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Catalyst materials based on plasma-processed alumina nanopowder

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Abstract: A platinum catalyst for glycerol oxidation by molecular oxygen has been developed applying an extractive-pyrolytic method and using, as a support, a fine alumina powder with an average particle size of 30–60 nm processed by plasma technology. The extractive-pyrolytic method (EPM) allows affixing small amounts of catalytic metals (1–5 %) with the particle size ranging from several nanometers to several tens of nanometers onto the surface of the support. The prepared material, 4.8 wt. % platinum on nano-sized alumina, could be used as a catalyst for glycerol oxidation by oxygen with conversions up to 84 %, in order to produce some organic acids (glyceric and lactic acid) with a selectivity of about 60 %.

Keywords: platinum catalyst; extractive-pyrolytic method; glycerol oxidation.

INTRODUCTION

The increasing global demand for biodiesel causes an excess of other important product, glycerol. It is the main by-product in the production of biodiesel fuel with a yield of 10 %. Glycerol is a very useful chemical compound utilized in pharmacy, cosmetics and the food industry, but the demand for glycerol is much smaller than its produced quantity; hence, glycerol utilization is a significant problem.^{1,2} Selective oxidation could be one of the preferred methods to convert glycerol to valuable compounds. Using supported Pt, Pd or Au catalysts, glyceric acid, tartronic acid, dihydroxyacetone, glyceraldehyde, glycolic acid, hydroxypyruvic acid, mesoxalic acid and oxalic acid can be produced from glycerol. Glycerol oxidation over these noble metal catalysts by air oxygen is environmentally friendly because the reactions occur in aqueous solutions under low temperatures and pressures, and the catalysts are recyclable.^{3,4} Alumina is often used as a

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support for catalysts containing noble metals. It is known that the particle size of the support influences the obtained metal particle size.^{5,6} The activity and selectivity of platinum catalysts loaded on a support in dependence on the size of particles are discussed in some papers,^{7,8}

The plasma technology developed at the Institute of Inorganic Chemistry of the Riga Technical University, Riga, Latvia, allows fine oxide powders, including alumina, with an average particle size of 30–60 nm to be produced.⁹ Such powders could be used as supports for metal particle catalysts. Fine particles of noble metals (Pt, Pd, Au, *etc.*) on different supports and substrates could be prepared by the developed extractive-pyrolytic method (EPM).¹⁰ Herein, the production of platinum catalysts on nano-sized alumina supports and the test results of glycerol oxidation using the prepared catalyst are described.

EXPERIMENTAL

Characteristics of the support

The plasma technology for the production of nano-sized powders developed at the Institute of Inorganic Chemistry of the Riga Technical University is based on the evaporation of coarse commercially available powders of chemical elements and their compounds and on subsequent condensation of the products to a radio-frequency inductively coupled nitrogen plasma. The experimental equipment and the procedure are described in more detail in the literature.⁹ The nano-sized alumina powder for catalyst application was manufactured from 99.7 % pure raw alumina. The alumina powder, as processed (Fig. 1), contains δ - and θ -Al₂O₃ transition crystallographic phases with sphere-shaped particles of an average size of 30–60 nm (the specific surface area is 50 m² g⁻¹).¹¹

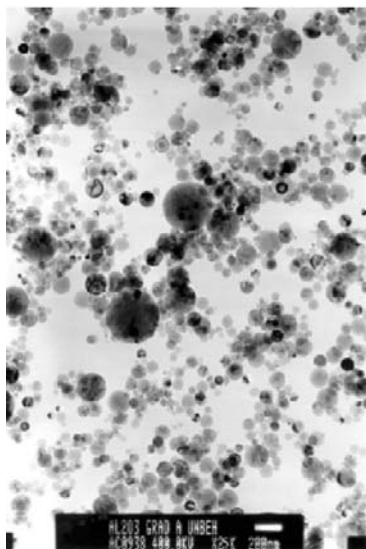


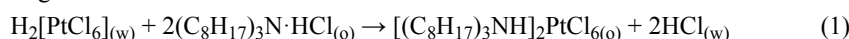
Fig. 1. Micrograph of plasma-processed alumina. Bar = 200 nm.

