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Liquid phase oxidation of glycerol over carbon supported gold catalysts

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Abstract

The heterogeneously catalysed liquid phase oxidation of glycerol over nanosized gold particles has been investigated. The effect of the support only was studied and no glycerol conversion could be detected whereas gold nanoparticles supported on different carbons (carbon black, activated carbon and graphite) and oxides (TiO_2, MgO and Al_2O_3) were active. Under the same reaction conditions and with comparable gold particle size, the carbon supported gold catalysts are highly active in the liquid phase oxidation of glycerol. The reaction conditions have been studied in a batch reactor with oxygen as oxidant and have been optimised. The different regimes have been determined by varying, e.g. catalyst amount, stirring speed and NaOH/glycerol ratio. The apparent activation energy of the Au/C catalysed glycerol oxidation was determined. Moreover, depending on the base concentration and the reaction time, the selectivity of the Au/C catalysed liquid phase glycerol oxidation could be controlled.

The structure-sensitivity of the glycerol oxidation was examined and discussed. Experiments with Au/C catalysts with gold particle sizes in the range from 2 to 45 nm indicate clearly that the reaction is structure-sensitive. In fact, a dependence of the catalytic activity and much more of the selectivity on the gold particle size has been observed.

Keywords: Oxidation of glycerol; Gold particles; Nanosize; Carbon support; Structure-sensitivity

1. Introduction

Glycerol is a compound of all natural fats and oils in form of fatty acid esters and is an important intermediate in the metabolism of living organisms [1]. It is obtained to 90% by the splitting of triglycerides. This simplest triol is the most important by-product of oleochemistry and its supply is increasing with oleochemical production [2]. Moreover, glycerol is a highly functionalised molecule. As a matter of fact, the oxidation of glycerol leads to a complex reaction pathway and a large number of products can be obtained (Fig. 1). These products are useful intermediates for the synthesis of fine chemicals and are still being obtained by either expensive processes or by an enzymatic way. As an example, glyceric acid is a useful compound as medicine because of its role as metabolite of glycolisis in the living body and is also used as a raw material for the synthesis of optical isomers from amino acids like L-serine [3]. Some Japanese patents describe the production of glyceric acid as important intermediate in the fine chemistry by biological routes [3–5]. Stoichiometric glycerol oxidation with mineral acids, like potassium permanganate to produce tatronic acid or nitric acid which yields glyceric acid, are known but harmful to the environment [1]. Thus, the heterogeneously catalysed glycerol oxidation is an environmentally friendly alternative to produce these valuable compounds [6]. Supported Pt and Pd catalysts are generally used for polyol oxidation; however, the main disadvantage is their deactivation with increasing reaction time. An improvement of activity, selectivity and stability can be obtained in presence of a second metal (e.g. Bi) and by the nature of the individual metal. Concerning the latter, gold on activated charcoal or on oxides is frequently used for the oxidation of OH and C=O groups of alcohols and aldehydes.

