

Selective oxidation of glucose versus CO oxidation over supported gold catalysts

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ABSTRACT

Two series of gold catalysts supported on TiO₂, SiO₂, and CeO₂ have been prepared by colloidal gold deposition with 2 wt% of nominal gold loading. The diameter of gold particle stabilized by polyvinylalcohol (PVA) or by tannic acid-citrate was 2–3 nm and 6–7 nm, which increased to 5–7 nm and 7–13 nm, respectively, after calcination in air. Catalytic activities were investigated and compared in CO oxidation and glucose oxidation reactions. Inverse correlation was found between the activities in glucose oxidation and CO oxidation suggesting that the mechanisms are different. Besides the high dispersion the nature of the support seems to play a significant role in the liquid phase reaction.

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1. Introduction

Since the discovery of the outstanding catalytic activity of gold nanoparticles in the CO oxidation several other gas and liquid phase oxidation reactions such as glucose oxidation have been investigated [1–8]. Until now no comparative data can be found about the behavior of the same catalysts in the CO oxidation and glucose oxidation.

Many efforts have been made to oxidize selectively the aldehyde group of D-glucose to produce gluconic acid which is a high value product for fine chemical industry [1,9]. During the last two decades Pt and Pd based catalysts exhibiting high activity but low selectivity in the oxidation of that multifunctional molecule have been extensively studied. The best catalytic performance was achieved with Bi promoted Pt–Pd catalyst supported on carbon but the metal leaching and self-poisoning effects could not be avoided [10,11].

First, Biella et al. published the highly efficient utilization of gold catalyst in the oxidation of glucose. They obtained gluconate with 100% selectivity using gold colloid particles as catalyst. Alkaline condition was essential for high activity but the reaction proceeded also under uncontrolled pH [12,13]. Catalytic activity inversely proportional to the diameter in the size range of 2.5–6 nm and a sudden loss of activity above 10 nm in size were

observed. The stability of the colloid particles was low, coagulation occurred after about 400 s [14]. To improve the stability, gold colloids were deposited on carbon support. The initial rates of the reaction were unchanged compared to the rates observed with non-supported particles operated under the same conditions, hence it was concluded that the support is of limited importance in the origin of the catalyst activity in the oxidation of glucose. However the gold–support interaction was declared to be essential for the formation of a stable catalyst system [15–17]. On the contrary other authors [9] reported different catalytic activity using different type of carbon supports with the same Au particle size indicating a specific metal–support interaction. Ishida et al. observed that gold particle size influences the catalytic effect more significantly than the nature of the support comparing carbon and different metal oxide supports such as Al₂O₃, ZrO₂, TiO₂, CeO₂ [18,19].

In CO oxidation high activity can be achieved with small gold particles, less than about 5 nm in size and the highest rates at sizes of about 2–3 nm. The support may take part in the reaction by oxygen activation and there is a specific role of the gold/support oxide perimeter in the case of some supports whereas – as seen above – many contradictions occur regarding the role of the support in glucose oxidation [9,16,20–23].

In the present paper gold catalysts supported on different oxides were synthesized with different sizes and characterized by XPS and TEM technique. Catalytic activities were investigated in both CO oxidation and glucose oxidation reactions in order to clarify the apparent contradictions reported earlier.

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2. Experimental

2.1. Materials

Aqueous solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich); polyvinylalcohol (PVA) (Aldrich); poly(diallyldimethylammonium) chloride (PDAA) (Aldrich); tannic acid (Aldrich); sodium citrate (Aldrich); commercial silica (Degussa Aerosil 200, Davisil), titania (Degussa P25 and Eurotitania from Tioxide International), ceria nanopowder (Aldrich) and NaBH_4 (Aldrich) were used as received for the preparation of the catalysts. Analytical grade D-glucose and analytical grade Na_2CO_3 and NaHCO_3 for the preparation of the buffer solution were purchased from Sigma–Aldrich and used as received. 0.8 wt% Au/C catalyst obtained from World Gold Council was used as a reference.

