Catalysis Today 158 (2010) 121–129

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Glycerol oxidation on gold catalysts supported on group five metal oxides—A comparative study with other metal oxides and carbon based catalysts

Izabela Sobczak*, Katarzyna Jagodzinska, Maria Ziolek

A. Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-780 Poznan, Poland

ARTICLE INFO

Article history:
Available online 18 May 2010

Keywords:
V_2O_5
Nb_2O_5
Ta_2O_5
Al_2O_3
TiO_2
Carbons – supports for Au
Glycerol oxidation

ABSTRACT

V_2O_5, Nb_2O_5 and Ta_2O_5 were used as supports for gold and their activity in the oxidation of glycerol was compared with that of gold loaded on Al_2O_3, TiO_2 and carbons. Different methods of gold loading were applied and they determined the gold particle sizes. The gold-sol method used for the modification of oxides ensured high gold dispersion and smaller Au crystallites than the deposition–precipitation one. The influence of acid–base properties of the supports on gold particle sizes and activity in oxidation of glycerol was considered. Au/Nb_2O_5 catalyst, prepared by gold-sol method and crystalline niobia as support, was attractive for the liquid phase oxidation of glycerol showing high selectivity to glyceric acid and the ability of reuse. Its catalytic properties in this process were comparable with those noted for Au loaded on carbon. A significant difference between the amorphous and crystalline niobia used as supports of gold was established and better performance of anhydrous crystalline Nb_2O_5 was shown.

1. Introduction

Glycerol is a co-product of triglyceride transesterification in the production of fatty acid esters employed as biodiesel [1]. For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed [2]. If the production of biodiesel increases as predicted, the supply of glycerol will be in excess of demand [3–6]. Therefore, glycerol should find new outlets to optimize the economy of biodiesel production and to rebalance supply and demand. Many valuable commodity chemicals can be formed from glycerol via oxidation, reduction, halogenation, and etherification [2,3]. One of the most intensively studied pathways of glycerol transformation into useful chemicals is the oxidation process [2,3,7,8]. Selective oxidation of glycerol leads to various valuable oxygenates (glyceric, tartronic, glycolic, hydroxypyruvic acids, and dihydroxyacetone). It is widely shown in literature [9–17], that these oxygenates can be obtained by oxidation with oxygen in the presence of carbon supported gold catalysts. Under mild reaction conditions (333 K, water as a solvent) on Au-carbon catalysts over 90% selectivity for glyceric acid at 90% glycerol conversion was obtained [9,10]. Moreover, it was found that glycerol oxidation is structure sensitive. It has been reported [11–13] that the size of the gold particle influences the catalytic activity and selectivity of the Au-carbon catalysts. The carbons with gold particle sizes between 2 and 47 nm were active, but those with smaller gold particles showed higher activities [11,12]. On the other hand, large Au particles (>20 nm) were more selective to glyceric acid, while for small gold particle size the selectivity to glyceric acid decreased and the glycolic acid selectivity increased.

As to the mechanism of the reaction, the important role of NaOH for initiation of the catalytic glycerol oxidation was confirmed [9–11,18,19]. The presence of OH^- is essential to observe any glycerol oxidation using gold containing catalysts. In the presence of the base, the proton is readily abstracted from one of the primary hydroxyl groups of glycerol. The initial dehydrogenation is proposed as the first step in the oxidation process [9]. The existence of two major routes, of which hydroxyacetone and glyceric aldehyde are the primary oxidation products and glycolic and oxalic acid are the end-members, respectively, is now firmly established. Moreover, rapid oxidation of glyceraldehydes favours glyceric acid rather than hydroxyacetone formation [13]. It was also found that the conversion of glycerol and the selectivity to the reaction products depend strongly on the amount of base used [9,11,13,20,21]. In general, the higher the base concentration the greater the glycerol conversion and higher selectivity to glyceric acid. However, at high NaOH/glycerol molar ratio (NaOH/Gly = 4) the oxidation of glyceric acid to tartronic acid is strongly favoured [11].

The effect of the support for gold was studied by Claus and coworkers [11,14]. They compared the activity of different types of carbons and the metal oxides supported (TiO_2, Al_2O_3, MgO, and CeO_2). Under the same experimental conditions the gold catalysts supported on carbon showed much higher activity in the liquid phase oxidation of glycerol than magnesia and ceria supported gold catalysts.

---

* Corresponding author. Tel.: +48 61 8291305.
E-mail address: sobiza@amu.edu.pl (I. Sobczak).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.04.022

Niobium containing materials are presently of a great interest in heterogeneous catalysis in which they are used as catalyst components or play a role of promoters [22]. Niobium compounds exhibit special properties which are not shown by the compounds of neighbouring elements in the periodic table. Some of them, like strong metal support interaction (SMSI) or unique reversible interaction with several reagents are very important for the design of catalysts. Moreover, it is known, that Nb_2O_5 is active catalysts in oxidation reactions [22].

The idea of this work is to apply Nb_2O_5 as well as V_2O_5, Ta_2O_5 as a new oxide supports for gold and to investigate the effect of group five metal oxides on the efficiency of the oxidation of glycerol (niobium *contra* V and Ta). Gold catalysts, based on carbons and Al_2O_3 and TiO_2 oxides, were also tested for comparison. Our interest was to study the influence of gold–support interaction on the activity and selectivity in glycerol oxidation. Moreover, the influence of preparation method, gold dispersion and the reaction conditions are considered.

2. Experimental

2.1. Modification of the catalysts

Commercial oxides (V_2O_5 – Aldrich, Nb_2O_5 (cr) – Alfa-Aesar, $Nb_2O_5 \times nH_2O$ (am) – CBMM-Brasil, Ta_2O_5 – Aldrich, Al_2O_3 – Sasol) and carbon supports (C (ALD) – Aldrich and C (POCH) – POCH-Poland) were modified by gold-sol method with tetrakis (hydroxymethyl) phosphonium chloride (THPC) as a reducing agent and $HAuCl_4$ as a source of gold (1 wt.% of Au) according to [11]. First, the metallic sols were prepared: H_2O (232 ml) with 0.2 M NaOH (7.5 ml) was stirred before adding 5 ml of diluted THPC (1.2 ml of the 78 wt.% solution diluted with 100 ml H_2O). After 2 min of stirring, the gold aqueous solution ($HAuCl_4$ – Johnson Matthey) was added (1 wt.% of Au). The gold-sols were then stirred for 1 h. Aqueous suspensions of the supports (5 g) were agitated for 15 min in an ultrasonic bath. The gold-sols were added into the support suspensions and stirred for 1 h for immobilisation. The suspension was filtered, washed until the filtrate was free of chloride ($AgNO_3$ test) and dried at 373 K. The materials prepared were calcined at 623 K for 4 h.

Moreover, Nb_2O_5 and Al_2O_3 oxides were modified by deposition–precipitation method with urea (DPU) [11]. An aqueous solution of $HAuCl_4$ (calculated as 1 wt.% of Au) was added to a stirred 0.84 M aqueous solution of urea (Fluka) and heated to 353 K while stirring. Then the support was added and the suspension was stirred at 353 K for 4 h. The suspension was filtered, washed until the filtrate was free of chloride ($AgNO_3$ test) and dried at 373 K. The catalysts were calcined at 623 K for 4 h.