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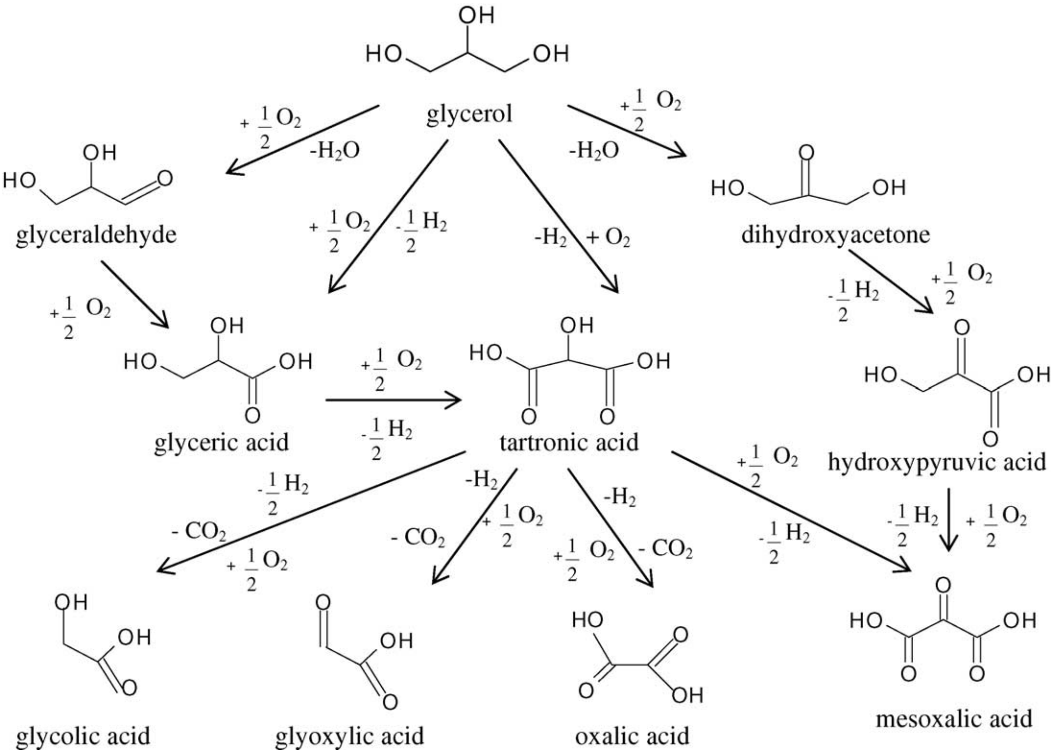

Fig. 1. Reaction network of the glycerol oxidation.

In the present work, we report on the heterogeneously catalysed liquid phase oxidation of glycerol with gold supported on carbon and show that the single steps of the oxidation pathway of glycerol can be controlled mainly via the reaction conditions and the catalyst properties. With respect to the latter, it was of special interest whether this reaction is structure-sensitive or not.

2. Experimental

2.1. Catalyst preparation

2.1.1. Materials

Urea (>99%) and magnesium citrate (>98%) from Fluka, NaOH (0.2 M), NaOH (>99%), Tetrakis-(hydroxymethyl)-phosphonium chloride (THPC, 78 wt.%) from Merck, $HAuCl_4 \cdot 3H_2O$ (99.99% ACS, Au 49.5% min), activated carbon (2 mm) and graphite (−50 + 140 mesh size) from Alfa Aesar were used. The carbon black "Black Pearls 2000" (GP 3755) was purchased from Cabot GmbH; glycerol (>99%) and MgO (>99%) from Sigma–Aldrich; Al_2O_3 (Puralox HP 14/150) from Sasol and TiO_2 (P25) from Degussa.

2.1.2. Preparation procedure

The gold catalysts were prepared via the gold-sol method with THPC as reducing agent (described below) and with a gold content in the range from 0.5 to 10 wt.% [7,8]. The deposition–precipitation method with urea was employed to prepare 1 wt.% gold catalysts supported on different materials [9].

2.1.3. Gold-sol method

First, the metallic sols were prepared: H_2O (232 ml) with 0.2 M NaOH (7.5 ml) was stirred before adding 5 ml diluted THPC (1.2 ml of the 78 wt.% solution diluted with 100 ml H_2O). After 2 min stirring, the gold aqueous solution was added. The $HAuCl_4$ concentrations were calculated according to the desired final gold content. The gold-sols were then stirred for 1 h. Aqueous suspensions of the carbon supports (1 wt.%) were agitated for 15 min in an ultrasonic bath. The gold-sols were added into the carbon suspensions and stirred for 1 h for immobilisation. The suspension was filtered, washed until the filtrate was free of chloride ($AgNO_3$ test), dried and mortared. After inert gas treatment (3 h/350 °C/N_2), the catalysts were activated by reduction (3 h/350 °C/H_2).