2.2. Sample preparation

The preparation of samples is described in [24,25]. Shortly, samples were prepared by two methods:

- (A) preparation of Au colloid (Au–PVA) reducing 27.5 mL 0.55 mM HAuCl_4 at room temperature with 3 mL 25 mM NaBH_4 in presence of 1 mL 2 g/L polyvinylalcohol (PVA) as stabilizer followed by adsorption of Au–PVA on (a) SiO_2 (Davisil) at pH 1.5 (Au– SiO_2 –PVA) (b) CeO_2 at pH 5–6 (Au– CeO_2 –PVA) (c) TiO_2 (P25) at pH 5–6 (Au– TiO_2 –PVA) and
- (B) preparation of Au colloid (Au–TC) reducing and stabilizing 16 mL 0.32 mM HAuCl_4 at 60 °C with the mixture of 3.2 mL 2 g/L sodium citrate and 0.8 mL 0.5 g/L tannic acid followed by adsorption of Au–TC assisted by PDAA addition (0.4 mL 20%) on (a) SiO_2 (Aerosil 200) (Au– SiO_2 –TC) (b) TiO_2 (Eurotitania) (Au– TiO_2 –TC) and at pH 1.5 (c) CeO_2 (Au– CeO_2 –TC).

All the preparation systems were filtered, washed thoroughly and dried at 60–80 °C. Different silica and titania supported samples were prepared to see that the different structure but same chemical composition could influence the activities.

2.3. Sample characterization

The Au content of the samples was determined by a double-focusing inductively coupled plasma mass spectrometer (ICP–MS, ELEMENT2). All measurements were made using a Scott-type spray chamber operating at room temperature and a Meinhard concentric nebulizer. The catalyst samples were dissolved in HNO_3 , HCl and HF acid mixture. Prior to the ICP–MS analysis the excess HF was removed. Au standards were used as reference.

The distribution and size of gold particles on TiO_2 , CeO_2 and SiO_2 was studied before and after reactions by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV equipped with energy dispersive spectrometer (EDS) for electron probe microanalysis. The aqueous suspensions of the samples were dropped on carbon-coated grid and after evaporating water the electron micrographs of the particles were taken. The gold particle size distribution was obtained by measuring the diameter of about 200–300 metal particles.

Surface concentrations of Au before and after reactions were determined by XPS performed by a KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber. Al K α characteristic X-ray line, 40 eV pass energy and FAT mode were applied for recording the XPS lines of Au 4f, Ce 3d, Si 2p and Ti 2p.

2.4. CO oxidation

The CO oxidation was measured in a quartz plug flow reactor of 4 mm inside diameter at atmospheric pressure connected to a Balzers Prisma QMS 200. Same amounts of catalysts (60 mg) were employed which were in situ calcined at 400 °C in 20% O_2 in He mixture for 1 h (10 K/min heating rate, 30 mL/min gas flow) for the removal of organic residues. Temperature programmed reaction was performed with a 55 mL/min gas flow of 0.5% CO and 9% O_2 in He with 4 K/min ramp rate. The conversion was calculated on the basis of the CO_2 production.

2.5. Glucose oxidation

Oxidation of glucose was carried out in a thermostated, magnetically stirred batch reactor, bubbling oxygen at atmospheric pressure through the liquid phase. The reaction was started by adding the calcined (400 °C in air for 1 h) catalyst to the O_2 saturated solution. Oxygen saturation was measured by Hanna HI 9143 dissolved oxygen meter. pH was kept at a constant value 9.5 by using carbonate–bicarbonate (volume ratio: 2:3) buffer solution. Typical reaction parameters were: $c_{\text{buffer}} = 0.1 \text{ M}$, $T = 35^\circ\text{C}$ stirring rate = 1000 rpm, $c_{\text{glucose}} = 0.1 \text{ M}$ in 30 mL water solution, O_2 flow = 100 mL/min (1 atm).

Analysis of the reaction products was performed by HPLC on a JASCO instrument equipped with a Jasco UV 2075 and an ERC 7515A RI detector. A Hamilton HC-75H+ form cation exchange column was used with aqueous succinic acid 0.11 mM as the eluent with 0.4 mL/min flowing rate. With this system it is possible to measure the concentration of glucose in the presence of gluconic acid. The conversion was calculated on the basis of the concentration of gluconic acid produced and glucose consumed. Under these conditions selectivity was always 100%.