Materials for EPM and tests of catalytic properties

Platinum powder ($\geq 99.9\%$; Aldrich), HCl (35 %) and HNO₃ (65%) (Lachema), *n*-trioctylamine (C₈H₁₇)₃N ($\geq 95\%$; Fluka) and toluene (analytical grade; Stanchem) were used to produce the precursors. NaOH (reagent grade, Sigma–Aldrich) and oxygen (98 %; AGA SIA) were used to oxidize glycerol ($\geq 98\%$; Fluka). DL-Glyceraldehyde dimer ($\geq 97\%$; Aldrich), 1,3-dihydroxyacetone dimer ($\geq 97\%$; Aldrich), glyceric acid calcium salt hydrate ($\geq 99\%$; Fluka), sodium β -hydroxypyruvate hydrate ($\geq 97\%$; Fluka), lithium lactate ($\geq 97\%$; Fluka), tartronic acid ($\geq 98\%$; Alfa Aesar), sodium mesoxalate monohydrate ($\geq 98\%$; Aldrich), glycolic acid ($\geq 99\%$; Acros Organics), glyoxylic acid monohydrate ($\geq 98\%$; Aldrich), oxalic acid (98%; Aldrich), acetate standard for IC (1,000 g L⁻¹; Fluka), formate standard for IC (1,000 g L⁻¹; Fluka) were used to analyze the products of glycerol oxidation.

Catalyst preparation

The EPM used to prepare fine metal particles (Pt, Pd, Au, *etc.*) on different supports and substrates was developed at the Institute of Inorganic Chemistry (Riga Technical University). This method allows small amounts of catalytic metals (1–5 %) with particle size ranging from several nanometers to several tens of nanometers to be affixed onto the surface of the support. The main advantages of this method are its simplicity and low costs, and it is possible to apply the method without sophisticated equipment.¹⁰ The method is schematically illustrated in Fig. 2. Previously, a solution of platinum acid hexachloride was prepared. An amount of the platinum powder was dissolved in *aqua regia* and evaporated adding concentrated HCl to the wet salt that was then diluted with 2 M HCl to the necessary concentration (0.5 mol L⁻¹). The organic precursor (extract) was prepared by extracting platinum from the HCl solution using the *n*-trioctylamine (C₈H₁₇)₃N solution (1 M) in toluene. The following chemical interaction occurred during the extraction:



where the subscripts w and o denote the aqueous phase and organic phase, respectively. As a result, a solution of tri-*n*-octylammonium hexachloroplatinate in toluene was obtained.

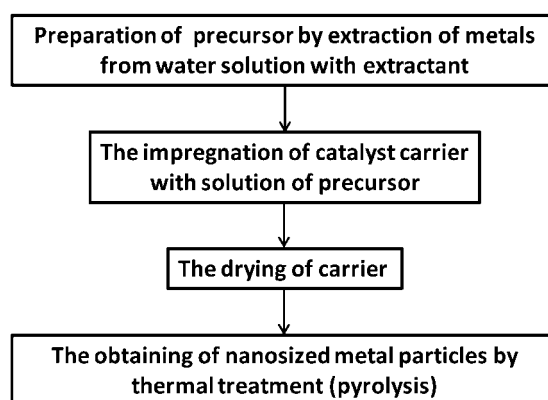


Fig. 2. Processing scheme of catalyst preparation by the extractive-pyrolytic method.

The results of the analysis of the aqueous solution after extraction using a HITACHI 180-50 atomic absorption spectrometer evidenced that the platinum had been completely extracted into the organic phase. Different volumes of the extract were used as the precursor

to impregnate the alumina nanopowder in order to produce catalysts with different platinum contents. After impregnation, the toluene was evaporated by drying at 90–110 °C. The materials were then heated in the air from room temperature to 300, 400 or 500 °C at a rate of 10 °C min⁻¹. The time of thermal treatment at these temperatures was varied from 5 to 120 min. The lowest temperature to ensure the complete decomposition of the precursor without contamination of the catalyst with organic pyrolysis products was 300 °C. This was established by recording the IR spectra of the produced materials.

The phase composition of the prepared catalysts was determined by XRD analysis using a D-8 Advance (Bruker AXS) diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The average crystallite size of platinum was computed from the (111) peak width by the Scherrer method. TEM investigations were performed using a JEM-1230 operating at 100 kV. The chemical composition of the prepared materials was determined by an X-ray fluorescence spectrometer S4 Pioneer (Bruker AXS).

Testing of the catalysts

Glycerol was oxidized by molecular oxygen in the presence of the catalysts in an alkaline medium in a thermostated slurry bubble column reactor operated in a batch mode. The oxidation was performed as follows: during thermostating (10 min), the required quantities of the dry catalyst, distilled water and an aqueous 3.0 M glycerol solution were fed into the reactor. The supply of oxygen into the reactor was turned on and the required volume of aqueous 5.0 M sodium hydroxide solution was added. The oxidation process started as soon as sodium hydroxide was added. The reaction conditions to test the catalyst were chosen based on preliminary experiments and are were the following: the initial glycerol concentration 0.3 M, the concentration of sodium hydroxide 1.5 M, the glycerol/Pt molar ratio 300 mol mol⁻¹, the reaction temperature 60 °C, the reactions time 7 h, the oxygen pressure 1 atm, and the rate of oxygen flow 300 cm³ min⁻¹. In order to determine the concentration of the reaction products, liquid samples were collected periodically from the reaction mixture in certain time intervals.

