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PHOTOCATALYTIC HYDROGEN PRODUCTION FROM GLYCEROL - PRELIMINARY STUDY USING Pt/TiO_2 AND Pd/TiO_2 AS CATALYSTS

FOTOKATALITYCZNA PRODUKCJA WODORU Z GLICERYNY - BADANIA WSTĘPNE Z WYKORZYSTANIEM Pt/TiO_2 ORAZ Pd/TiO_2 JAKO KATALIZATORÓW

Abstract: Concern for the environment and the use of renewable energy sources are the two main priorities of energy policy combined with the environmental policy based on the principles of sustainable development. Many aspects should be taken into account in the case of energy production based on biomass/biofuels, in particular the possibility of additional by-products formation. When it comes to biodiesel production, the formation of huge amounts of surplus crude glycerol may be such a problem. The well-known, traditional methods of glycerol utilization are ineffective, which was proved by the big price drop in the glycerol market. High hopes to solve this problem are placed in new technologies: bio-conversion of glycerol to various chemicals or energy carriers and photocatalytic conversion to hydrogen. The paper presents the results of some preliminary studies of photocatalytic glycerol conversion to hydrogen. The investigation was focused on proper selection of catalysts and on the search for the optimum conditions of the photocatalytic process using TiO_2 doped with platinum or palladium (0.1, 0.5, 1 wt.%). The initial glycerol concentration in the solution was 4.5%. Photocatalysts were obtained by the sol-gel method. The effect of irradiation intensity was achieved by using 2-4 xenon lamps, the power of 75 W each. Gas product was analyzed by gas chromatography. The highest efficiency of hydrogen production (19.33 mmol/g of catalyst·h) was obtained for Pt doped TiO_2. The production rate of hydrogen depended on catalyst concentration, the amount of the noble metal in the catalysts, the concentration of glycerol in the solution and the intensity of irradiation.

Keywords: glycerol, hydrogen, photocatalysis

Introduction

Biodiesel is produced by transesterification of vegetable oils [1, 2]. The increase of biodiesel production observed all around the world contributes to the surplus of glycerol on the market. Therefore, nowadays, much emphasis is placed on the development of new technologies of glycerol utilization. Unfortunately, effective utilization of large amounts of waste fractions creates serious economic and technological problems [2]. One of the most promising processes seems to be its photocatalytic conversion into hydrogen, which is considered to be a modern and environmentally friendly method. The idea to apply this method emerged from the previous studies on the degradation of other organic pollutants

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(*eg* alcohols) into hydrogen. Photoconversion of glycerol is described by the below reaction [3, 4]:

$$C_3H_8O_{3(liquid)} + 3H_2O_{(liquid)} \xrightarrow[hv]{cat.TiO_2} 7H_{2(gas)} + 3CO_{2(gas)} \quad (1)$$

Photocatalysis is based on the absorption of light by the catalyst or by the substrate. Photoexcitation of the catalyst is based on the transfer of an electron from the valence band to the conduction band after it has absorbed an adequate portion of radiant energy. As a result of the process, we obtained one electron with reduction properties in the conduction band and a hole with oxidation properties in the valence band [1, 2, 5].

Photocatalytic conversion of glycerol to hydrogen is a promising way to convert solar energy into chemical energy [1, 5]. Titanium dioxide (TiO_2) is the most frequently used catalyst for the conversion of organic compounds (pollutants or wastes - including glycerol) into hydrogen. Surface modification of TiO_2 leads to the reduction in the band-gap energy and produces catalysts, which are active in the visible light and UV. Photocatalysts (*eg* TiO_2) that should be active over the entire visible spectrum are obtained by doping with nonmetals (N, S, C, B, P, F, I) and adding noble metals (or other metals) [4, 5]. The benefits of using TiO_2 as a basic support are its chemical and photochemical stability, low cost and non-toxicity [1, 5].

The aim was to test the catalysts (based on TiO_2) that were doped with Pt or Pd in the process of photoconversion of glycerol to hydrogen.

Materials and methods

Chemicals

Titanium(IV) isopropoxide (TIP) (97%) was purchased from Aldrich Chem. and used as the source of titanium for the preparation of TiO_2 nanoparticles. A commercial form of TiO_2 (P25, crystalline composition: 80% anatase, 20% rutile, surface area 50 g/m^2) was purchased from Evonik, Germany. 99.9% chloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$), 5 wt.% solution in 10 wt.% HCl palladium(II) chloride ($PdCl_2$) were provided by Aldrich Chem.