The following notation is used for the catalyst samples we prepared: (sol) denotes gold-sol method, (DPU) stands for the deposition–precipitation method with urea, (ALD) for carbon from Aldrich, (POCH) stands for carbon from POCH company, (cr) for crystalline niobia, and (am) denotes amorphous niobia.

In addition, for comparison, we used a reference gold catalyst prepared by the World Gold Council – Au/TiO_2 (1 wt.% of Au).

2.2. Catalysts characterisation

All the materials were characterised by the use of standard techniques: N_2 adsorption/desorption, XRD, ultraviolet–visible (UV–vis), TEM, and test reactions.

The texture parameters of the samples were measured by nitrogen adsorption at 77 K, using the conventional procedure on a Micromeritics 2010 apparatus.

The XRD patterns were obtained on aD8 Advance diffractometer (Bruker) using CuK_α radiation ($\lambda = 0.154$ nm), with a step size of 0.05° in the $2\Theta = 6–60°$ range.

The UV–vis spectra were recorded on a Cary 300 Scan (Varian) spectrometer. Catalysts in the form of powders were placed in the cell equipped with a quartz window. The Kubelka–Munk (F(R)) was used to convert reflectance measurements into equivalent absorption spectra using the reflectance of SPECTRALON as a reference. The spectra were recorded in the range from 800 to 190 nm.

For transmission electron microscopy (TEM) measurements the powders were deposited on a grid covered with a holey carbon film and transferred to JEOL 2000 electron microscope operating at 80 kV.

The surface properties were characterised by test reactions – acetonylacetone (AcoAc) cyclisation and 2-propanol decomposition.

A tubular, down-flow reactor was used in AcoAc cyclisation reaction that was carried out at atmospheric pressure, using nitrogen as the carrier gas. The catalyst bed (0.05 g) was first activated for 2 h at 623 K under nitrogen flow (40 $cm^3\,min^{-1}$). Subsequently, 0.5 cm^3 of acetonylacetone (Fluka, GC grade) was passed continuously over the catalyst at 623 K. The substrate was delivered with a pump system and vaporized before being passed through the catalyst with the flow of nitrogen carrier gas (40 $cm^3\,min^{-1}$). The reaction products were collected for 30 min downstream of the reactor in the cold trap (mixture of 2-propanol and liquid nitrogen) and analysed by gas chromatography (CHROM -5, Silicone SE-30/Chromosorb G column).

The 2-propanol conversion (dehydration and dehydrogenation) was performed, using a microcatalytic pulse reactor inserted between the sample inlet and the column of a CHROM-5 chromatograph. The catalyst bed (0.05 g) was first activated at 623 K for 2 h under helium flow (40 $cm^3\,min^{-1}$). The 2-propanol (Aldrich) conversion was studied at 423, 473, 523 and 573 K using 3 μl pulses of alcohol under helium flow (40 $cm^3\,min^{-1}$). The reactant and the reaction products: propene, 2-propanone (acetone) and diisopropyl ether were analysed using CHROM-5 gas chromatograph on line with microreactor. The reaction mixture was separated on 2 m column filled with Carbowax 400 (80–100 mesh) at 338 K in helium flow (40 $cm^3\,min^{-1}$) and detected by TCD.

2.3. Glycerol oxidation

The glycerol oxidation experiments were performed in a 300 cm^3 batch reactor from Parr. The oxidation reactions were carried out with oxygen under pressure 6 atm, at 333 and 363 K. NaOH (NaOH/glycerol molar ratio = 2) and 0.2 g of gold catalyst (glycerol/Au molar ratio = 980) were added to a 1 M aqueous solution of glycerol. The reaction mixture was stirred (1500 rpm) for 5 h (and for selected samples additionally for 1 and 15 h). The quantitative analyses of the reaction mixtures were performed by high performance liquid chromatography (HPLC). The analysis was carried out using HPLC chromatograph (Waters) equipped with ultraviolet (UV) and refractive index (RI) detectors. The reactant and the products were separated on an ion exclusion column (IC-Pak Ion Exclusion 7.8 × 300 mm – Waters) heated at 343 K. The eluent was a solution of H_2SO_4 (0.0004 M). The samples were taken at the end of the reactions, 1 ml of the sample was diluted in 10 ml of water and 5 μl of this solution was analysed.

3. Results

3.1. Catalysts characterisation

3.1.1. Textural properties of the supports

The results of BET analysis of the oxides and carbons used as supports for gold are shown in Table 1. The BET surface areas of

Table 1
Texture parameters of the catalyst's supports.

Catalyst	Surface area BET, $m^2\,g^{-1}$	Average pore volume BJH, (ads.) $cm^3\,g^{-1}$	Average pore diameter, BJH, (ads.) nm
Nb_2O_5 (cr)	7	0.02	12.3
Nb_2O_5 (am)	30	0.09	4.2
V_2O_5	10	0.05	24.7
Ta_2O_5	4	0.01	12.9
Al_2O_3	190	0.49	7.7
C (ALD)	118	0.85	33.9
C (POCH)	700	0.34	6.2

Nb_2O_5 (cr), Ta_2O_5 and V_2O_5 are comparable, whereas Nb_2O_5 (am) shows a much greater surface area. The surface areas of alumina and carbons are above 100 m^2/g. The greatest surface area (700 m^2/g) was observed for carbon from POCH.

The pore sizes of the supports ranged from 4 to 34 nm. Nb_2O_5 (cr), V_2O_5 (cr) and C (ALD) exhibited the greatest pore sizes (12, 25 and 34 nm, respectively) among the supports chosen. It is worthy of notice that the carbon from ALD is mainly a macroporous material with wide pore size distribution, whereas POCH carbon shows meso-macroporosity (domination of mesopores) as deduced from its N_2 adsorption isotherm.

3.1.2. *The state of gold and the size of gold crystallites*

The state of gold in the catalysts prepared was studied by UV–vis, XRD and TEM techniques. The results clearly indicate that metallic gold crystallites are formed on all materials and their size is determined by the chemical composition of the support and the method of Au introduction.

UV–vis spectroscopy, commonly used for identification of metallic gold, shows the presence of metallic gold on the surface of all gold modified oxides (Fig. 1A–C). The observed intense UV–vis band at 500 nm is typical of metallic gold [23].

The difference in the Au particle sizes on different carbons and oxides is visible on TEM images (examples are shown in Figs. 2 and 3).