2.1.4. Deposition–precipitation method

A 4.2 mM aqueous solution of $HAuCl_4$ was added to a stirred 0.84 M aqueous solution of urea and heated to 80 °C while stirring. Then, a 6.9 mM solution of magnesium citrate was added. The support (carbon or magnesia) was added and the suspension was stirred by 80 °C for 4 h. The suspension was then filtered, washed until the filtrate was free of chloride ($AgNO_3$ test), dried (2 h at 100 °C under vacuum) and mortared. The catalysts were activated by calcination with air at 300 °C for 4 h.

2.2. Catalyst characterisation

The characterisation data of the used supports had been reported elsewhere [10]. The gold content of the prepared catalysts was analysed with ICP-OES analysis. The gold particle sizes were determined by transmission electron microscopy (TEM, Philips CM 20, 200 kV) and the mean diameter of the particles was calculated by counting at least 300 particles onto the micrographs. Laser diffraction analysis was carried out to determine the average catalyst particle size, however, with this method it was only possible to determine that the catalyst particle size is smaller than 1 μm (manufacturer data: 12 nm for the support Black Pearls). The surface areas of the untreated support, of the catalyst before and after activation (reduction with H_2) and of the catalyst after it has been used two times in the glyc- erol oxidation have been measured by N_2 physisorption (Quantachrome) yielding 1539, 1545, 1545 and 1481 $m^2\,g^{-1}$, respectively.

2.3. Oxidation experiments

The glycerol oxidation experiments were performed in a 300 ml batch reactor from Parr. The reactor is equipped with pressure and temperature sensor, pressure controller and sample outlet. The oxidation reactions were carried out with oxygen under pressure up to 10 bar, at temperatures from room temperature to 100 °C and by varying catalyst amount, stirring speed and NaOH/glycerol molar ratio. NaOH (NaOH/glycerol molar ratio = 0, 1, 2 and 4) and the gold catalyst (glycerol/Au molar ratio in the range from 1500 to 20,000) were added to a 1.5 M aqueous solution of glycerol. The reaction was started after heating under Argon by switching from inert gas to oxygen and starting stirring. The reaction course was controlled during the 3 h reaction time by taking samples (0.5 ml) at regular time intervals and analysing them by high performance liquid chromatography (HPLC). The carbon mass balance was proved for the experiments with a maximal difference of 5 wt.%.

Because the very low catalyst particle size makes the experimental investigation of internal diffusion difficult, a theoretical approach according to [15] was applied. The calculations of the ϕ-modulus indicated that intraparticle diffusion is not a limiting step (ϕ_{exp} always $\ll 0.2$ [15]).

Examination of the reaction rates of two experiments in which the catalyst was recycled indicated that no catalyst deactivation is occurring during the reaction. Also from measurements of the specific surface area (Section 2.2), it is obvious that catalyst deactivation does not play a significant role because the data for the catalyst after activation and after activation plus two oxidation cycles are nearly constant (relative difference: 4%).

2.4. Analysis of products

The quantitative analyses of the reaction mixtures were performed by high performance liquid chromatography. The chromatograph (HP 1100 Agilent Technologies) is equipped with an ion exchange column (Aminex HPX-87C) from Biorad and a refractive index detector. Diluted H_2SO_4 (0.01 M) was employed as eluent. For the analysis, the samples were diluted with the eluent with a dilution factor of 30. An injection volume of 10 μl and a measure time of 30 min were adjusted.

Table 1
Gold content of the prepared catalysts (ICP-OES analysis) and mean gold particle size calculated from TEM analysis

Catalyst	Au content (wt.%)	$\bar{d}_{\mathrm{Au}}$ (nm)
Au_0.5/BP	0.33	2.7 ± 0.9
Au_1/BP	0.75	3.7 ± 1.4
Au_5/BP	3.99	22.5 ± 3.5
Au_10/BP	7.2	42.3 ± 4.8
Au_1/MgO	0.65	3.5 ± 0.7

BP: carbon black "Black Pearls 2000".

