Ag-Pd nanoparticles prepared by laser ablation for selective oxidation of propylene glycol to lactic acid

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Abstract. Silver/palladium composite nanoparticles (NPs) obtained by pulsed laser ablation in liquid (PLAL) technique catalyze oxidation of propylene glycol (PG) to lactic acid (LA) in alkaline media. The PLAL technique allows obtaining silver/palladium NPs with different silver/palladium molar ratio. Addition of palladium increases PG conversion (up to 52%) and LA selectivity (up to 88%). The reaction temperature and silver/palladium molar ratio strongly affects the catalytic activity of the silver/palladium composite NPs.

1. Introduction

Recently, the challenge of reduction of carbon sources by chemical synthesis from fossil hydrocarbons is widely discussed. Propylene glycol (PG) can be synthesized by catalytic hydrogenolysis of biomass-derived polyols, such as glucose, glycerol, sorbitol, etc. [1]. One of the most valuable products that can be obtained through PG oxidation is lactic acid (LA), which finds in a wide range of fields, especially in production of biodegradable plastics [2]. There are a lot of valuable products that can be obtained by PG catalytic oxidation: methylglyoxal [3], hydroxyacetone [4], lactic acid [5], etc.

Silver NPs are promising alternative to noble metals used as catalysts in reaction of catalytic oxidation of polyols [6]. Recently, Xue et al. [5] developed a green chemical route for selective LA synthesis through aerobic oxidation of PG over Ag-Pd NPs in alkaline medium. Tentative reaction mechanism consists of 2 steps: in the first step PG oxidizes to methylglyoxal (MGO) on the metal NPs, and in the second step MGO converts into sodium lactate via intramolecular Cannizarro reaction in an alkaline media. The catalysts were prepared by wet chemical reduction method. However, in this case to form the NPs, both template and toxic reducing agent hydrazine were used that led to additional steps of centrifugation, washing and drying of Ag-Pd NPs prior to the application.

Pulsed laser ablation in liquid (PLAL) attracts growing attention as a facile and “green” one-step method to synthesize nanomaterials to be used in catalysis [7]. High-energy PLAL allows obtaining “pure” and active NPs directly as colloid solutions in pure solvents without the addition of any surfactants or stabilizers. Additional advantages of this method are relative simplicity, a broad variation of materials for ablation and the opportunity to produce composite NPs [8]. PLAL technique allows obtaining bimetallic Ag-Pd NPs [9].

In the present work, we aimed to use PLAL to prepare monometallic (Ag and Pd) and bimetallic (Ag-Pd) NPs and estimate their catalytic activity in selective oxidation of PG with oxygen in alkali media.

2. Methods
2.1. Catalyst preparation.
The PLAL was carried out using Q-switch Nd:YAG laser source operating at a repetition rate of 20 Hz, with a laser duration, wavelength and energy of 7 nanosecond, 1064 nm and 150 mJ, respectively. Silver and palladium targets with purity of not less than 99.97% were used. Focused radiation was introduced through the side wall of a 100 ml cylindrical glass reactor. Detailed experimental conditions of PLAL are described in Ref. [10]. The concentration of NPs in the dispersion was 50 mg/L determined by the loss of target mass. The operation was repeated several times to obtain the desired amount of dispersion.

To synthesize the silver/palladium NP composite in water, the as-prepared PLAL dispersions of silver and palladium in water were mixed in the given ratio, placed in a 100 ml cylindrical glass reactor with a diameter of 50 mm and then irradiated through the side wall by focused laser irradiation (lens with F = 50 mm) of the same Q-switch Nd:YAG laser. The focus of the lens was in the center of the reactor. Irradiation was carried out during 30 min with a continuous magnetic stirring.

2.2. Catalysts characterization.
SEM images were obtained by TEM CM12 (Phillips, Netherlands). Dispersions were deposited on copper grids with an amorphous carbon coating and dried. UV-vis DR spectra were obtained by Carry 100 (Varian, Australia) in the transmission mode in a quartz cuvette with a thickness of 2 mm in the spectral range of 200-800 nm.