The results obtained clearly indicate the effect of the method of Au introduction on the size and dispersion of gold. The TEM images indicate that the size of gold crystallites on the surface of the samples prepared by DPU method is much greater than that on catalysts modified by gold-sol method. The average particle size estimated from TEM images for the Au/Nb_2O_5 prepared by DPU method is about 25 nm, whereas in the sample prepared by gold-sol method it is of about 10 nm. THPC used during gold-sol method stabilizes the colloid gold solutions and that is why gold particle sizes are smaller and their dispersion is greater. Among the supports mod-

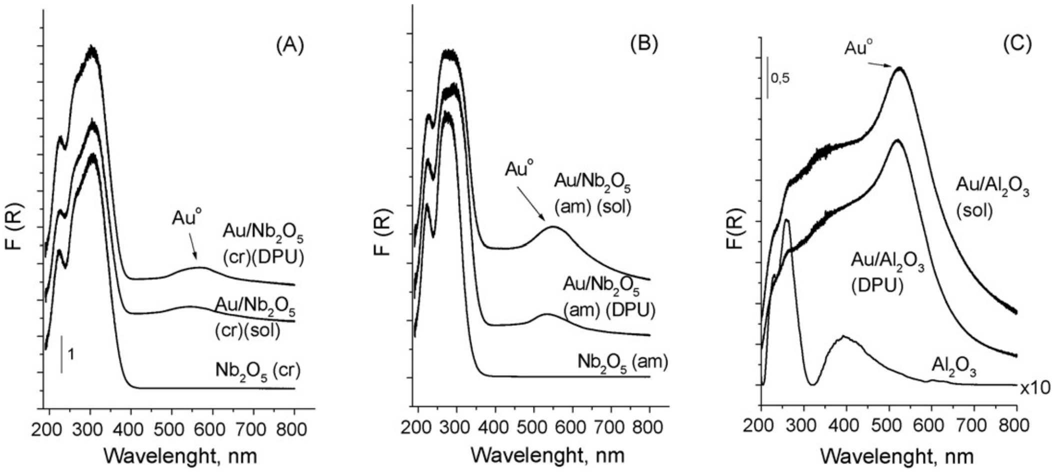


Fig. 1. UV–vis spectra of oxides and gold modified catalysts.

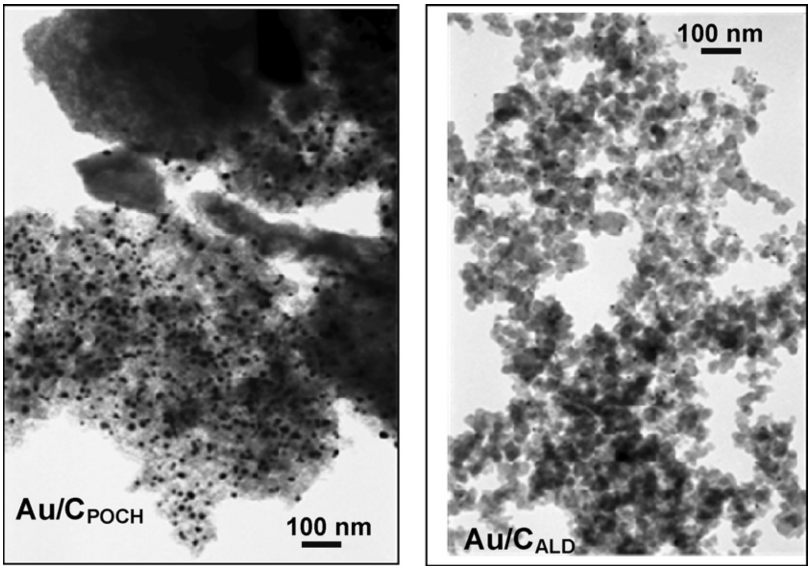


Fig. 2. TEM images of gold-sol modified carbons.

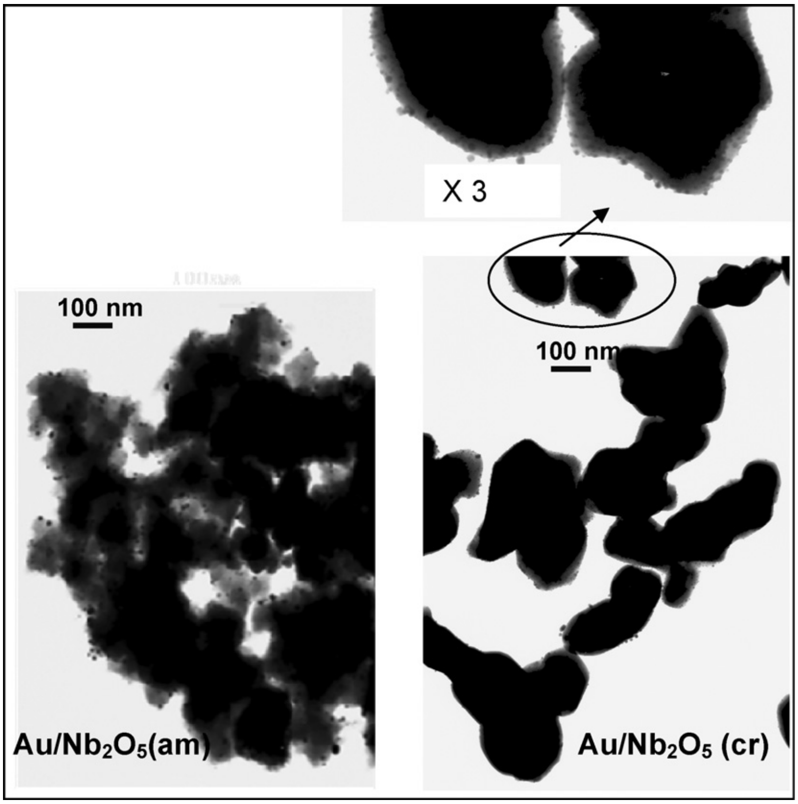


Fig. 3. TEM images of gold-sol modified Nb_2O_5 samples.

ified with the use of THPC, higher dispersion and smaller average gold particle size were obtained on niobia (~6 nm for Au/Nb_2O_5 (cr) (sol) and ~10 nm for Au/Nb_2O_5 (am) (sol) and vanadia (~10 nm) as well as on C (ALD) (~8 nm) than on Ta_2O_5 and C (POCH) (~15 nm)) (Figs. 3 and 4). However, one cannot exclude that in the crystalline oxides much smaller gold particles are hidden inside the crystal and are not visible in TEM images. Interestingly, on Au/Al_2O_3 (DPU) the Au particles observed in TEM image exhibit different sizes giving the average Au particle size of 80 nm.

XRD patterns (not shown here) confirm the influence of preparation method on the size and dispersion of gold. The reflections characteristic of metallic gold (at $2\Theta = 38.2^\circ$ and 44.4°) [24,25] are well visible for the catalysts prepared by DPU method. In contrast, only very low intense and broad XRD reflections from metallic gold are present in the XRD patterns of the catalysts with all group five metal oxides modified by gold-sol method.

