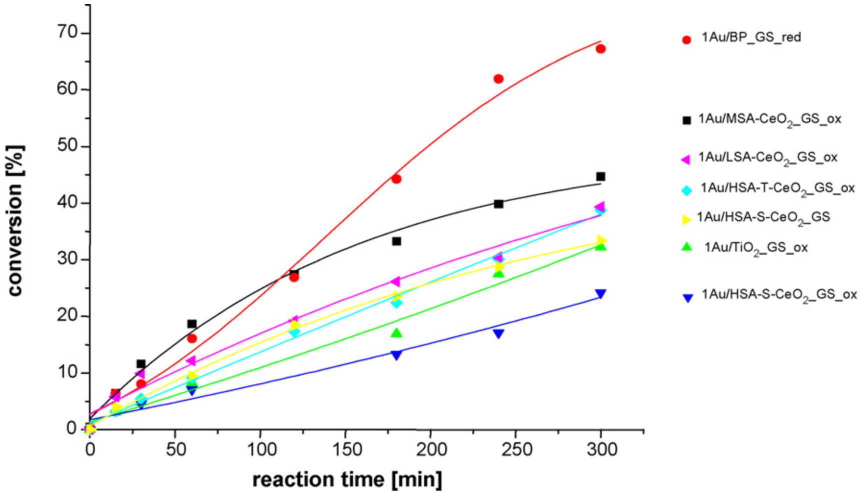

Fig. 15. Activity of supported gold catalysts in the glycerol oxidation. Reaction conditions: [glyceroll]$_0$ = 1.5 M, glycerol/Au [mol/mol] = 2460, pH = const = 12, $T = 60\,^{\circ}\mathrm{C}$, $p_{O_2} = 1$ atm.

active than the carbon supported gold catalyst in the glycerol oxidation. Furthermore, it was not possible to influence the selectivity behaviour of the Au/CeO_2 catalysts neither by the catalyst and support preparation method nor by the activation conditions. In opposition to this result, the carbon supported gold catalysts have significantly different selectivity behaviour in dependency of e.g. the carbon support [23].

4. Conclusions

The heterogeneously catalysed liquid-phase oxidation of polyalcohols, propylene glycol and glycerol has been investigated and evaluated in comparison to the oxidation of the corresponding monoalcohol, *n*-propanol. The motivation of this study is to elucidate under which catalytic conditions a secondary alcohol group can be selectively oxidised in presence of a primary group. Though the ceria supported gold catalysts were highly active in the oxidation of the investigated alcohols, the selectivity was almost independent on influencing factors as e.g. specific surface area of the support and preparation method. Only a significant change in the activity is achieved by these ways. Thus, focusing on the selective glycerol oxidation, which is the target reaction, carbon supported gold catalysts are, at the moment, still the best system to elaborate the selective glycerol oxidation. In fact, the reaction parameters and the preparation conditions of these carbon supported catalysts have an influence not only on the activity but also on the selectivity.

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