3. Results and discussion

3.1. Catalysts characterisation

Table 1 summarises the gold content and the mean diameter of the gold particles of the different catalysts prepared.

3.2. Investigation of the support effect in the glycerol oxidation

In order to evaluate dependence of the catalytic activity on the support, oxidation experiments were carried out in a batch reactor with first glycerol aqueous solution without support and catalyst, second with the different investigated supports and at least with the prepared gold catalysts. In fact, carbons have been already reported to be active catalyst per se in liquid phase oxidation reactions [11]. These experiments show that the conversion of glycerol only occurs in the presence of catalyst. In fact, by blank experiments (with and without support) no glycerol conversion could be detected whereas gold nanoparticles supported on different carbons (Vulcan XC 72, Black Pearls 2000) and oxides (Al_2O_3, TiO_2) show high activity (full conversion within the 3 h oxidation time) by comparable mean gold particle sizes. Under the same experimental conditions and with comparable gold particle size, the gold catalysts supported on carbon show higher activity in the liquid phase oxidation of glycerol than a magnesia supported gold catalyst (Fig. 2). Moreover, it could be shown that the carbon black supported gold catalysts are more active than gold on activated carbon or graphite. In fact, the glycerol conversion with the catalyst supported on activated carbon achieves only 17% and with the graphite supported catalyst 5% after 3 h oxidation. It can be concluded that the reported catalytic activities are only due to the catalyst and not to the support.

3.3. Structure sensitivity of the glycerol oxidation

On particle size effect of Au/C catalysts in liquid phase oxidation reaction has already been reported, e.g. the

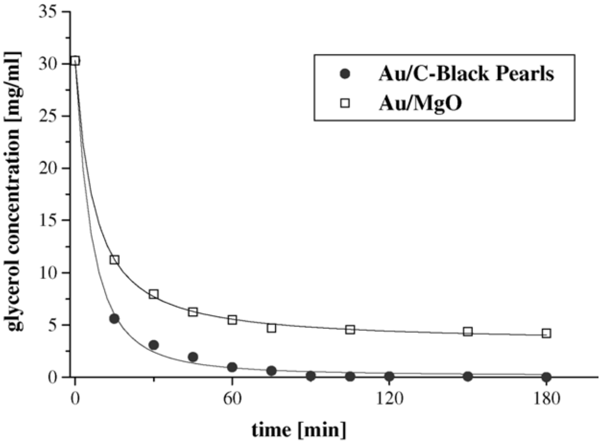

Fig. 2. Support dependent catalytic behaviour of the prepared gold catalysts. Reaction conditions: 100 ml of a 0.3 M glycerol solution, glycerol/Au = 1000 [mol/mol], NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

oxidation of D-glucose to D-gluconic acid [10]. In this case, the initial reaction rate could be strongly increased by decreasing the mean gold particle size of the investigated Au/C catalysts, but almost no influence on the selectivity was detected. In order to examine the structure sensitivity of the Au/C catalysed liquid phase oxidation of glycerol, which has not been investigated so far, Au/C catalysts with gold particle sizes in the range from 2 to 45 nm were prepared (Table 1) by using the gold-sol method and achieving different gold contents. The carbon black "Black Pearls 2000" was used as carbon support. Under comparable experimental conditions the catalysts Au_1/BP, Au_5/BP and Au_10/BP show higher activities with smaller gold particle size (Table 2). Moreover, the mean gold particle size influences not only the catalytic activity but also the selectivity of the catalyst. The selectivity (compared for different catalysts at constant conversion of 30%) is increased with decreasing gold particle size but only until to a maximum value which is achieved with $\bar{d}_{\mathrm{Au}} = 3.7\,\mathrm{nm}$ (Au_1/BP catalyst) where the selectivity to glyceric acid is 75% (Table 2). With smaller gold particle size (Au_0.5/BP catalyst, $\bar{d}_{\mathrm{Au}} = 2.7\,\mathrm{nm}$), a decrease of the selectivity to glyceric acid was observed (S_{30} = 40%). Furthermore, from Table 2, it is obvious that with the smallest gold particle size the highest selectivity to glycolic acid was obtained. The metal particle size seems to play an important role particularly in the oxidation of glyceric acid. Nevertheless, these experiments indicate clearly an influence of the metal particle size of the gold catalysts on their catalytic activity and selectivity so that the Au/C catalysed liquid phase oxidation of glycerol is structure-sensitive.