The reaction is carried out under alkaline conditions where silica supported samples might have been dissolved. Experiment was made for checking the dissolution of silica as follows. 90 mg Davisil silica was mixed with 0.1 M carbonate–bicarbonate buffer then it was stirred for 3 h. The mixture was filtered through a 0.2 μm porous diameter filter then the Si content of the filtrate was measured by ICP–OES. 13 wt% of the silica dissolved after 3 h of reaction. If we consider a linear dissolution rate of silica, the amount of dissolved silica is less than 1 wt% in the first 10 min where the initial reaction rate was calculated for comparison of the samples.

Utilization of buffer solution is very convenient compared to titration with NaOH. The possible negative effect of the buffer was investigated. The buffer reduced the reaction rate when its concentration was above 0.1 M. Below this concentration (0.05 M) the reaction rate did not change within the experimental error. For comparison the reaction was performed with NaOH titration and the reaction rate was slightly higher: we obtained 10% higher reaction rate in the first 10 min in the case of the most active sample.

3. Results and discussion

3.1. Catalyst characterization

Two series of catalyst samples were prepared by colloidal gold deposition on different supports (CeO_2 , TiO_2 and SiO_2) with 2 wt% of nominal gold loading. The diameter of the particles and the gold content of the samples were determined by TEM and ICP–MS, respectively (Table 1). After deposition on the support followed by calcination the particle sizes of the pre-prepared gold sols increased to 5–7 nm in case of the PVA stabilized samples and 7–13 nm in case of the tannin–citrate stabilized samples due to sintering (during calcinations). However, the sintering during the calcination neces-

Table 1

Sample properties and catalytic activities in CO oxidation and glucose oxidation.

Samples	Support	Au content (wt %)	Surface area/pore size (m ² /g)/nm	d_{Au} (TEM) after calcination (nm)	Catalytic activity			
					CO oxidation	Glucose oxidation		
					T at 50% CO conversion ^a	Reaction rate (μmol/min)	Spec. activity (μmol/mg _{Au} /min)	TOF ^b (1/h)
WGC sample								
Au/C	Activated carbon	0.8	1200/0.8–0.9	10.5	–	35	147	14901
Sols								
Au–PVA		–	–	2.2 ± 0.9	–	–	–	–
Au–TC		–	–	6.7 ± 1.8	–	–	–	–
Samples								
Au–SiO ₂ –PVA	Davisil	1.7	300/15	7.8 ± 2.8	400	34	66	5210
Au–TiO ₂ –PVA	P25	2.3	55/non-porous	5.3 ± 2.1	30	6	10	514
Au–CeO ₂ –PVA	Aldrich	2.2	80–100/non-porous	5.6 ± 3.5	57	6	10	563
Au–SiO ₂ –TC	Aerosil	2	200/non-porous	6.8 ± 2.8	308	25	42	2864
Au–TiO ₂ –TC	Eurotitania	2.3	125/0.3	13.0 ± 5.6	130	12	18	2349
Au–CeO ₂ –TC	Aldrich	2	80–100/non-porous	8.0 ± 3.8	46	14	23	1889

^a Ref.: A. Beck, A. Horváth, G. Stefler, M.S. Scurrell, L. Guzzi, Top. Catal. 52 (2009) 912–919.^b TOF values were calculated on the basis of the number of surface gold atoms estimated from mean diameter of Au considering spherical shape particles.

sary for the removal of organic materials results in bigger size and broader distribution compared to the size of the original colloid this method allows us to use the same procedure in case of all support and application of the pre-prepared colloidal particles for the preparation ensures that the gold particles are in metallic state.