Experimental procedure

Reactions were carried out in a semi-batch quartz reactor (the volume of 40 cm^3). The reactor was charged with the mixture of glycerol aqueous solution (15 cm^3). The reaction mixture containing glycerol, water and catalyst was irradiated using xenon lamps (4 lamps Xe-arc XBO 75 W each), (4.5 wt.%) and photocatalysts - Pt/TiO_2 or Pd/TiO_2 (70 mg). Characteristics of photocatalyst are shown in Table 1. The temperature of the reaction mixture was in the range of 40-55ºC. Argon was used as a carrier gas, at the flow rate of 30 cm^3/min, to remove air from the reactor before the start of the reaction, to mix the liquid and to remove gas products from the reactor when performing the process. The almost homogeneous slurry of the catalyst was obtained by magnetic stirring and the flow of argon through a special distributor. Each of the experiments lasted approximately

4-6 hours. Gaseous phase was analyzed every 15 minutes. The scheme of laboratory set-up is presented in Figure 1.

Table 1

Photocatalysts characteristics for photoconversion of glycerol

Photocatalyst type	Preparation method	The type of metal precursor	Content of metal precursor [wt.%]	BET surface area [m^2/g]
0.1 Pt	sol-gel	$H_2Cl_6PtxH_2O$	0.1	92
0.5 Pt		$H_2Cl_6PtxH_2O$	0.5	148
1 Pt		$H_2Cl_6PtxH_2O$	1	130
0.1 Pd		$PdCl_2$	0.1	126
0.5 Pd		$PdCl_2$	0.5	86
1 Pd		$PdCl_2$	1	81

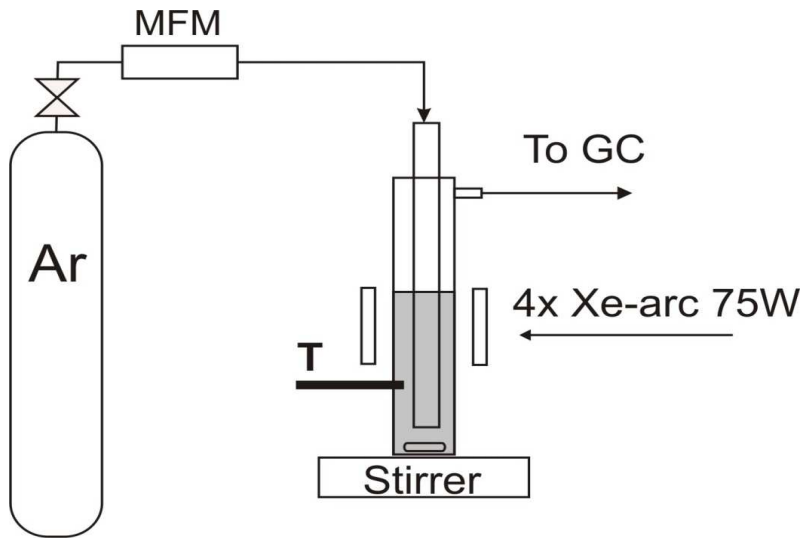

Fig. 1. The layout of laboratory set-up (Ar - inert gas; GC - the gas chromatograph; magnetic stirrer - 500 rpm)

Results and discussion

The main goal of the part of the study presented in this article was to compare the efficiency of hydrogen production for the two catalysts in the experiments carried out under the same conditions. Each time the amount of catalyst added to the solution was 70 mg. The volume of glycerol in water solution at the concentration of 4.5 wt.% was equal to 15 cm^3. Two types of catalysts were used in the experiments - TiO_2 doped with platinum or the second TiO_2 doped with palladium. In both cases the amount of the above metals in the TiO_2 was the same, respectively 0.1 and 0.5 representing 1% by weight. In each experiment we used four xenon lamps, the power of 75 W each. Operational conditions for each experiment are shown in Table 2. The comparison of hydrogen production efficiencies obtained in the experiments is presented in Figures 2 and 3.

Table 2

Experimental conditions and efficiency of glycerol photoconversion

Photocatalyst type	Photocatalyst amount [mg]	Glycerol initial concentration [wt.%]	Irradiation time [min]	Power of the light source [W]	Average hydrogen productivity [mmol/g_{cat} h]
0.1 Pt	70	4.5	180	300	17.35
0.5 Pt			210		11.18
1 Pt			195		6.12
0.1 Pd			150		13.41
0.5 Pd			180		6.20
1 Pd			180		1.41