2.3. Catalytic tests.
In the first mode (opened reactor) 20 ml of water dispersions of the metal NPs (50 mg/ml) was placed in a three-necked flask equipped with a condenser, then the calculated amount of propylene glycol (99.3 wt%) and sodium hydroxide were added to the reaction mixture. The reaction flask was placed in an oil bath with a thermocouple and heated up to the given reaction temperature. Oxidation reaction was started by pumping of molecular oxygen throughout the reaction mixture (P(O₂) = 1 bar, oxygen flow rate = 80 ml/min). At the end of the reaction, metal NPs were separated by centrifugation and the reaction mixture was analyzed by GC and HPLC. In the second mode of testing (closed reactor), 20 ml of water dispersion of the metal NPs (50 mg/ml) was placed in a glass reactor, then the calculated amount of PG and sodium hydroxide were added to the reaction mixture. The reactor was purged with oxygen (P(O₂) = 3 bar), placed in an oil bath with a thermocouple and heated up to the desired temperature.

3. Results and discussion

3.1. Catalyst characterization.
According to TEM data, the bimetallic NPs with a different Ag/Pd ratio are formed as a result of the focused laser beam treatment of the mixture of silver and palladium NPs (Fig. 1). To study the structure and morphology of the prepared NPs, TEM method was used. Both composite NPs have spherical shape with a diameter below 15 nm for Ag and 60 nm for Pd.
In the present work we studied the optical properties of the obtained metal NP dispersions (Fig. 2). Basic dispersions obtained by the PLAL technique (50 mg/ml) from monometallic silver and palladium targets in water possess the characteristic peaks of the surface plasmon resonance with a maximum at 410 nm for silver colloid solution (curve 1) and 205 nm for palladium solution, respectively (curve 2). In addition to a pronounced narrow peak at 205 nm, a wide band with the maximum at 250–400 nm appears in the palladium colloid probably due to the incorporation of hydrogen [11] into the palladium NPs as a result of high-energy synthesis and repeated interaction of palladium particles with the laser radiation [6]. The increased optical density in the long-wavelength range results from the scattering of the particles due to their agglomeration.

Figure 1. TEM image of Ag-Pd NPs with 50/50 ratio.

Figure 2. UV-Vis absorption spectra of NPs dispersions.
1 – Ag dispersion, 2 – Pd dispersion, 3 – a mixture of Ag and Pd dispersions before laser irradiation, 4 – a mixture of Ag and Pd dispersions after laser irradiation.
UV-vis DRS spectra of the initial mixture of silver and palladium NP dispersions (25 mg/ml of each component) are close to the superposition of the spectra of monometallic dispersions. Intensity of the characteristic peaks are lower due to decreasing of the concentration of Ag and Pd NPs in the resulting mixture (curve 3). Optical properties of the mixture change after the powerful laser irradiation (curve 4). The intensity of absorption (scattering) is increased in the entire investigated range. Characteristic peak of the silver surface plasmon resonance completely disappears, while the characteristic peak position of the palladium surface plasmon resonance does not change. According to Ref. [12], the presence of palladium in the bimetallic alloy suppresses plasmon resonance of silver NPs. Thus, the disappearing of the characteristic peak of silver plasmon resonance after laser irradiation confirms the formation of Ag-Pd alloy. Visually, the solution becomes more saturated with a dark brown tint.

3.2. Catalytic properties.

The result of PG catalytic conversion strongly depends on the catalyst nature. Low PG conversion in runs 1-4 (Table 1) may be due to low O₂ pressure. Ag/Pd molar ratio in the catalyst composition strongly affects the PG conversion pathway. The composite of Ag-Pd NPs synthesized by addition of 30% (mol) Pd dispersion to the Ag one results in a sharp increasing of the LA selectivity in comparison with the individual Ag NPs (Table 1, runs 1-2). Further enhancement of palladium content in the catalyst up to 100 % leads to increasing of both PG conversion and LA selectivity. Xue et al. [5] obtained similar dependence in the case of PG conversion and an opposite dependence in the case of LA selectivity. This fact may be due to different catalyst preparation methods used, which leads to the formation of another type of active surface. The overall carbon mass balance was poor in runs 1-2, probably, due to the formation of undetected lactaldehyde and carbon oxides. Hydroxyacetone is not found in the products that allow suggesting the PG oxidation only through the primary hydroxyl group.