XPS spectra were recorded on the samples after calcination, before glucose oxidation and on the spent catalysts after glucose oxidation. The results confirmed the presence of gold on the surface of each samples. The surface atomic ratio of gold and the support cation were calculated and presented in Table 2. The same amount of gold was found on the surface before and after glucose oxidation except Au–SiO₂–PVA (Davisil supported Au sample) and Au–TiO₂–TC (Eurotitania supported Au sample). Thus, we can declare that there is neither metal leaching nor sintering during liquid phase glucose oxidation except of those samples, where the surface Au/Si, Ti ratio decreased.

Regarding the silica supported samples the Au/Si ratio decrease was not observed in the case of Au–SiO₂–TC (Aerosil 200 supported) sample. The difference between the behaviors of the silicas might be due to their different structure. Aerosil 200 is a non-porous, very small particle size (12 nm average primary particle size) support material which might be able to stabilize the gold particles via surrounding it. The gold could not move easily on its surface because of this steric effect. This explanation was supported by the negligible change in the average particle size during calcination, too: In the case of Au–SiO₂–PVA (Davisil) the size increased from 2.2 to 7.8, while in the case of Au–SiO₂–TC (Aerosil 200) the average particle size only slightly increased. The difference between the silicas in the surface Au/Si ratios before glucose oxidation might be again due to their different structure. In the case of Aerosil support, where Au particles are surrounded, covered by SiO₂ particles similar in size, part of them may be hidden for XPS but not for the glucose molecules.

Table 2

Surface Au content of samples (measured by XPS).

Samples	Surface atomic ratio Au/M (M = Ce, Si, Ti) (%)	
	Before glucose oxidation	After glucose oxidation
Au–CeO ₂ –PVA	1.6	1.7
Au–CeO ₂ –TC	2.2	2.2
Au–SiO ₂ –PVA	1.2	0.6
Au–SiO ₂ –TC	0.5	0.5
Au–TiO ₂ –PVA	1.4	1.4
Au–TiO ₂ –TC	2.4	1.9

In the case of Au–SiO₂–PVA after glucose oxidation where no other species that may cover Au was found on the surface by XPS, metal leaching or sintering during the reaction remain to explain the Au/Si ratio decrease. In order to elucidate the reasons TEM images were taken and gold content was measured after glucose oxidation. Based on the gold content measurement by ICP–MS leaching of the metal can be excluded. Figs. 1 and 2 show typical TEM images (a) and particle size distributions (b) of the Au–SiO₂–PVA sample before and after glucose oxidation. Comparing the figures some very large gold particles (aggregates) of 30–40 nm can be observed besides the smaller particles after the reaction. Biella et al. also observed similar change in the particle size and explained by the dissolution and reprecipitation of the particles [12]. In our case Au particle migration, increased mobility and aggregation may be the reasons of the decrease in the surface Au/Si atomic ratio. However, particle migration into the pores cannot be excluded because Davisil is a porous support.

In the case of Au–TiO₂–TC (Eurotitania supported sample) the results show slight decrease in surface Au/Ti ratio after glucose oxidation that could be due to some sintering or metal leaching again. TEM images were taken after the reaction but no significant change was observed neither in the average particle size nor in the distribution. The particle size of that Au–TiO₂–TC sample was large after calcination and the distribution is quite broad that is why TEM images did not show much changes. It could be possible that the small gold particles migrated into the pores, which causes decrease in surface Au/Ti ratio. Taking into account that in our case Au/Si or Au/Ti ratio decrease was observed only on the porous samples some particle migration into pores is supposed.

3.2. Catalytic activity

The catalysts were tested and their performance was compared in CO oxidation and glucose oxidation reactions.

3.2.1. CO oxidation

Au supported on both TiO₂ and CeO₂ was very active with a temperature of 50% conversion (T_{50}) of 30 °C, 130 °C and 57 °C, 46 °C in case of PVA and TC stabilized samples, respectively (Table 1). The behavior of Au–SiO₂ catalysts was different, they were less active.