Table 2
Selectivity to glyceric acid at 30% conversion with different Au/C catalysts

	Catalyst			
	Au_10/BP	Au_5/BP	Au_1/BP	Au_0.5/BP
$\bar{d}_{\mathrm{Au}}$ (nm)	42	23	3.7	2.7
X^{a} (%)	84.7	92.5	100	100
S_{30} glyceric acid (%)	49	62	75	40
S_{30} glycolic acid (%)	21	19	15	36
S_{30} dihydroxyacetone (%)	20	10	<DL[b]	15

Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

[a] Gylcerol conversion after 3 h oxidation time.

[b] DL: detection limit.

3.4. Optimisation of the reaction parameters

In order to optimise the glycerol oxidation, several reaction conditions have been varied. These reactions were carried out in a batch reactor with molecular oxygen as oxidising agent, the most selective catalyst (Au_1/BP) and 100 ml of a 1.5 M glycerol aqueous solution. First aim was to determine the different regimes of this reaction under these conditions, so that the next optimisation experiments could be performed out of the mass transfer limited regime.

3.4.1. Influence of the catalyst amount

For that purpose, the influence of the catalyst amount was studied first. The glycerol/Au molar ratio was varied in the range from 1500 to 20,000 while the other reaction parameters were kept constant as follows: p_{O_2} = 10 bar, T = 60 °C, molar ratio NaOH/glycerol = 2, stirring speed = 1500 rpm and t = 3 h. Fig. 3 shows the initial reaction rate of the glycerol oxidation dependent on the catalyst amount. From the course of this dependency, it results that the mass transfer limited regime occurs below a glycerol/Au molar ratio of 2500. Therefore, the next optimisation experiments were carried out with a molar ratio of 3500. At catalyst amounts lower than ca. 1 g, the initial reaction rate remains nearly constant. Because we have verified by measurements of specific surface area and recycling experiments that deactivation does not play a role,

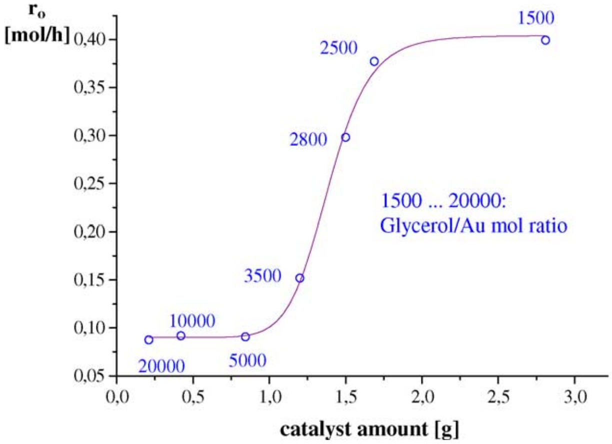

Fig. 3. Initial reaction rates of the glycerol oxidation with 1% Au/C at different catalyst amount. Reaction conditions: 100 ml of a 1.5 M glycerol solution, NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

we attributed this behavior to the formation of foam during the reaction, in which the hydrophobic catalyst is preferentially located. The formed foam, which is essentially on the gas/liquid phase interface, has been observed at the end of the reactions and also by using a glass reactor.