3.1.3. Acidity/basicity of the catalysts – test reactions

3.1.3.1. Acetonylacetone cyclisation. The cyclisation of acetonylacetone was used as a test reaction for acid/base properties. This reaction was proposed by Dessau [26] as Brønsted acid–base test. The formation of 2,5-dimethylfuran (DMF) occurs on acidic centres, whereas basic centres take part in the production of 3-methyl-2-cyclopentenone (MCP). On the basis of the ratio of the selectivity to MCP to the selectivity to DMF, the catalysts prepared can be ordered according to increasing basicity. According to literature [26,27] the catalyst is considered basic if MCP/DMF $\gg$ 1. When MCP/DMF $\ll$ 1 the catalyst exhibits acidic properties, while for MCP/DMF $\approx$ 1 the acid–base character of the catalysts is postulated.

Table 2 summarises the results of this test reaction. Crystalline forms of group five metal oxides and carbons show very low activity in AcoAc cyclisation. The amorphous Nb_2O_5 shows significantly higher activity than the crystalline Nb_2O_5 (cr). The modification with gold increases the activity of the catalysts irrespective of the method of gold introduction. It indicates that the modification generates new active centres responsible for the activity increase. For all gold containing catalysts based on group five metal oxides and carbons. DMF is the only product of the reaction that points to the acidic (Brønsted acid sites) character of these materials. Contrary, it is noteworthy that alumina based catalysts exhibit the highest activity in AcoAc cyclisation among the samples studied and basic properties concluded from MCP/DMF ratio (MCP/DMF > 1). One can see the prevalence of MCP in the reaction products (Table 2), indicating the domination of basicity in both types of these gold catalysts (sol and DPU). The basicity originates from the support – Al_2O_3 [28] – and it is partially reduced by gold loading.

Table 2
The results of acetonylacetone (AcoAc) cyclisation at 623 K.

Catalyst	Conversion, %	Selectivity DMF, %	Selectivity MCP, %	MCP/ DMF
Nb_2O_5 (cr)	1.0	100	0	0
Au/Nb_2O_5 (cr) (sol)	1.1	100	0	0
Au/Nb_2O_5 (cr) (DPU)	1.9	100	0	0
Nb_2O_5 (am)	7.6	100	0	0
Au/Nb_2O_5 (am) (sol)	10.5	100	0	0
Au/Nb_2O_5 (am) (DPU)	13.3	100	0	0
V_2O_5	0.4	100	0	0
Au/V_2O_5 (sol)	0.6	100	0	0
Ta_2O_5	0.7	100	0	0
Au/Ta_2O_5 (sol)	0.9	100	0	0
Al_2O_3	26.0	6.1	93.9	15.5
Au/Al_2O_3 (sol)	13.4	7.3	92.7	12.8
Au/Al_2O_3 (DPU)	32.0	10.3	89.7	8.8
C (Ald)	0	0	0	0
Au/C (Ald) (sol)	7.5	100	0	0
C (POCH)	1.2	100	0	0
Au/C (POCH) (sol)	12.2	100	0	0

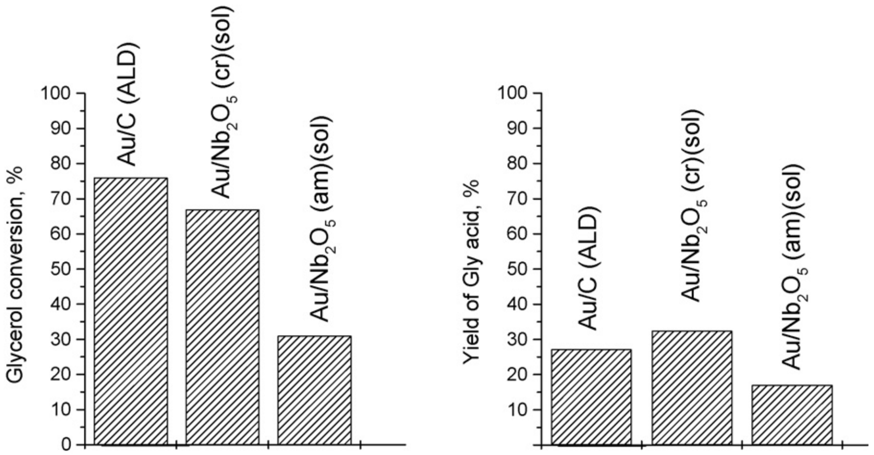


Fig. 4. Glycerol conversion and the yield of glyceric acid production on Au/C (ALD), Au/Nb_2O_5 (cr) (sol) and Au/Nb_2O_5 (am) (sol) catalysts (reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, stirring = 1500 rpm, T = 333 K, $p_{O_2} = 6$ bar, time = 5 h).

Table 3
The results of 2-propanol decomposition at 473 K.

Catalyst	Conversion i-PrOH [%]	Selectivity [%] towards		
		Propene	Ether	Acetone
Nb_2O_5 (cr)	9	76	24	0
Au/Nb_2O_5 (cr) (sol)	6	65	5	30
Au/Nb_2O_5 (cr) (DPU)	1	100	0	0
Nb_2O_5 (am)	13	100	0	0
Au/Nb_2O_5 (am) (sol)	49	90	2	8
V_2O_5	39	74	8	2
Au/V_2O_5 (sol)	89	6	90	4
Ta_2O_5	0	0	0	0
Au/Ta_2O_5 (sol)	0	0	0	0
Al_2O_3	61	0	100	0
Au/Al_2O_3 (sol)	1	28	0	72
Au/Al_2O_3 (DPU)	1	30	0	70
C (Ald)	0	0	0	0
Au/C (Ald) (sol)	17	99	0	1
Au/C (POCH) (sol)	10	96	0	4

3.1.3.2. 2-Propanol decomposition. The 2-propanol decomposition is a test reaction for characterisation of acidic (Brønsted or Lewis) and/or basic properties of solids [29]. Dehydration of alcohol to propene and/or diisopropyl ether requires acidic centres (Lewis or Brønsted), whereas the dehydrogenation to acetone occurs on the basic sites. It is noteworthy that ether production requires the presence of pairs of Lewis acid–base centres. Some authors (e.g. [30]) have reported that acetone formation takes place on redox centres. The conversion of 2-propanol is much higher in the presence of acidic centres on the catalyst surface than that on basic catalysts.

The alcohol conversion on gold containing samples differs depending on the nature of the support (Table 3). Among the metal oxide supports, Ta_2O_5 is inactive in the reaction of i-propanol at 473 K and gold loading does not change this feature. The lack of activity is observed also on pure carbon samples. However, the modification of carbons with Au species enhances the activity by generating acidic centres as deduced from a very high selectivity to propene. This behaviour can be caused by the use of auric acid as gold source and carbon treatment with acid leads to the generation of acid centres. Among the metal oxides used as supports the highest conversion of i-propanol is observed on alumina that exhibits the presence of pairs of Lewis acid–base centres active in the formation of diisopropyl ether. Interestingly, the gold loading by both methods (sol and DPU) diminishes significantly the activity of alumina as well as Nb_2O_5 (cr). That phenomenon can be interpreted as a result of the strong interaction of Lewis acid–base centres with gold species. Different behaviour is noted for gold modified vanadia and amorphous niobia, for which Au loading leads to increased activity and changes in selectivity. Especially important for further study of glycerol oxidation, is the generation of Lewis basicity on both materials, leading to the formation of ether (mainly on Au/V_2O_5 (sol) in which both acid and basic sites are active) and acetone from i-propanol. It is important to stress the high selectivity to acetone observed on Au/Nb_2O_5 (cr) (sol), which indicates the accessibility of basic centres for the reagents on this catalyst based on crystalline niobia.