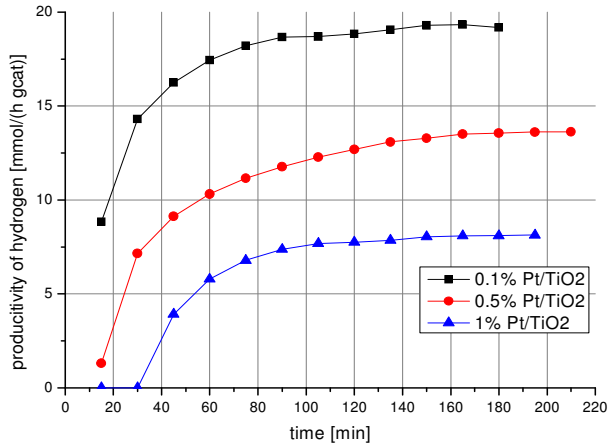

Fig. 2. Efficiency of hydrogen production during irradiation of aqueous glycerol solution in the presence of photocatalyst obtained by sol-gel method depending on the TiO_2 doped with Pt (0.1, 0.5, 1 wt.%)

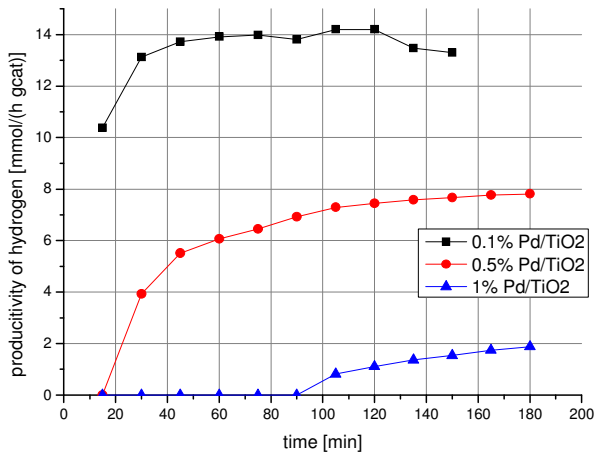

Fig. 3. Efficiency of hydrogen production during the irradiation of aqueous glycerol solution in the presence of photocatalyst obtained by sol-gel method depending on the TiO_2 doped with Pd (0.1, 0.5, 1 wt.%)

Hydrogen production yield obtained for Pt catalyst was higher than for Pd (catalysts prepared by the sol-gel method and photodeposition). The lower metal dopant content, the higher the efficiency of hydrogen production. The most optimal process conditions offering the highest H_2 productivity were found for 4.5 wt.% of glycerol concentration of aqueous solution and 0.07 g of the catalyst weight. The highest production efficiency of hydrogen for the 0.1% Pt (TiO_2) catalyst prepared by sol-gel for 4.5% glycerol solution was found to be 19.33 mmol/g_{cat} h. Hydrogen was identified in all the studied samples while carbon dioxide was not detected.

Conclusions

Results of the present study show that the highest efficiency of hydrogen production was achieved for the catalyst $Pt(TiO_2)$ rather than for Pd/TiO_2. Generation of hydrogen largely depends on the content of dopant metal and on the type of the catalyst.

Acknowledgments

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Abstrakt: Efektywna produkcja energii oparta na biomasie/biopaliwach powinna uwzględniać wiele aspektów, w szczególności możliwość powstania dodatkowych produktów ubocznych. W przypadku produkcji biodiesla takim problemem może być zagospodarowanie dużych ilości odpadowej gliceryny powstającej w tym procesie. Dotychczas stosowane tradycyjne metody jej utylizacji okazują się nieefektywne, o czym świadczy duży spadek cen na rynku surowej gliceryny. Duże nadzieje jej korzystnego zagospodarowania wiązane są z nowymi

technologiami - biokonwersją do różnych produktów chemicznych i energetycznych oraz fotokatalityczną konwersją do wodoru. W pracy przedstawiono badania przeprowadzone w celu selekcji katalizatorów, które mogą być wykorzystane do konwersji gliceryny, oraz znalezienia optymalnych warunków procesowych. Rozkład gliceryny badano, stosując jako katalizator TiO_2 domieszkowany platyną lub palladem (0,1, 0,5, 1% wag.). Stężenie gliceryny w roztworze wynosiło 4,5%. Fotokatalizatory otrzymano metodą zol-żel. Jako źródło światła wykorzystano od 2 do 4 lamp ksenonowych o mocy 75 W. Produkt gazowy analizowano metodą chromatografii gazowej. Najwyższą wydajność produkcji wodoru (19,33 mmola/g kat·h) otrzymano dla fotokatalizatora TiO_2 domieszkowanego 0,5% Pt. Efektywność generowania wodoru zależy od rodzaju katalizatora, jego stężenia w roztworze, zawartości metalu szlachetnego w katalizatorze, stężenia gliceryny oraz intensywności naświetlania.

Słowa kluczowe: gliceryna, wodór, fotokataliza