3.4.2. *Influence of the stirring speed*

The influence of the stirring speed, as another parameter influencing the mass transfer, was also studied and has been varied in the range from 500 to 2000 rpm. These oxidation experiments were carried out with the glycerol/Au molar ratio of 3500, $p_{O_2} = 10$ bar, NaOH/glycerol = 2 and $T = 60$ °C. The respective initial reaction rates have been examined and they increase from 9.1 to 285.3 mmol/h in the range from 500 to 1000 rpm. Above 1000 rpm, the initial reaction rate increases slightly only until the two-fold value at 2000 rpm. By examining the selectivities at different stirring speeds, it appears that the stirring speed does not influence the selectivity to glyceric acid above a value of 1000 rpm. By considering these behaviours and in order to avoid working at the maximum stirring speed, a stirring speed of 1500 rpm was used in the next optimisation experiments.

3.4.3. *Influence of pressure and temperature*

Furthermore, the influence of the oxygen pressure on the reaction course has been examined. The aim of this investigation was to verify the dependency of the reaction rate and of the catalyst selectivity on the oxygen pressure. Oxidation experiments were carried out with the glycerol/Au molar ratio of 3500 and stirring speed of 1500 rpm, with NaOH/glycerol = 2 and at 60 °C first. The oxygen pressure has been varied between 4 and 10 bar. Under the described conditions, the oxygen pressure does nearly not influence the reaction rates of the glycerol oxidation (Fig. 4). From Fig. 4, it is obvious that the temperature influences the reaction course much more than the oxygen pressure does. To get further information on this behaviour, oxidation experiments have been carried out from room temperature to 100 °C with $p_{O_2} = 10$ bar (Fig. 5). From these investigations, the reaction rate constant k of the glycerol oxidation could be determined under the assumption of a first order reaction concerning the glycerol concentration (Fig. 6). Table 3 shows the calculated reaction rate constant k at different temperatures, so that from these results the apparent activation energy of the Au/C catalysed liquid phase oxidation of glycerol could be estimated to 50 ± 5 kJ/mol.

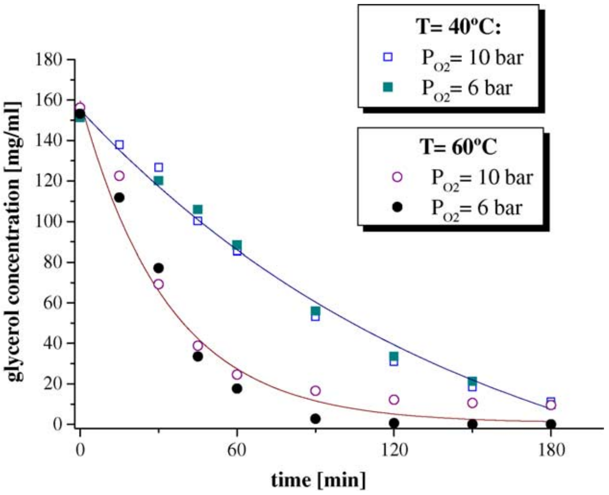

Fig. 4. Oxygen pressure dependent glycerol conversion with 1% Au/C at different temperatures. Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], NaOH/glycerol = 2 [mol/mol], rpm = 1500.

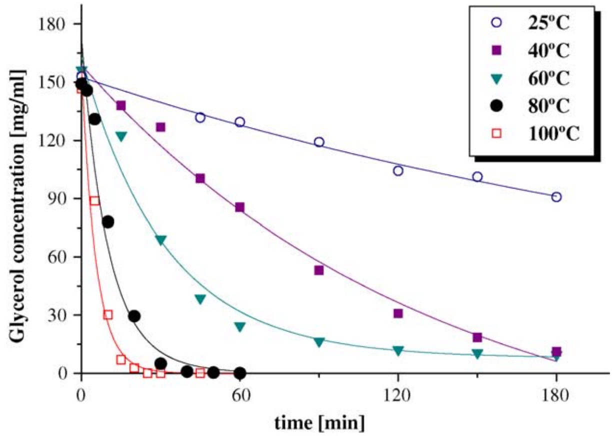

Fig. 5. Glycerol conversion with 1% Au/C at different reaction temperatures. Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, rpm = 1500.