3.2. Glycerol oxidation

3.2.1. Effect of the stirring speed

For our experiment we have selected the commonly used conditions, i.e. NaOH/glycerol molar ratio = 2, oxygen pressure of 6 atm and 333 K as the standard reaction conditions. The choice of the stirring speed (1500 rpm) was made on the basis of the experiment performed with stirring speeds from the range 800–2200 rpm. As shown in Table 4 for Au/C (ALD) the lowest stirring speed (800 rpm)

Table 4
Liquid phase oxidation of glycerol using Au-supported catalysts – effect of stirring speed.

Catalyst	Stirring speed, rpm	Glycerol conv. %	Selectivity, %				
			Glyceric acid	Tartronic acid	Glycolic acid	Formic acid	Oxalic acid
Au/C (ALD) (sol)	800	49	16	9	8	4	3
Au/C (ALD) (sol)	1500	76	36	8	7	4	1
Au/C (ALD) (sol)	2200	97	25	5	9	4	2
Au/Nb_2O_5 (cr) (sol)	1500	67	47	5	5	4	–
Au/Nb_2O_5 (cr) (sol)	2200	84	34	4	4	3	–
Au/Nb_2O_5 (am) (sol)	1500	31	55	2	1	1	–
Au/Nb_2O_5 (am) (sol)	2200	50	27	1	2	1	–

Reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, T = 333 K, $p_{O_2} = 6$ bar, time = 5 h.

gives the lowest activity and the selectivity to glyceric acid. The increase in the stirring speed from 1500 to 2200 rpm results in increase in the activity of Au/C (ALD) catalyst but decrease in the selectivity to glyceric acid. The same behaviour was observed when the tests were performed on amorphous and crystalline Nb_2O_5 based gold catalysts. The porosity of all these three tested samples significantly differs (Table 1) and the effect of stirring speed was the same for all of them (the increase in activity by ca. 20%). Therefore, one could suggest that the growth of activity with the increase in the stirring speed does not originate from the increase in the diffusion rate in pores but rather from the transport of products from solid to liquid. Our choice for further study was the stirring speed of 1500 rpm because it ensured the highest selectivity to glyceric acid.

3.2.2. *Effect of the support and the method of gold introduction*

The oxidation of glycerol with oxygen was investigated using the 1% Au-containing catalysts at 333 K and the results are given in Table 5. Group Five metal oxides (V_2O_5, Nb_2O_5, and Ta_2O_5) were used as supports for gold. Moreover, two types of different carbons (POCH and ALD) and alumina catalysts were used for a comparative study. Similarly as shown in the literature for carbons and oxides (MgO and CeO_2) modified with gold [11,14], the activity of gold catalysts studied in this work in glycerol oxidation strongly depends on the preparation method. The gold-sol method that leads to the better gold dispersion and smaller gold particle size gives catalysts more active than the catalysts prepared by DP method with the use of urea. It confirms the earliest results that smaller gold particles (<20 nm) are more active in glycerol oxidation [11,12].

Moreover, the results obtained indicate that among group V metal oxides the highest activity was obtained for crystalline niobium oxide modified with gold by the gold-sol method (Au/Nb_2O_5 (cr) (sol)). The conversion of glycerol on this catalyst is comparable to the conversion reached for gold supported on carbon from ALD. Amorphous Nb_2O_5 modified with Au (Au/Nb_2O_5 (am) (sol)) is less active than the crystalline form, but its activity is higher than that of gold catalysts based on other group five metal oxides. The Au/Ta_2O_5 (sol), Au/V_2O_5 (sol) oxides, as well as Au/Al_2O_3 (sol) show lower activity in glycerol oxidation. It indicates the role of Au–Nb interactions in Au/Nb_2O_5 catalysts (SMSI between gold and niobium). The Au–Nb interaction in the crystalline Nb_2O_5 is stronger than in amorphous Nb_2O_5 because niobium in the crystal phase occupies also the positions in the corners and edges of the crystals in which Nb species is unsaturated. Such unsaturated niobium species strongly interact with gold particles and stabilize them. It is the reason for better gold dispersion on crystalline niobia than on amorphous ones.

Considering the specific surface area and average pore diameter of the different supports with respect to the corresponding activity, no direct correlation can be found (Tables 1 and 5). A similar behaviour was found earlier for different carbons [15] and CeO_2 oxides [14]. It was shown that no specific surface area of carbon and CeO_2 supports determines the catalytic properties of gold. The results presented in Table 5 confirm this statement. When the glycerol conversion is calculated as mmol Gly/m^2 of the catalyst the activity of gold-loaded carbons and alumina is much lower than the activity of group five metal oxides modified with gold, especially Au/Nb_2O_5 (Table 5).

The highest activity (91% of glycerol conversion) in oxidation of glycerol was observed for commercial MINTEK catalyst – gold supported on TiO_2 (Table 5). The conversion obtained with Au/TiO_2 was exactly the same as observed in the oxidation experiment described in [16].

As shown in Table 5, all gold supported oxides and carbons activate the reaction mainly towards glyceric acid. Other products of oxidation formed besides glyceric acid include: glycolic, tartronic,

Table 5
Liquid phase oxidation of glycerol using Au-supported catalysts – effect of the support and the method of Au introduction.

Catalyst	Glycerol conv., %	Glycerol conv., mmol/m^2 × 10^{-2}	Selectivity, %					Yield, %				
			Glyceric acid	Tartronic acid	Glycolic acid	Formic acid	Oxalic acid	Glyceric acid	Tartronic acid	Glycolic acid	Formic acid	Oxalic acid
Nb_2O_5 (cr)	6	42	22	Traces	Traces	0	0	4	Traces	Traces	0	0
Au/Nb_2O_5 (cr) (sol)	67	478	47	5	5	4	0	32	4.0	3.0	2.0	0
Au/Nb_2O_5 (cr) (DPU)	11	78	15	4	6	4	0	2.0	0.5	0.6	0.4	0
Nb_2O_5 (am)	4	7	2	6	Traces	0	0	0.1	0.3	Traces	–	–
Au/Nb_2O_5 (am) (sol)	31	52	55	2	1	1	0	16.9	0.7	0.4	0.3	0
Au/Nb_2O_5 (am) (DPU)	10	17	3	Traces	5	0	0	0.3	Traces	0.5	0	0
V_2O_5	5	25	1	Traces	1	22	0	0.1	Traces	0.1	3.2	0
Au/V_2O_5 (sol)	20	100	29	1	4	3	0	6.0	0.2	0.8	0.5	0
Ta_2O_5	2	25	3	Traces	6	2	0	0.3	Traces	0.5	0.2	0
Au/Ta_2O_5 (sol)	13	163	6	3	6	3	0	0.8	0.3	0.8	0.4	0
Al_2O_3	3	0.8	1	Traces	0	0	0	0.1	Traces	0	0	0
Au/Al_2O_3 (sol)	28	7.4	28	1	6	4	0	7.6	0.2	1.7	1.2	0
Au/Al_2O_3 (DPU)	13	3.4	14	1	3	2	0	1.8	0.1	0.4	0.3	0
Au/C (ALD) (sol)	76	32	36	8	7	4	1	27	6.6	5.1	3.3	1
Au/C (POCH) (sol)	17	1.2	49	1	13	11	0	8.6	0.2	2.2	1.9	0
Au/TiO_2[a]	91	–	38	7	4	3	2	34.6	6.1	3.8	3.2	1

Reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, T = 333 K, p_{O_2} = 6 bar, stirring = 1500 rpm, time = 5 h.