The reaction mixture was analyzed in a Waters 2487 high performance liquid chromatograph (HPLC) equipped with ultraviolet (UV 210 nm) and refractive index detectors. The possible products were identified by comparing with original samples.

RESULTS AND DISCUSSION

Dependence of the platinum particle size on processing parameters

The microscopic studies of the samples showed (Figs. 1 and 3) that it is impossible to identify the platinum particles correctly in the presence of alumina nanoparticles, since the metal particles and the carrier particles are difficult to distinguish. The XRD phase analysis of the platinum-containing composites showed that the peaks for Pt overlap, at least partially, with those of the carrier at all diffraction angles, which makes it difficult to determine precisely the mean size of platinum crystallites when the content of the metal in the composite was small ($\leq 2.4 \text{ wt. \%}$) (Fig. 4). Therefore, the average crystallite size was determined only for the composites containing 4.8 wt. % Pt using the most intensive peak (111).

The most important parameters of the catalyst preparation affecting the platinum crystallite size are the thermal treatment (pyrolysis) temperature and du-

ration. The results of investigations of the catalyst with 4.8 wt. % Pt testify that increasing the thermal treatment temperature and treatment duration leads to enlargement of the average crystallite size (Figs. 5 and 6).

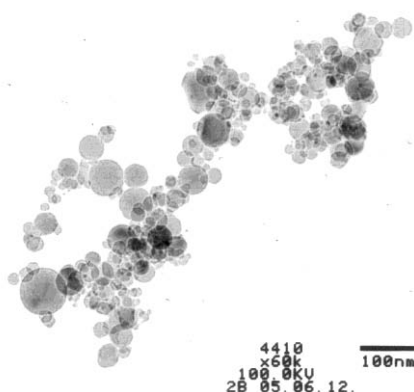


Fig. 3. Micrograph of the 2.4 % Pt catalyst on nano-sized alumina.

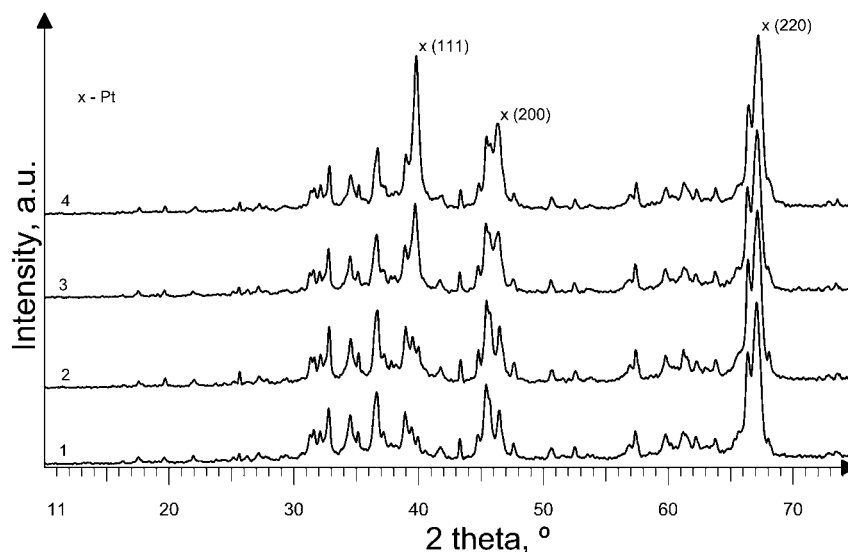


Fig. 4. XRD Patterns of plasma-processed alumina and catalyst powders, 1 – alumina nanopowder as processed, 2 – 1.2 wt. % platinum; 3 – 2.4 wt. % platinum, and 4 – 4.8 wt. % platinum on nano-sized alumina. Thermal treatment temperature 300 °C, treatment time 5 min.

Influence of catalyst synthesis parameters on glycerol oxidation

The obtained catalyst samples were tested for use in the process of glycerol oxidation. From Table I, it can be seen that the 4.8 % platinum-containing catalyst prepared at the lowest pyrolysis temperature 300 °C and having the smallest

average crystallite size demonstrates the highest activity (in terms of glycerol conversion) and selectivity to glyceric acid. Increasing the pyrolysis temperature from 300 to 500 °C decreased both the glycerol conversion from 75 to 22 % and the selectivity to glyceric acid from 53 to 15%. It is important to note that the catalysts prepared at a higher thermal treatment temperature exhibit very good selectivity to lactic acid, which attained 65–67 %. The data in Table II show that the increase of thermal treatment duration from 5 to 120 min led to an increase in catalyst activity. The glycerol conversion increased in this case by 9 %. The catalysts with a thermal treatment time of 120 min are more selective to glyceric acid, but their selectivity to other products is similar and low (<20 %).