3.2.2. Glucose oxidation

The evaluation of the results of liquid phase reactions is more complicated than that of the gas phase reactions. Metal leach-

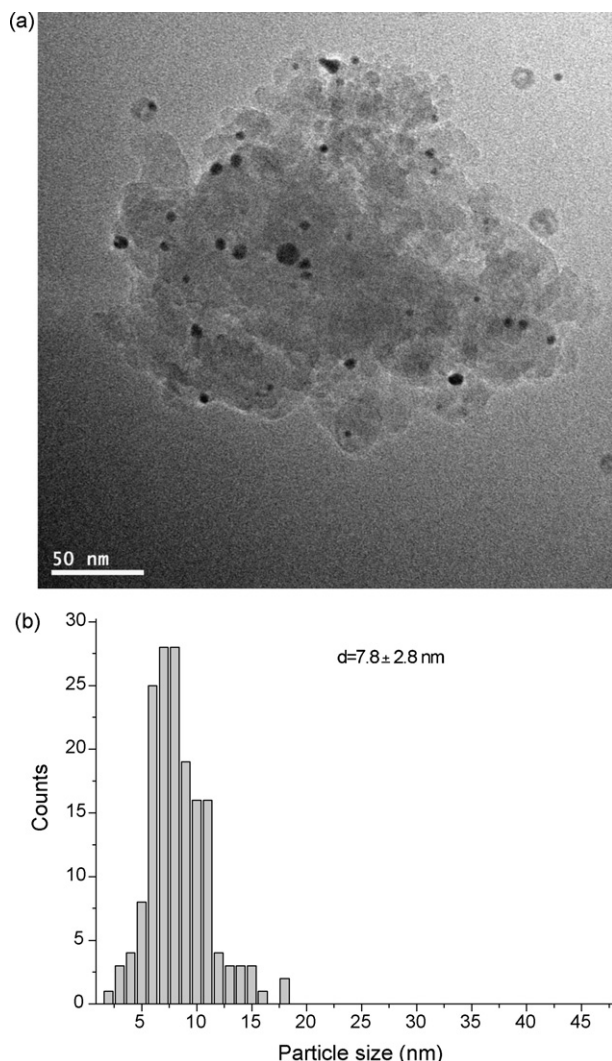


Fig. 1. TEM image (a) and the size distribution (b) of Au-SiO₂-PVA before glucose oxidation.

ing and poisoning by the products may occur during the reaction. Avoiding those effects the reaction is suggested to carry out under controlled pH and temperature. The required temperature is below 60 °C, the appropriate pH is between 9 and 10 [9]. Under the actual reaction conditions only gluconic acid as product was observed in its gluconate form at alkaline conditions. No isomerization products occur.

3.2.3. Effect of catalyst mass

In case of the most active Au/C catalyst the effect of catalyst amount was studied between 10 and 40 mg. Reaction parameters, such as buffer concentration, temperature, stirring rate, glucose concentration and oxygen flow rate were kept constant. Fig. 3 shows the effect of catalyst amount in terms of activities. The activity increases linearly indicating that the reaction proceeds under kinetic control in the whole range. In further experiments 30 mg catalyst was used.

3.2.4. Effect of oxygen concentration

The effect of oxygen concentration was studied by choosing two different values of oxygen concentration, 8 mg/L and 40 mg/L provided by using 20% O₂/N₂ and pure O₂ bubbling. The experiments were carried out using $c_{\text{buffer}} = 0.1$ M, pH 9.5, $T = 35$ °C, stirring rate = 1000 rpm, $c_{\text{glucose}} = 0.1$ M. The reaction rate increases