3.4.4. *Influence of the base concentration*

As already reported, the presence of a base in the reaction mixture during an alcohol oxidation reaction is essential for the start of the reaction [12]. In fact, an oxidative dehydrogenation mechanism of the alcohol oxidation reaction has been generally accepted [13]. The first step

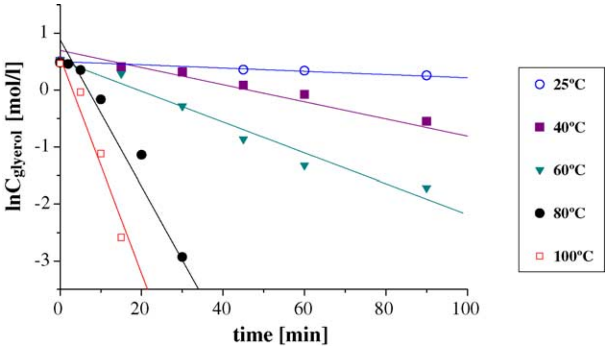

Fig. 6. Temperature dependent conversion of glycerol with 1% Au/C. Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, rpm = 1500.

Table 3
Temperature dependency of the reaction rate constant k of the glycerol oxidation

T (°C)	k (h^{-1})
25	0.17 ± 0.01
40	0.90 ± 0.04
60	1.6 ± 0.2
80	6.8 ± 0.7
100	12.3 ± 1.8

Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], NaOH/glycerol = 2 [mol/mol], p_{O_2} = 10 bar, rpm = 1500.

of this mechanism consists of the dehydrogenation of the alcohol function followed by the oxidation of the formed intermediate. It has also been reported that the type and concentration of the base play a major role in the reaction course [14]. Therefore, the influence of the base concentration in the glycerol oxidation has been studied. For this purpose, the course of the glycerol conversion has been examined at different NaOH/glycerol ratios (0, 1, 2 and 4). The results are shown in Fig. 7. In a first experiment carried out without NaOH, it could be verified that the presence of the base is required to start the oxidation of glycerol. This reaction course confirms that the first step of the alcohol oxidation mechanism, namely the dehydrogenation step of the hydroxyl group, does not take place in the absence of the base [12]. These results show clearly that the base concentration has an important influence on the reaction rate. The higher the base concentration the greater the conversion rate of glycerol. To quantify this effect, the initial reaction rates have been plotted against the respective NaOH/glycerol molar ratio as shown in Fig. 8. The initial reaction rate increases strongly by increasing the base concentration until a molar ratio NaOH/glycerol of 2 and above this ratio converges to a maximum value (Fig. 8). A larger effect has been observed in the selectivity. In opposition to the experiments with NaOH/glycerol molar ratios up to 2, the selectivities, obtained with a ratio of 4, do not remain constant during the 3 h oxidation time (Fig. 9). In this last case, the oxidation of glyceric acid to tartronic acid is strongly favoured. Thus, the investigation of the influence of the base concentration shows that the selectivity to glyceric acid and to tartronic acid, respectively could be controlled depending on the base amount.

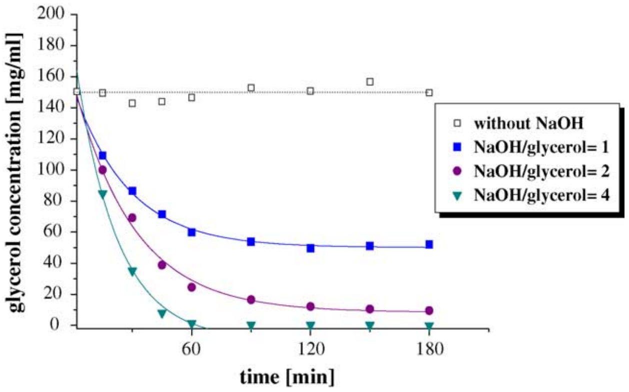

Fig. 7. Influence of the NaOH/glycerol molar ratio on the glycerol conversion with 1% Au/C. Reaction conditions: 100 ml of a 1.5 M glycerol solution, glycerol/Au = 3500 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

