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Stearic acid hydrodeoxygenation over Pd nanoparticles embedded in mesoporous hypercrosslinked polystyrene

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ABSTRACT

Stearic acid hydrodeoxygenation into n-heptadecane on the catalyst containing Pd nanoparticles incorporated in the hypercrosslinked polystyrene matrix was studied. The used catalysts were characterized using TEM, CO chemisorption, low-temperature nitrogen physisorption and XPS. A clear hydrogen pressure dependent induction period was noticed. Kinetic regularities were studied for the indicated reaction in the presence of polymer based catalysts. A mathematical model for decarboxylation was suggested which was able to adequately describe experimental data at different temperatures, hydrogen pressures and initial concentrations of stearic acid. Kinetic constants were calculated and their statistical analysis was performed.

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Introduction

The growing interest to clean technologies based on renewable resources is due to the diminishing of petroleum resources, price volatility of crude oil and environmental hazards connected with the emissions from the fossil fuels. The increase in energy production and consumption is directly correlated with the increase in population and welfare. Due to many factors such as capital interests, oil prices fluctuations and other geopolitical problems, there is a significant growth in biofuel industry all over the world [1–4]. A substantial amount of research is devoted to bio-based fuels production from non-eatable, waste cooking oils and algae [5–8].

The processing of vegetable oils and fats is one of the permissive ways to obtain low-sulphur, low-oxygen, aromatic free and ecologically friendly automotive fuels. Methods of oils treatment can be classified into chemical and physical methods. Physical upgrading consists of char removal, hot vapour filtration, solvent addition and extraction of organic acids [9,10]. Chemical upgrading methods include catalytic etherification [11], hydrothermal liquefaction, deoxygenation and catalytic hydroprocessing [12,13]. Among the oil treatment processes catalytic hydrodeoxygenation is the most intensively studied one.

Oxygen content of bio resources has a significant effect on the resulting fuel properties. The high oxygen content of vegetable oils (up to 50 wt.%) leads to such disadvantages as low heating value, thermal and chemical instability and immiscibility with fossil fuels. Hydrodeoxygenation is a process of oxygenated compounds removal from fatty acids typically in the form of water [1].

Normally, catalytic hydrodeoxygenation of fatty acids and their derivatives is carried out at 200–500 °C and pressure of 0.1–6 MPa. Depending on the composition of the initial feedstock, the process duration is in the range of 60–400 min. No additional solvents in general are necessary. In the majority of cases, n-heptadecane is the desired product.

Typically the industrial Co–Mo and Ni–Mo catalysts are used in hydrodeoxygenation [14]. These catalysts have high activity and show good selectivity towards the desirable saturated hydrocarbons with the carbon number C_{12}–C_{20}. The main drawback of such catalysts is the necessity of activation by sulphur which can pollute the final product. Moreover, high oxygen and low sulphur content of vegetable oils can cause oxidation of the catalyst active

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sites and thus deactivate the sulphide catalysts [15,16]. Therefore recent investigations are focused on a search of new sulphur free catalytic systems.

Application of palladium catalysts in carboxylic acids deoxygenation was pioneered in Refs. [16–18]. More lately Lercher and co-workers proposed to use supported sulphur free Ni catalysts [19,20] in hydrodeoxygenation of fatty acids. The latter catalysts showed high activity and selectivity towards hydrocarbons in comparison with traditional sulphured NiMo and CoMo catalysts. Further investigations were focused on the development of catalytic systems on the basis of Co [21], Ni [4,5,8,22–29], Mo [30], Pt [31], Pd [6,7,32–35]. The most investigated catalysts Ni and Pd supported on inorganic materials (zeolites and carbon) showed rather high activity in the terms of turnover numbers (TON). These catalysts can be ranged in comparison with traditional catalysts as following Ni > Pd > sulphided NiMo giving TOF 50 g g_{cat}^{-1} h^{-1} [36], 46 g g_{cat}^{-1} h^{-1} [37] and 39 g g_{cat}^{-1} h^{-1} [38] respectively.