**Table 1.** Catalytic properties of bimetallic silver/palladium composite NPs with different ratio in the PG to LA oxidation reaction.

| Reactor type | O₂ flow rate/pressure, (ml/min / bar) | Reaction temperature (°C) | Ag/Pd ratio | PG conversion (%) | LA (%) | FA (%) | AA (%) | PA (%) |
|--------------|---------------------------------|--------------------------|-------------|------------------|--------|--------|--------|--------|
| Opened       | 80                              | 75                       | 100/0       | 11               | 10     | 1      | 2      | 1      |
| Opened       | 80 ml/min                       | 75                       | 70/30       | 8                | 53     | 0      | 2      | 0      |
| Opened       | 80 ml/min                       | 75                       | 50/50       | 13               | 84     | 1      | 9      | 5      |
| Opened       | 80 ml/min                       | 75                       | 30/70       | 16               | 92     | 1      | 9      | 5      |
| Opened       | 80 ml/min                       | 75                       | 0/100       | 70               | 90     | 0      | 2      | 0      |
| Closed       | 3 bar                           | 75                       | 50/50       | 13               | 85     | 0      | <1     | 0      |
| Closed       | 3 bar                           | 85                       | 50/50'      | 21               | 85     | 1      | 3      | 0      |
| Closed       | 3 bar                           | 90                       | 50/50'      | 27               | 85     | 1      | 11     | 1      |
| Closed       | 3 bar                           | 100                      | 50/50'      | 58               | 81     | 1      | 11     | 0      |

Reaction time = 4 h, C(NaOH) = 0.6 M, C(PG) = 0.3 M, C (Ag/Pd) = 50 mg/ml
FA – formic acid, AA – acetic acid, PA – pyruvic acid, * - reaction time = 7 hours

In order to compare the influence of the oxygen pressure on the catalytic activity of the Ag-Pd NPs we tested the composite catalyst with a silver/palladium ratio of 50/50 under the same reaction conditions (T = 75 °C, C(PG) = 0.3 M, C(NaOH) = 0.6 M). Table 1 shows the results of the experiments (runs 6-9). PG conversion is higher at the increased O₂ pressure. We conclude that application of the closed reactor is more effective in the case of PG to LA oxidation on the silver-palladium NPs as a catalyst.

Increasing of the reaction temperature from 75°C to 90 °C leads to growth of PG conversion and LA selectivity (Table 1, runs 6-8). Further enhancement of the reaction temperature up to 100 °C results in LA selectivity decrease at much increased PG conversion (Table 1, run 9). The amount of AA rises as
the temperature increases. However, the selectivity to another product of C-C cleavage, FA, does not change. This can result from the high susceptibility of FA to decomposition at elevated temperatures.

4. Conclusions
Powerful laser irradiation of the mixtures of silver and palladium water NP dispersions allowed forming the bimetallic NP composites. The obtained Ag/Pd composites demonstrated high activity in the PG oxidation to LA in alkaline media. Increasing of the reaction temperature up to 90 °C led to increase of both PG conversion and LA selectivity. However, further rising of the reaction temperature up to 100 °C resulted in the decrease of the selectivity towards LA up to 80 % due to the oxidative cleavage of C-C bound in the propylene glycol molecule. The highest catalytic activity and selectivity towards LA was demonstrated by monometalic Pd, the addition of silver in Ag/Pd ratios from 30/70 to 70/30 leads to a decreasing of the catalytic activity of the bimetallic catalyst. The enhancement of oxygen pressure up to 3 bar and reaction temperature up to 90 °C led to increasing in the LA selectivity.

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