[a] Reference catalyst supplied by World Gold Council.

Table 6
Liquid phase oxidation of glycerol using Au–supported catalysts – effect of the reaction time.

Catalyst	Time, h	Glycerol conv., %	Selectivity, %				
			Glyceric acid	Tartronic acid	Glycolic acid	Formic acid	Oxalic acid
Au/Nb_2O_5 (cr) (sol)	1	36	31	3	6	4	–
Au/Nb_2O_5 (cr) (sol)	5	67	47	5	5	4	–
Au/Nb_2O_5 (cr) (sol)	15	94	43	5	7	5	Traces
Au/C (ALD) (sol)	1	71	34	6	10	6	2
Au/C (ALD) (sol)	5	76	36	8	7	4	1
Au/TiO_2[a]	1	65	38	3	4	3	1
Au/TiO_2[a]	5	91	38	7	4	3	2

Reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, T = 333 K, p_{O_2} = 6 bar, stirring = 1500 rpm.

[a] Reference catalyst supplied by World Gold Council.

Table 7
Liquid phase oxidation of glycerol using Au-supported catalysts – effect of the reaction temperature.

Catalyst	Temp., K	Glycerol conv., %	Selectivity, %				Yield, %			
			Glyceric acid	Tartronic acid	Glycolic acid	Formic acid	Glyceric acid	Tartronic acid	Glycolic acid	Formic acid
Au/Nb_2O_5 (am) (sol)	333	31	55	2	1	1	16.9	0.7	0.4	0.3
Au/Nb_2O_5 (am) (sol)	363	79	42	3	0.1	1.1	32.8	2.7	0.1	0.9
Au/Ta_2O_5 (sol)	333	13	6	3	6	3	0.8	0.3	0.8	0.4
Au/Ta_2O_5 (sol)	363	50	21	1	16	8	10.3	0.3	7.9	4.1
Au/Al_2O_3 (sol)	333	28	28	1	6	4	7.6	0.2	1.7	1.2
Au/Al_2O_3 (sol)	363	78	30	4	5	5	23.1	2.7	3.8	3.7

Reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, p_{O_2} = 6 bar, stirring = 1500 rpm, time = 5 h.

glycolic, oxalic and formic acids. However, the yields of these products are low.

Fig. 4 presents a comparison of glycerol conversion and the yield of glyceric acid production on the most active catalysts: gold supported on carbon and on niobia. It is clearly seen that even if the activity of carbon supported gold catalysts is a little higher than that of Au/Nb_2O_5 (cr) (sol) the yield of glyceric acid is higher on the latter catalyst.

The sum of the selectivities towards products of glycerol oxidation is lower than 100%. It could be due to the polymerization of the reaction products to compounds not detected by the HPLC analytical method, oxidation of the reaction products to CO_2 or the adsorption of products on the supports surface as was mentioned in [10].

3.2.3. *Effect of the reaction time*

The effect of the reaction time was also investigated for the selected samples. The results of glycerol oxidation after 1, 5 and 15 h are shown in Table 6. The data indicate a significant decrease in the activity when the reaction time decreases from 5 to 1 h, except for the gold catalysts based on activated carbon. In the last case a high conversion was reached after 1 h and remained almost the same as after 5 h. Probably it is caused by the highest pore volume in this catalyst.

The increase in the reaction time to 15 h, for the most active among group V metal oxides sample, i.e. Au/Nb_2O_5 (cr) (sol), causes a significant increase in the activity. The conversion of glycerol is almost total. It indicates that the increase in the contact time allows obtaining a very high activity, comparable to that obtained on gold supported carbons.

Moreover, it is worth noting that the reaction time has almost no influence on the selectivity towards the products of glycerol oxidation.

3.2.4. *Effect of the reaction temperature*

To get further information on the behaviour of the catalysts, oxidation experiments were carried out at different temperatures. The studies were performed for the gold/oxides catalysts showing low activity at 333 K. The increase in the reaction temperature from 333 to 363 K causes a significant increase in the glycerol conversion shown in Table 7.

Simultaneously, the increase in glyceric acid yield is observed. Like at 333 K, glyceric acid is the main product of the reaction at 363 K. However, it is worth noting that when using the niobia catalyst Au/Nb_2O_5 (am) (sol), the selectivity to glyceric acid decreases, whereas the selectivities to and yields of tartronic and formic acids are enhanced at higher temperature. It means that temperature promotes the oxidation of glyceric acid to other products of oxidation (mainly tartronic acid) showing that the glyceric acid is a by-product in the formation of tartronic and formic ones.