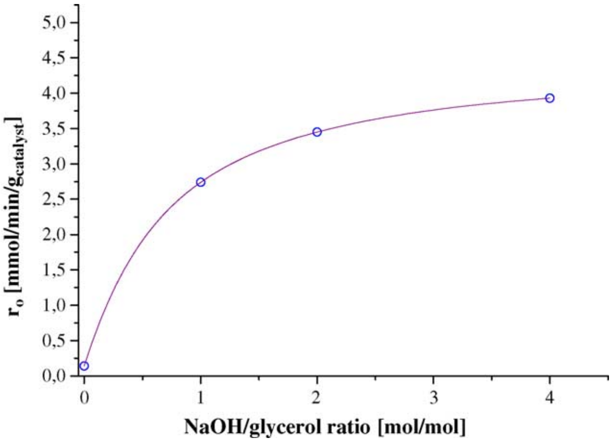

Fig. 8. Initial reaction rates of the glycerol oxidation at different NaOH/glycerol molar ratios. Reaction conditions: 100 ml of a 1.5 M glycerol solution, catalyst: 1 wt.% Au/C, glycerol/Au = 3500 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

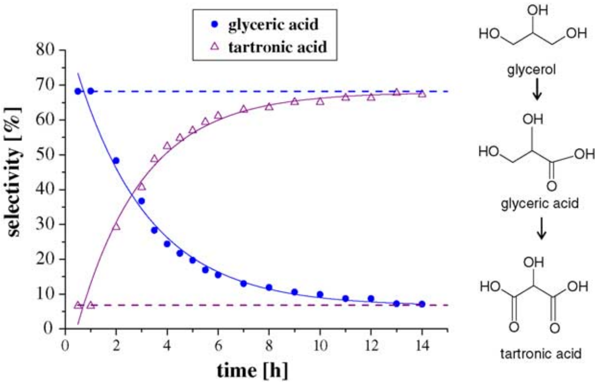

Fig. 9. Time dependent selectivity to glyceric acid and tartronic acid with NaOH/glycerol molar ratio = 4. Reaction conditions: 100 ml of a 1.5 M glycerol solution, catalyst: Au_1/BP, glycerol/Au = 3500 [mol/mol], p_{O_2} = 10 bar, T = 60 °C, rpm = 1500.

4. Conclusions

From our investigations of the heterogeneously catalysed liquid phase glycerol oxidation arises that the support strongly influences the catalyst properties. The carbon supported gold catalysts show high activity and the investigated carbon black support is more active than activated carbon or graphite. Moreover, comparing the catalytic behavior of Au/C catalysts with different mean gold particle sizes in the range from 2.7 to 42 nm, it could be shown that the glycerol oxidation is structure-sensitive. In fact, the selectivity to glyceric acid was increased to 75% with smaller gold particle size until the optimum value of $\bar{d}_{\mathrm{Au}} = 3.7\,\mathrm{nm}$. With smaller mean gold particle size ($\bar{d}_{\mathrm{Au}} = 2.7\,\mathrm{nm}$) the selectivity to glyceric acid decreased to 40% for the benefit of glycolic acid whose selectivity increased from 15 to 36%. Consequently, the metal particle size of the Au/C catalyst plays a major role in the oxidation of glyceric acid. Furthermore, within the optimisation of the reaction conditions which can influence the mass transfer, we could determine the different regimes of the Au/C catalysed glycerol oxidation, so that we could discriminate between the kinetic regime and the mass transfer regime. In addition, the investigation of the influence of the base concentration shows that this reaction parameter plays an important role not only in the oxidative dehydrogenation mechanisms, but as well for the catalyst selectivity. Depending on the base concentration and the reaction time the selectivity of the Au/C catalysed liquid phase glycerol oxidation could be controlled.

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