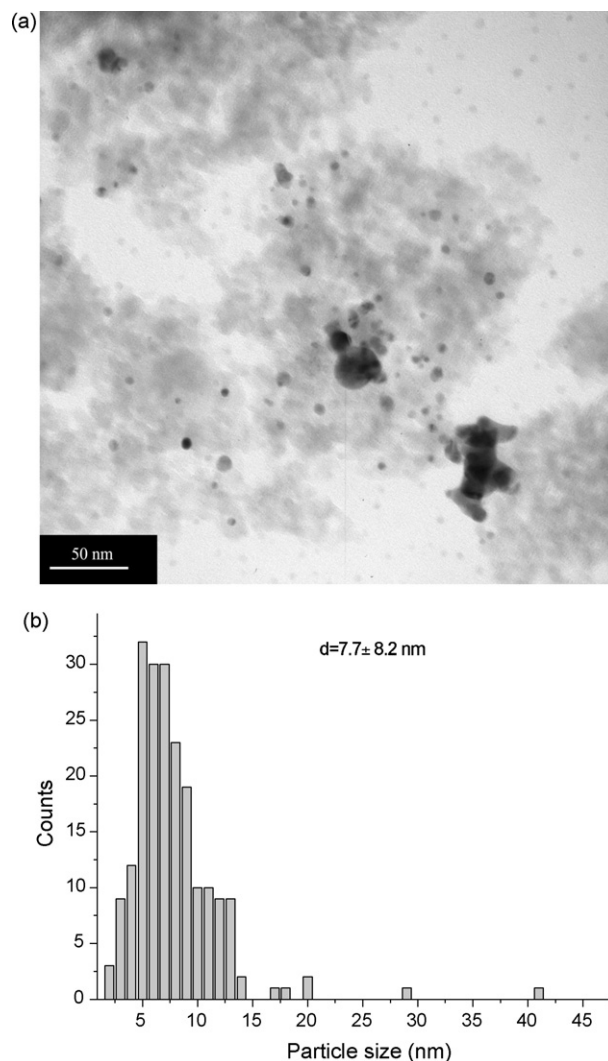


Fig. 2. TEM image (a) and the size distribution (b) of Au-SiO₂-PVA after glucose oxidation.

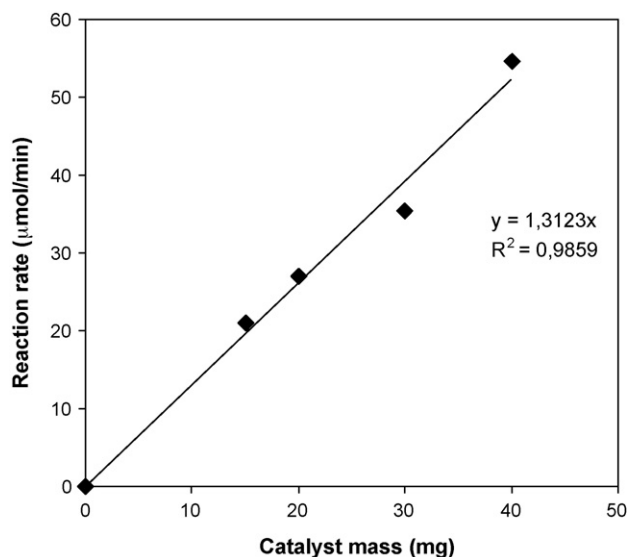


Fig. 3. Effect of catalyst loading on glucose oxidation with Au/C, $c_{\text{buffer}} = 0.1$ M, pH 9.5, $T = 35$ °C, stirring rate = 1000 rpm, $c_{\text{glucose}} = 0.1$ M, O₂ flow = 100 mL/min (1 atm).

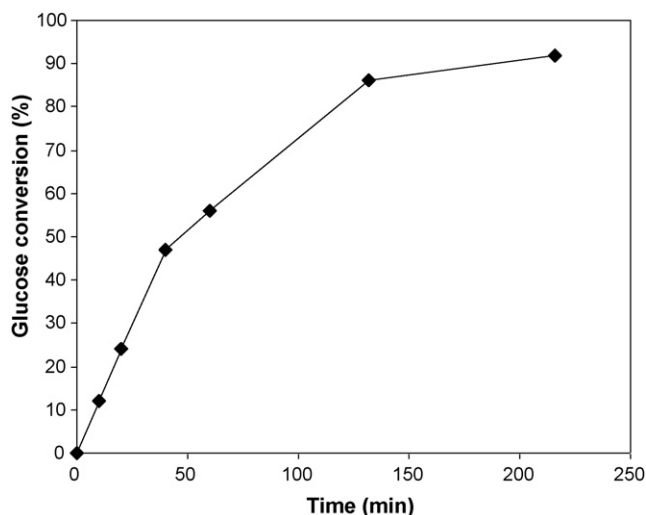


Fig. 4. Glucose oxidation conversion curve, catalyst: 0.8 wt% Au/C, $c_{\text{buffer}} = 0.1$ M, pH 9.5, $T = 35^\circ\text{C}$, stirring rate = 1000 rpm, $c_{\text{glucose}} = 0.1$ M, O_2 flow = 100 mL/min (1 atm).

with oxygen concentration as follows: 14 $\mu\text{mol/min}$ at 20% O_2/N_2 ; 35 $\mu\text{mol/min}$ at 100% O_2 .