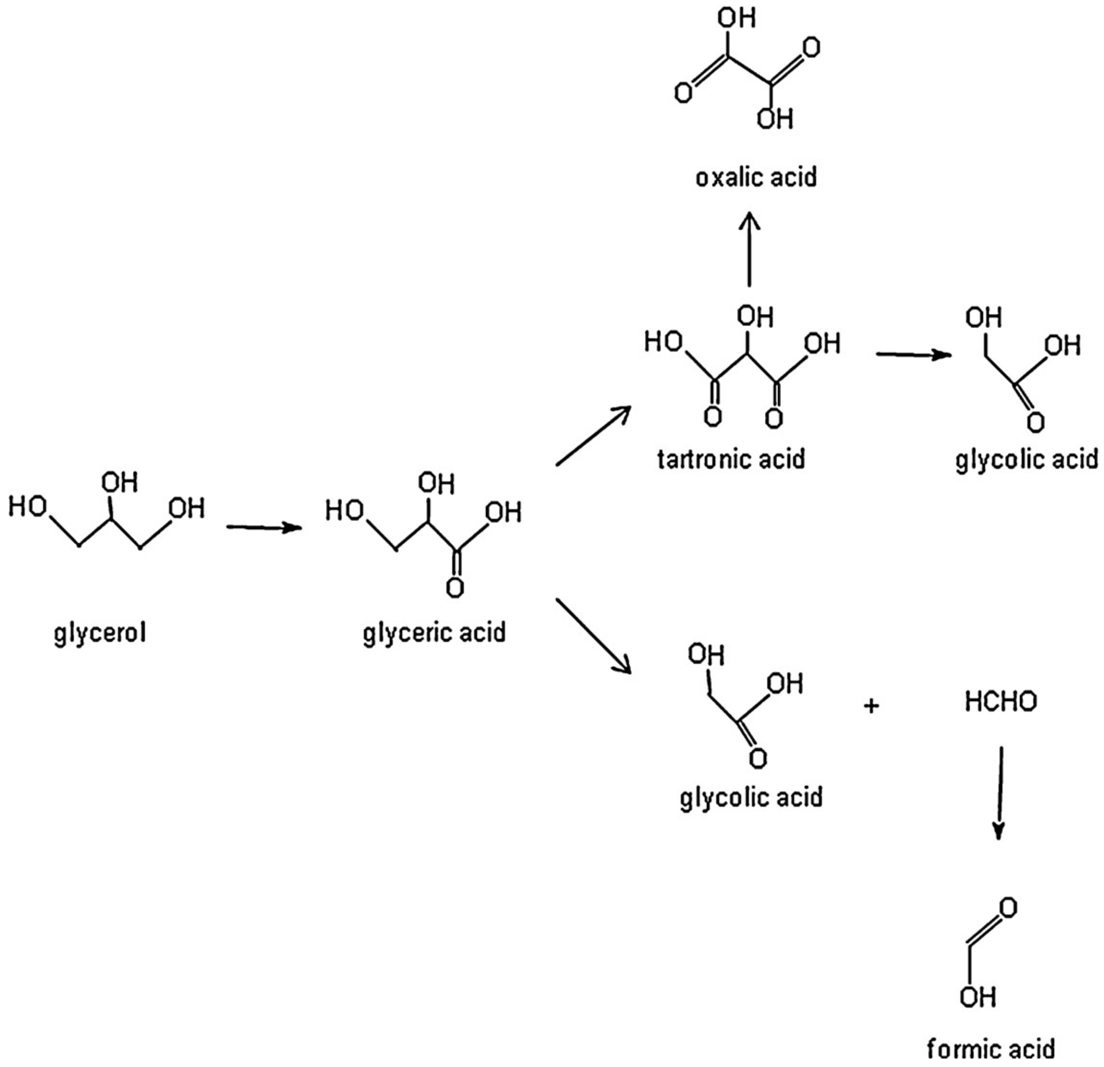
3.2.5. *Reuse of the catalysts*

It is know from literature that Au/carbon catalysts used in glycerol oxidation can be used several times without deactivation [31]. Gold on carbon shows the best stability in recycling tests (greater than palladium or platinum on carbon catalysts), showing neither

Table 8
Liquid phase oxidation of glycerol using Au/Nb_2O_5 (cr) (sol) catalyst – reuse of catalyst.

Catalyst	Glycerol conv., %	Selectivity, %			
		Glyceric acid	Tartronic acid	Glycolic acid	Formic acid
Au/Nb_2O_5 (cr) (sol) first reaction	67	47	5	5	4
Au/Nb_2O_5 (cr) (sol) second reaction	61	46	4	5	4

Reaction conditions: glycerol 100 mmol/kg, NaOH/glycerol molar ratio = 2, T = 333 K, p_{O_2} = 6 bar, stirring = 1500 rpm, time = 5 h.



Scheme 1. Possible reaction pathway for glycerol oxidation.

deactivation nor metal leaching. The results of the reuse experiments for Au/Nb_2O_5 (cr) (sol) are shown in Table 8. It is worth emphasizing that the catalyst used in the first reaction was simply recovered by decantation of the solvent after the reaction and reused without any washing and drying. The data in Table 8 indicate only slightly decrease in glycerol conversion, with no considerable changes in the selectivity. The small decrease in the activity can be ascribed to a small loss of the catalyst during the workup.

4. Discussion

The idea of this study was to compare the activity and selectivity of gold catalysts supported on various oxides with the catalytic properties of Au supported on carbons in the oxidation of glycerol. Results of our study confirmed the earlier reports for Au deposited on carbons [11,14] showing that the gold-sol method used for modification of the metal oxides ensures higher gold dispersion than that obtained by the deposition–precipitation one. Therefore, our further considerations concern the catalysts prepared by the gold-sol technique.

The nature of metal oxides used as supports of gold species determines their acid–base properties which influences both, the particle size of metallic gold loaded on their surface and the final activity and selectivity in the oxidation of glycerol. Alumina applied in this study exhibits basic character as follows from the test reactions. Therefore, $AuCl(OH)_3^-$ (formed from $AuCl_4^-$ at pH 6–8) ions used for the modification are not strongly anchored on its surface, which results in a higher agglomeration of metallic gold during calcination. It leads to greater particle size of gold. In contrast, vanadium and niobium oxides showing the domination of acidic character of the surface, formed stronger connections with $AuCl(OH)_3^-$ ions and as a consequence the dispersion of gold on them after calcination was higher. Another important parameter is the crystallinity of the oxide. Anhydrous niobium(V) oxide is a crystalline material, whereas the hydrous oxide is amorphous. The first contains unsaturated niobium atoms at the corners and edges of the crystals that stronger interact with gold precursor than saturated Nb species in amorphous niobia. Such interaction could increase the activity of oxygen from Nb_2O_5 active in the abstraction of proton from glycerol. The overall selectivity of the reaction is a resultant of combination of various factors. Among them the basicity and acidity of gold catalysts play an important role because these parameters determine the product stability.

Considering the mechanisms of glycerol oxidation process presented in literature [9,11,13] the oxidation of glycerol to glyceric acid on gold containing group five metal oxides most probably proceeds via initial formation of glyceraldehyde, which is rapidly oxidised to glyceric acid. The presence of tartronic acid and C2 or C1 by-products among the reaction products indicates that the further oxidation of glyceric acid leads to tartronic acid which would be expected to undergo facile decarboxylation to give glycolic acid [16]. The origin of formic acid is less obvious. However, as was suggested in [16], it is possible that the initially formed glyceric acid could undergo a reverse-aldol fragmentation to give glycolic acid directly and formaldehyde, oxidation of which would then account for the formic acid. The relative rates of each step of the reaction are determined by the nature of gold supports and therefore, depending on the support, various selectivities are reached. The possible reaction pathways for the partial oxidation of glycerol with gold loaded on group five metal oxides are shown in Scheme 1.

The first step of the reaction is the abstraction of a proton from the glycerol molecule, which usually involves the presence of Lewis basic centres on the catalyst. Such a process leads to glyceric aldehyde or hydroxyacetone. Interconversion between these dehydrogenation products occurs. The next step is aldehyde oxidation to glyceric acid and it is very fast, faster then the oxidation of ketone, and therefore the glyceric acid dominates among the reaction products. Among the metal oxides based catalysts, the highest basicity, deduced from the test reactions applied in this work, exhibit Au/Al_2O_3 (sol), Au/Al_2O_3 (DPU) and Au/Nb_2O_5 (cr) (sol) but their activity is not simply related to basicity because of different gold dispersion (much higher for niobia based catalyst). It confirms that oxidation of glycerol is a complex process and many parameters determine the activity and selectivity of the catalysts used. Interestingly, Au/C (Ald) (sol), which reveals acidic character in test reactions, demonstrates the highest activity and a very high yield of glyceric acid. This phenomenon is understood taking into account the basic medium of the reaction. The role of acidity of this catalyst is demonstrated by the relatively high yield of glycolic acid (5.1%). For the formation of this product the cracking of the C–C bond is necessary. Cracking is catalysed by the acidic centres on the catalyst surface. Such centres also exist on Au/Nb_2O_5 (cr) (sol) along with basic sites. Therefore, glycolic acid is also formed on this catalyst (yield of 3%) in the amount higher than on the other oxide based gold catalysts (yield below 3%).

