Synthesis and study of Au/TiO$_2$ and Au/CeO$_2$ nanocomposites for their physical properties and catalytic activity

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Abstract. The effect of the gold nanoparticles size, gold load, nature of support and composites’ specific surfaces area on the nanocomposites catalytic activity and selectivity was studied. It was demonstrated that glycerol conversion increased from 62% to 100% in the presence of the nanocomposites when Au particle size decreased from 26 to 1 nm. Glyceric acid was obtained as a main product with high selectivity.

1. Introduction

Supported gold catalysts are applicable in the hydrogenation processes [1], catalytic oxidations of CO [2, 3], alcohols [4, 5] and aldehydes [6]. There is also growing interest to apply such catalysts for water purification [7], air pollutions decreasing [8] as well as cars’ exhausting gases emission decrease [9]. Glycerol is a bio-diesel manufacturing by-product, its amount reaching up to 10% of the total mass of the products mixture, thus making it important to find a solution for the glycerol utilization problem. The glycerol catalytic oxidation by oxygen demonstrates great potential in this regard. A number of important products can be obtained in this process. Platinum group metals are classical supported heterogeneous catalysts [4-6] used in liquid-phase oxidation process of alcohols and aldehydes, including glycerol. It is known [10-15], that supported gold catalysts can be used in the processes of glycerol catalytic oxidation by molecular oxygen. The advantage of gold based catalysts in comparison to the classic Pt and Pd systems is in the absence of the gold catalysts’ surface deactivation by molecular oxygen in the process of oxidation [16, 17]. Gold catalyst can be used many times without regeneration required, so catalyst’s life time becomes longer [18, 19]. Catalysts activity and selectivity depends significantly on the support nature, size of the gold particles on the surface, catalyst's synthesis conditions as well as the oxidation process parameters. Gold catalysts supported on carbon materials or metal oxides are mostly used [20 – 22]. Metal oxide-supported Au catalysts can be grouped into two categories, with respect to glycerol oxidation, which depend on the support material: gold catalysts with inert support materials, such as SiO$_2$, Al$_2$O$_3$, or MgO, and gold catalysts with active support materials, such as Fe$_2$O$_3$, TiO$_2$, CeO$_2$, ZrO$_2$, NiO$_x$, CoO$_x$. Oxygen is adsorbed in large quantities on active support materials in a molecular form, probably as a superoxide (O$_2^-$) species [23]. This explains the high surface mobility of adsorbed oxygen so that diffusion to the gold particles is not rate-limiting. It has been demonstrated [24] that supported gold catalysts are active in the basic
environments only. The glycerol oxidation process has usually been studied at pH = 11-12, $P_{O_2} = 3\text{–}10$ atm and temperature of 298-373 K [11, 13, 24]. Glyceric acid is the currently only product that can be obtained with both high yield and selectivity. Authors of paper [11] report 100% selectivity by glyceric acid achieved in presence of 1%wtAu/C catalyst with glycerol conversion rate of 54-56% ($P_{O_2} = 3$ atm, 333 K, 3 h). There are works [10, 25] reporting about glycerol oxidation at the atmospheric oxygen pressure in presence of 1%wtAu/C or 1%wtAu/CeO$_2$ catalysts. Authors of the work [25] report that full glycerol conversion with selectivity by glyceric acid less than 53% has been achieved after two hours of oxidation in presence of 1%wtAu/C catalyst. Meanwhile, authors of the paper [10] report about glycerol conversion rate of just 38% with selectivity by glyceric acid 43% achieved after five hours of oxidation in presence of 1%wtAu/CeO$_2$. However, it is hard to find an appropriate catalyst and reaction conditions necessary to selectively obtain glycerol oxidation products other than glyceric acid.

This work is devoted to the synthesis and the study of the physical properties of Au/CeO$_2$ and Au/TiO$_2$ nanocomposites, as well as testing their catalytic activity in the reaction of glycerol oxidation and comparison of synthesized catalysts property to those of commercial Au/TiO$_2$ catalyst. The glycerol oxidation was studied at the atmospheric oxygen pressure.