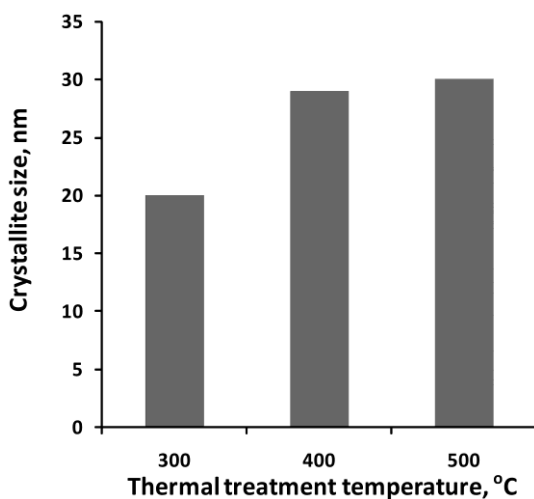


Fig. 5. Influence of the thermal treatment temperature on the average crystallite size of the platinum particles. Thermal treatment time 5 min. Catalysts with 4.8 wt. % Pt.

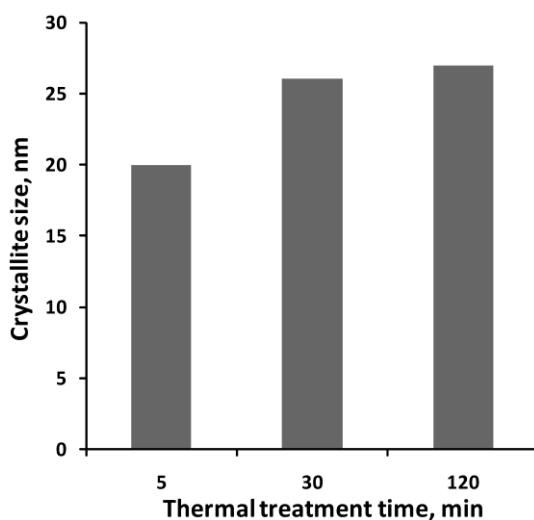


Fig. 6. The average platinum crystallite size vs. the pyrolysis time. Thermal treatment temperature 300 °C. Catalysts with 4.8 wt. % Pt.

TABLE I. Glycerol oxidation vs. the thermal treatment (pyrolysis) temperature, the treatment time was 5 min; GLYA – glyceric acid, TART – tartronic acid, LACT – lactic acid, GLYC – glycolic acid, OXAL – oxalic acid, FORM – formic acid

Pyrolysis temperature, °C	Glycerol conversion, %	Selectivity, mol %					
		GLYA	TART	LACT	GLYC	OXAL	FORM
300	75	53	13	19	10	3	2
400	16	15	2	65	15	0	3
500	22	15	3	67	12	0	3

TABLE II. Glycerol oxidation vs. the thermal treatment time at 300 °C; GLYA – glyceric acid, TART – tartronic acid, LACT – lactic acid, GLYC – glycolic acid, OXAL – oxalic acid, FORM – formic acid

Treatment time, min	Glycerol conversion, %	Selectivity, mol %					
		GLYA	TART	LACT	GLYC	OXAL	FORM
5	75	53	13	19	10	3	2
120	84	59	10	20	7	1	3

CONCLUSIONS

The employed extractive-pyrolytic method allowed nano-sized platinum particles on a nano-sized alumina support to be prepared.

The size of platinum crystallites in the catalyst with 4.8 wt. % Pt varied from 20 to 30 nm depending on the thermal treatment conditions.

The produced catalysts could be used for glycerol oxidation by oxygen for the preparation of glyceric or lactic acid with a glycerol conversion of up to 84 %.

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ИЗВОД

КАТАЛИЗАТОРИ БАЗИРАНИ НА ПЛАЗМА-ОБРАЂЕНОМ НАНОПРАХУ АЛУМИНИЈУМА

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Платински катализатор за оксидацију глицерола молекуларним кисеоником је развијен применом екстрактивно-пиrolитичке методе, и коришћењем носача од финог алуминијумског праха (величине честица 30–60 nm), процесираног плазма технологијом. Екстрактивно-пиrolитички метод (ЕРМ) омогућава додавање малих количина каталитичког метала (1–5 %) величине честица од неколико до неколико десетина нанометара, на површину подлоге. Добијени материјал – 4,8 тежинских процената платине на нано честицама алуминијума – може се употребити као катализатор за оксидацију глицерола кисеоником, са конверзијом до 84 %, у циљу добијања неких органских киселина (глицеринска и млечна), са селективношћу од око 60 %.

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