The oxidation of glycerol is a typical consecutive reaction proceeding according to the rake model. In such a process the selectivity is strongly determined by the adsorption and desorption rate of each product. Thus, the relation between the rate of desorption of glyceric acid and the rate of its oxidation to tartronic acid determines the selectivity to one or the other product. The faster the desorption of glyceric acid the lower the selectivity to tartronic acid. The rate of desorption increases with the increasing temperature and chemisorption of glyceric acid on the catalyst surface. Therefore, the higher yield of tartronic acid is noted at higher temperatures (Table 7). Glyceric acid can be chemisorbed on both, Lewis basic centres interacting with OH groups and Brønsted acid sites. So, the difference in the acid–base properties of the catalysts used in this study implies the difference in the tartronic acid production. However, in all experiments performed within this study the main reaction product is glyceric acid suggesting that the chemisorption of glyceric acid is relatively week.

5. Conclusions

The most important conclusion following from this study is that Au/Nb_2O_5 (cr) (sol) catalyst is attractive for the liquid phase oxidation of glycerol showing high selectivity to glyceric acid and the ability of reuse. Its catalytic properties in this process are comparable with those noted for Au loaded on carbon, known as the best catalyst of this process. Similar activities and selectivities of both samples were observed in spite of the different acid–base properties of their surfaces. It indicates that many parameters determine the effectiveness of glycerol oxidation. The influences of the nature of the support and its crystallinity as well as the method of gold loading and acidic–basic properties of gold catalysts were considered. The gold-sol method used for the modification of oxides ensures high gold dispersion and smaller Au crystallites than the deposition–precipitation one. That is why the modification with Au with THPC as a reducing agent is recommended. Moreover, a significant difference between the amorphous and crystalline niobia used as supports of gold was established and better performance of anhydrous crystalline Nb_2O_5 was shown.

Acknowledgements

COST action D36, WG No D36/0006/06 and the Polish Ministry of Science (Grant Nos. 118/COS/2007/03 and N N204 032536) are acknowledged for the financial support of this work. Acknowledge is made also to Project AuTEK as source of Au/TiO_2 catalyst and Johnson Matthey (UK–USA) and SASOL (Germany) for supplying $HAuCl_4$ and Al_2O_3, respectively.

References

[1] G. Centi, R.A. van Santen (Eds.), Catalysis for Renewables—from Feedstock to Energy Production, Wiley-VCH Verlag GmbH & Co. KGaA, 2007.
[2] Y. Zheng, X. Chen, Y. Shen, Chem. Rev. 108 (2008) 5253–5277.
[3] Ch.-H. Zhou, J.N. Beltramini, Y.-X. Fan, G.Q. Lu, Chem. Soc. Rev. 37 (2008) 527–549.
[4] Biofuels for Transport. An International Perspective, International Energy Agency, Paris, France, 2004, p. 169.
[5] K.S. Tyson, J. Bozell, R. Wallace, E. Petersen, L. Moens, Biomass Oil Analysis, Research Needs and Recommendations, NREL/TP-510-34796, 2004, pp. 74–75.
[6] http://beag.ag.utk.edu/pp/biodiesel.pdf.
[7] L. Prati, P. Spontoni, A. Gaiassi, Top. Catal. 52 (2009) 288–296.
[8] N. Dimitratos, J.A. Lopez-Sanchez, G.J. Hutchings, Top. Catal. 52 (2009) 258–268.
[9] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Chem. Commun. (2002) 696–697.
[10] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, CH.J. Kiely, G.J. Hutchings, PCCP 5 (2003) 1329–1336.
[11] S. Demirel-Gülen, M. Lucas, P. Claus, Catal. Today 102–103 (2005) 166–172.
[12] W.C. Ketchie, Y.-L. Fang, M.S. Wong, M. Murayama, R.J. Davis, J. Catal. 250 (2007) 94–101.
[13] F. Porta, L. Prati, J. Catal. 224 (2004) 397–403.
[14] S. Demirel, P. Kern, M. Lucas, P. Claus, Catal. Today 122 (2007) 292–300.
[15] S. Demirel, K. Lehnert, M. Lucas, P. Claus, Appl. Catal., B 70 (2007) 637–643.
[16] N. Dimitratos, J.A. Lopez-Sanchez, J.M. Anthonykutty, G. Brett, A.F. Carley, R.C. Tiruvalam, A.A. Herzing, Ch.J. Kiely, D.W. Knight, G.J. Hutchings, Phys. Chem. Chem. Phys. 11 (2009) 4952–4961.
[17] S.D. Pollington, D.I. Enache, P. Landon, S. Meenakshisundaram, N. Dimitratos, A. Wagland, G.J. Hutchings, E.H. Stitt, Catal. Today 145 (2009) 169–175.
[18] W.C. Ketchie, M. Murayama, R.J. Davis, Top. Catal. 44 (2007) 307–317.
[19] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037–3058.
[20] R. Garcia, M. Besson, P. Gallezot, Appl. Catal., A: Gen. 127 (1995) 165–176.
[21] N. Dimitratos, A. Villa, L. Prati, Catal. Lett. 133 (2009) 334–340.
[22] I. Nowak, M. Ziolek, Chem. Rev. 99 (1999) 3603–3624.
[23] D.L. Feldheim, C.A. Foss, Metal Nanoparticles. Synthesis, Characterization and Applications, Basel Marsel Dekker, Inc, New York, 2002.
[24] C. Kan, W. Cai, Z. Li, G. Fu, L. Zhang, Chem. Phys. Lett. 382 (2003) 318–324.
[25] A.C. Gluhoi, X. Tang, P. Marginean, B.E. Nieuwenhuys, Top. Catal. 39 (2006) 101–110.
[26] R.M. Dessau, Zeolites 10 (1990) 205–206.
[27] J.J. Alcaraz, B.J. Arena, R.D. Gillespie, J.S. Holmgren, Catal. Today 43 (1998) 89–99.
[28] V. Calvino-Casilda, R. Martin-Aranda, I. Sobczak, M. Ziolek, Appl. Catal., A: Gen. 303 (2006) 121–130.
[29] A. Gervasisni, J. Fenyvesi, A. Auroux, Catal. Lett. 43 (1997) 219–228.
[30] C. Lahousse, J. Bachelier, J.C. Lavalley, H. Lauron-Pernot, Le A.M. Govic, J. Mol. Catal. 87 (1994) 329–332.
[31] L. Prati, M. Rossi, J. Catal. 176 (1998) 552–560.