2. Experimental

2.1. Catalyst preparation and characterisation

Two different types of nanocomposites, supported on TiO$_2$ or on CeO$_2$, were synthesised. TiO$_2$ nanoparticles were prepared by hydrolysis of titanium isopropoxide. The as-prepared powder consisted of anatase crystalline phase with crystallite size ($d_{kr}$) of 7-8 nm. The carrier synthesized was dispersed in ethanol and tetrachloroauric acid water solution diluted by C$_2$H$_5$OH (pH = 6-8) was added. After impregnating a carrier with tetrachloroauric acid, gold was reduced by formaldehyde or by hydroquinone ethanol solution (pH = 5-6). CeO$_2$ was prepared by the sol-gel combustion technique-ethylene glycol was used as a fuel and nitrate as oxidant. Cubic CeO$_2$ with $d_{kr}$ 16 nm is obtained. The carrier obtained was dispersed in deionized H$_2$O and tetrachloroauric acid water solution (pH = 7) was added. After impregnating a carrier with tetrachloroauric acid, gold is reduced by formaldehyde water solution. Suspensions obtained after gold reducing were filtered, washed by water or ethanol and dried under the temperature 80-90 °C. Phase composition of prepared nanocomposites was determined by the X-ray diffraction analysis (D8 Advance, Bruker AXS). The crystallite size was calculated from broadening of diffraction maxima using Scherrer Equation (software Topas 3). Chemical analysis was performed by means of the S4 Pioneer X-ray Spectrometer (Bruker AXS). Specific surface area (SSA) of the powders was measured using HROM-3 chromatograph by BET method at temperature of liquid nitrogen. TEM measurements were carried out with by means of transmission electron microscope JEOL JEM 2100 at 200 kV accelerating voltage and at magnifications 40 000-200 000x. Histograms of Au particle size distribution were obtained by the counting of at least 200 particles from the micrographs, and the mean particle diameter ($d_{Au}$) was calculated as $d_{Au} = \sum (d_i n_i) \cdot \left(\sum n_i\right)^{-1}$, where $n_i$ was the number of particles of specific diameter.

2.2. Glycerol oxidation

Oxidation of glycerol by molecular oxygen in the presence of supported gold catalysts was performed at atmospheric pressure in a thermostated glass batch reactor equipped with gas supply system and magnetic stirrer (2500 rpm). Reaction conditions, such as initial glycerol concentration $c_0$(glycerol) = 0.3 M, oxygen pressure $P(O_2) = 1$ atm, NaOH initial concentration $c_0$(NaOH) = 1.5 M, glycerol and gold molar ratio n(glyc.)/n(Au) = 300 mol/mol, temperature 60 °C and oxidation time 1 hours were kept constant. Reaction mixture samples were filtered for separation of catalysts. The filtered samples were analyzed by high-performance chromatograph UFLC Shimadzu Nexera. Activity of the catalysts
was estimated by glycerol conversion. Selectivity (mol%) of the products was calculated using the formula 
\[
\text{selectivity} = P_i \cdot 100\% \cdot \left( \sum P_i \right)^{-1},
\]
where \( P_i \) was the yield by a single product (mol%).

3. Results
Typical TEM microphotography and the corresponding histograms of synthesized nanocomposites are presented in figure 1. The morphology of the catalytic material, consisting of support and Au nanoparticles as an active phase, is visible (figures 1a,b,d,e). The support CeO₂ exhibits crystalline structure with less contrast. The support TiO₂ exhibits granular structure with less contrast. The metal nanoparticles possess higher contrast and sphere-like shape. In some regions of the sample they are coalesced, thus forming big aggregates. Very big Au particles with diameters about 30 - 50 nm are visible in some aggregates of the catalyst. They are not typical for the samples' studied structure. The corresponding size distribution histogram of Au nanoparticles in the 1wt%Au/CeO₂ and 5wt%Au/TiO₂ catalysts is shown in figure 1c, 1f. Electronic microscopy revealed that the average size of Au nanoparticles in 1wt%Au/CeO₂ catalyst is 8.7 nm and in 5wt%Au/TiO₂ catalyst – 9.9 nm.

Figure 1. TEM images of Au nanocomposites with particle size distribution (a,b,c – 5wt%Au/TiO₂; d,e,f – 1wt%Au/CeO₂)

The prepared nanocomposites were tested in glycerol oxidation processes. The results of study of catalyst synthesis parameters effect on the catalyst's activity and selectivity, demonstrated that the Au/TiO₂ nanocomposites synthesized with hydrochinon as a reducer are inactive compared with the nanocomposites where formaldehyde is used. Therefore, all the gold nanocomposites used in later studies were synthesized using formaldehyde as a gold reducer. According to the data presented in the table 1 in all cases glycerol catalytic oxidation main product in the presence of the Au/CeO₂ or
Au/TiO$_2$ nanocomposites is the glyceric acid, by-products are – tartronic, lactic, glycolic, oxalic, acetic and formic acids. It is visible from the data presented in the table 1 that the size of gold particles defines catalytic activity and selectivity of nanocomposites in the process of glycerol oxidation. When Au particle size decreased from 26 to 1 nm, glycerol conversion increased from 62 to 100%. In presence of Au/GeO$_2$ with Au particle size decreased from 9 to 1 nm the process selectivity by glyceric acid decreased from 52 to 44%. At the same time in the presence of catalyst Au/TiO$_2$ the process selectivity by glyceric acid practically did not depend on the size of Au particles. The results obtained in this work in presence of Au/GeO$_2$ are consistent with the data of works [11, 14, 26, 27]. According to the data presented in the mentioned works, the Au/C catalysts activity increases with the decrease of the gold particles size, although selectivity by glyceric acid decreases as well. For example, according to the data [14] with d$_{Au}$ increased from 12 to 20 nm the activity of the 1wt% Au/C catalyst decreases 8 times but selectivity by glyceric acid increased from 69 to 78% at the same time. The results obtained in this work in presence of Au/TiO$_2$ are consistent with the data of [12]. It is demonstrated in the work [12] that no obvious Au particles size impact on the catalyst activity and selectivity is found in case of glycerol oxidation in presence of 1wt% Au/TiO$_2$ catalyst.