Dissolved oxygen meter was used to estimate the rate of oxygen dissolution. The reaction mixture was saturated by oxygen in 15 min, up to about 40 mg/L oxygen concentration (saturation concentration at the used temperature [26]). The rate of oxygen dissolution in the reaction media was estimated to be the same or higher than the rate of glucose oxidation reaction over the most active Au/C sample. This result confirms that the overall reaction rate is not limited by oxygen dissolution.

A typical glucose oxidation conversion curve is presented in Fig. 4. The curve is linear up to 50% glucose conversion then the rate started to decrease. This behavior can be interpreted either by a non-zero order reaction with respect to glucose or the buffer capacity is close to its maximum value at about 50% conversion, the pH starts to decrease and for this reason the reaction rate also decreases. This deviation from linearity in the curve above 50% conversion does not influence the activities which were calculated from the reaction rate extrapolated to zero.

3.3. Comparison of the activity in CO oxidation and in glucose oxidation

Fig. 5 shows correlation between the T_{50} in CO oxidation and reaction rate in glucose oxidation that demonstrates the relation between the activities in the two reactions. The higher the temperature of 50% CO conversion the lower the activity of the sample is. The more active samples in CO oxidation are less active samples in glucose oxidation. Reducible oxides – ceria and titania – ensure the high activity in CO oxidation, whereas silica is much less effective support. In accordance with previous studies [1,19] the activity increases with decreasing particle size. In contrast, in glucose oxidation inverse activity order was found. Similar behavior was observed by Edwards et al. [27] in the oxidation of hydrogen, where a quite precise inverse correlation between the rates of hydrogen peroxide synthesis and carbon monoxide oxidation was established. In our case silica and carbon supported samples were more effective than the reducible oxide supported samples and higher activity was observed over catalysts with larger gold particles on each support. Fig. 6 shows the activity of catalysts in glucose oxidation as the function of particle size.

Considering the possible explanations of the diverse behavior of the same samples in the two reactions it is hardly to be expected

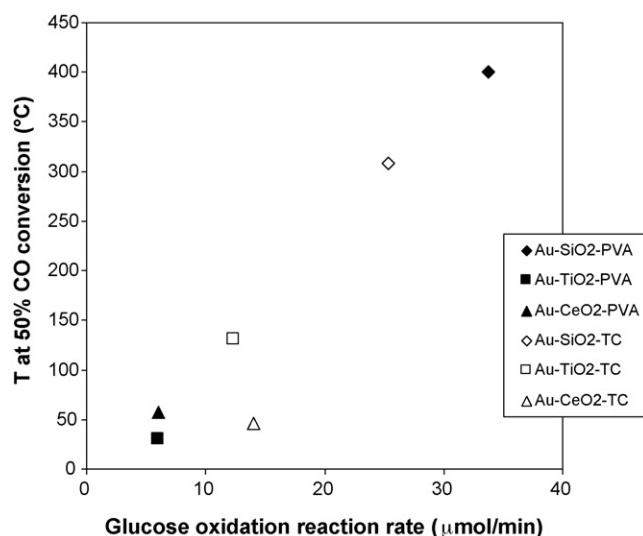


Fig. 5. Comparison of activities in CO oxidation and glucose oxidation. The higher the T of 50% CO conversion the lower the activity is.

that the activity is in correlation with the presence of very small c.a. 0.5 nm bilayer clusters as reported by Hutchings and co-workers because the most probable shape of the pre-prepared colloid particles is spherical [28]. The effect of the ionic species is also excluded based on the application of pre-prepared sol and XPS results. The difference between the surface geometry of the small particles and the large particles could be the reason of why the larger particles are more active in glucose oxidation and small ones in CO oxidation. Glucose is a large multifunctional molecule compared to CO. For its adsorption different surface arrangements and sites are needed.