### Table 1. Glycerol oxidation over supported gold catalysts

| Catalyst       | TEM d$_{Au}$ (nm) | XRD d$_{Au}$ (nm) | SSA. (m$^2$/g) | Glycerol conv., (mol%) | Selectivity, (mol%) |
|----------------|-------------------|-------------------|----------------|-----------------------|---------------------|
|                |                   |                   |                | GLIC                  | TAR                 |
| 1wt% Au/GeO$_2$| 9                 | 20-23             | 27             | 83                    | 52                  |
| 1.5wt% Au/GeO$_2$ | 1             | 29                 | 27             | 100                   | 44                  |
| 2.7wt% Au/GeO$_2$ | -              | 36                 | 27             | 74                    | 53                  |
| 1.5wt% Au/TiO$_2$ (commer.) | 2              | 2-5                | -              | 93                    | 62                  |
| 2wt% Au/TiO$_2$ | -                 | 10-15              | 122            | 59                    | 64                  |
| 5wt% Au/TiO$_2$ | 10                | 10-15              | 117            | 78                    | 62                  |
| 5wt% Au/TiO$_2$ | 26                | 22-25              | 101            | 62                    | 67                  |

* – oxidation time is 0.5 h, GLIC – glyceric acid, TAR – tartronic acid, LAC – lactic acid, GLY – glycolic acid, OXA – oxalic acid, ACE – acetic acid, FOR – formic acid

From the data collected in table 1 it could be concluded that Au/GeO$_2$ nanocomposites are more active but significantly less selective at the same time comparing to Au/TiO$_2$ nanocomposites having approximately same size of Au particles. For example, glycerol conversion equals to 83% (selectivity by glyceric acid is 52%) in presence of 1wt%Au/GeO$_2$ (d$_{Au}$ = 9 nm), but glycerol conversion equals to 78% in presence of 5wt%Au/TiO$_2$ (d$_{Au}$ = 10 nm) with selectivity by glyceric acid equals to 62%. The results obtained in this work are consistent with the data of [10]. It has been demonstrated in the work [10] that the 1wt%Au/GeO$_2$ catalyst is more active than 1wt%Au/TiO$_2$ catalyst in the oxidation of the glycerol with oxygen at the atmospheric pressure. However, the authors of the work [10] were capable to reach glycerol conversion of just 38% and 30% in five hours in presence of 1wt%Au/GeO$_2$ and 1wt%Au/TiO$_2$ catalysts respectively. Our work reports conditions for full glycerol conversion in presence of 1.5wt%Au/GeO$_2$ and 93% conversion in presence of 1.5wt%Au/TiO$_2$ in one hour (see table 1).

According to the data in table 1, it can be also concluded that there is no direct correlation between the catalysts activity and their specific surface area or gold content. Available reports on the subject are contradictory. The same conclusions (that there is no direct correlation between catalyst activity and specific surface area of the support) were also made in the works [10, 18] during the study of glycerol oxidation in the presence of Au based catalysts with different supports. The effect of the gold content is studied in the works [11, 13]. It is found in the work [11] that changing the gold content percentage from 0.25 to 1wt% does not affect d$_{Au}$ (25 nm). However, authors explain the decrease of the Au/C catalyst activity with the decrease of the gold content by the decrease of the gold particles quantity per catalyst’s surface unit. At the same time, work [13] demonstrates that with the increase of
the gold content from 0.33 to 7.2wt% Au/C catalysts activity decreases, but the d_{Au} increases from 2.7 to 42.3 nm.

By comparing the data presented in table 1, it could be concluded that the most effective catalysts for glycerol oxidation to glyceric acid were commercial 1.5wt%Au/TiO$_2$ and 5wt%Au/TiO$_2$ (synthesized in this work) catalysts.

4. Conclusions.
Au/Co$_2$ and Au/TiO$_2$ composites synthesized in this work as well as commercial 1.5wt%Au/TiO$_2$ are catalytically active in the process of glycerol oxidation under mild conditions. In comparison to the best results reported in literature, glyceric acid with high yield and selectivity is obtained at atmospheric pressure, using simple thermostated glass batch reactor. It was found that Au based catalysts activity depends from the size of gold nanoparticles, gold load and nature of the support.

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