Considering the effect of the particle size we cannot separate that from the possible role of the support. However in this study the Au/C reference catalyst gives higher activity (Fig. 6) the silica supported catalysts also work well indicating that weak-metal support interaction and high surface area favor the reaction. The pore structure should also play a role in the accessibility of the smaller particles in the pores by glucose. In our system Davisil silica, Eurotitan and Activated carbon are porous supports. Davisil silica has

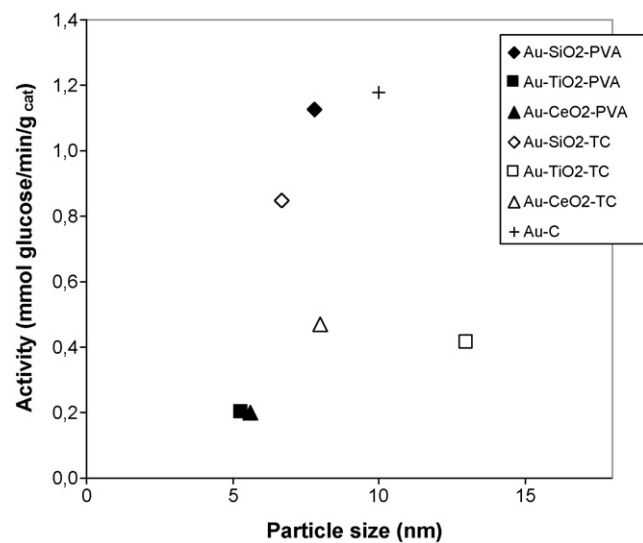


Fig. 6. Comparison of the activities in glucose oxidation as the function of Au size determined by TEM, $c_{\text{buffer}} = 0.1$ M, pH 9.5, $T = 35^\circ\text{C}$, stirring rate = 1000 rpm, $c_{\text{glucose}} = 0.1$ M, O_2 flow = 100 mL/min (1 atm).

15 nm pore size and gold particles could penetrate into the pores. However, if the stabilized Au particles penetrate into the pores and stabilized there in the calcined sample after the removal of large organic stabilizer there should be enough accessibility of the much smaller glucose but in this case pore diffusion can occur. Even so the activity of this sample is the highest in glucose oxidation compared to the other samples. Eurotitania is also a porous support with 3.6 nm pore size. This support was used with 6–7 nm particle size gold sol considering that most of the particles are outside of the pores but some of them could be small enough to penetrate into the pores. The role of the surface area of the support could be that the support may adsorb the reacting glucose molecule facilitating the reaction as it was discussed by Okatsu et al. [19].

The Au/C catalyst in CO oxidation did not show activity until 190 °C where the carbon support started to burn.

Deposition of the same Au sol on different supports resulted different particle size after calcination at 400 °C depending on the support due to particle moving and sintering. This behavior can be observed also at low temperature in the liquid phase reaction in case of Au–SiO₂–PVA sample, where larger particles or aggregates are shown in TEM images (Figs. 1 and 2). Particle migration on the surface is hindered on reducible oxides after calcination because of stabilization of the Au particles by metal–support interaction. On SiO₂ support weak metal–support interaction is supposed compared to ceria or titania.

The opposite support effect observed in the glucose oxidation as compared in CO oxidation suggests different O₂ activation mechanism in the two reactions and/or the presence of a metal–support interaction in case of reducible oxides that modifies the ability of Au for activating glucose and O₂.

4. Conclusion

In gold catalyzed total oxidation reactions as e.g. CO the smaller gold particle size and the reducible oxide supports favor the activity. On the contrary, our results in glucose oxidation using SiO₂, CeO₂ and TiO₂ supported sol derived two different size gold particles show that the SiO₂ supported larger size gold is more active.

Inverse correlation was found between the activities in CO oxidation and in glucose oxidation suggesting that the mechanisms are different which is explained by geometrical and support effects.

The results show that the effect of the support is more significant than the small gold particle size.

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