Previously it was demonstrated that palladium nanoparticles incorporated in hypercrosslinked polystyrene (HPS) are efficient catalytic systems in hydrogenation and oxidation of various substrates [39–42].

In this paper Pd/HPS catalytic systems were explored for the first time in hydrodeoxygenation of fatty acids using stearic acid as the model compound.

Experimental

Materials

Hypercrosslinked polystyrene MN-270 with the specific surface area 1350–1400 m^2/g (Purolite, UK), Na$_2$PdCl$_4$·6H$_2$O (99.9%, Sigma-Aldrich), tetrahydrofuran (98.0%, Sigma-Aldrich), methanol (99.0%, Sigma-Aldrich), stearic acid (98.0%, KhimMedServis, Russia), and dodecane (99.9% Sigma-Aldrich) were used as received.

Catalyst synthesis

HPS (fraction below 70 μm, mass 3 g) first pretreated with acetone and dried, was thereafter impregnated for 8–10 min with 6 mL of the solvent mixture consisting of 4 mL of tetrahydrofuran, 1 mL of methanol, and 1 mL of water as well as of the predetermined amount of Na$_2$PdCl$_4$. Then the polymer was dried at 70 ± 2 °C for 30 min. The sample obtained was treated with the solution of sodium carbonate, Na$_2$CO$_3$, with the concentration 2.76 g/L for 15 min, washed with distilled water and dried again for 1.5 h at 70 ± 2 °C. Metal-polymer systems with the palladium content (by loading) of 5 wt.% (5%-Pd/HPS), 3 wt.% (3%-Pd/HPS), and 1 wt.% (1%-Pd/HPS) were synthesized. All the synthesized catalysts were reduced with hydrogen at 300 °C for 3 h. Thermogravimetric analysis described in Ref. [43] showed that reaction temperature and temperature of preliminary reduction did not affect the stability of the polymeric matrix.

Hydrodeoxygenation procedure and the reaction mixture analysis

Stearic acid hydrodeoxygenation was carried out in a stainless steel temperature-controlled autoclave reactor Parr—4307 with the total volume 50 mL (Parr Instrument, USA). The liquid load was 30 mL. The reactor was equipped with a heating jacket and a stirring device. The suspension of a heterogeneous catalyst in dodecane (20 mL) was introduced into the autoclave through the side fitting. Before the reaction the catalyst was saturated with hydrogen at a preselected temperature and pressure for 30 min, and then the substrate in dodecane (10 mL) was introduced. Hydrodeoxygenation was carried out at constant stirring of 400–700 rpm with varying the size of catalyst granules (60–100 μm).

Upon completion of each experiment the selectivity was determined, i.e. the molar percent of n-heptadecane to the corresponding amount of consumed stearic acid. The main by-product of the reaction was n-pentadecane.

For a detailed kinetic study, several series of single-factor experiments were performed by varying the catalyst loading ([cat]$_0$), initial concentrations of stearic acid [C]$_0$ = 0.05–0.2 mol/L, temperature (230–260 °C), and hydrogen partial pressure (0.2–1.8 MPa), which was maintained constant through an adjustable valve (experimental series 1–4, respectively) thus allowing the reactor to operate in a semi-batch mode. For calculations of the hydrogen partial pressure the partial pressure of dodecane was subtracted from the overall pressure.

Samples were periodically taken and analysed by GC–MS, using tGC-2010 chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan). The analysis duration was 81 min using the following conditions: initial column temperature of 50 °C was withstood for 1 min, then the temperature was increased up to 210 °C with a heating rate 2 °C/min; injector temperature: 280 °C; automatic split; pressure of He 53.6 kPa; common stream of He 81.5 mL/min; linear gas velocity 36.3 cm^3/s; chromatographic column type HP-1MS: L = 30 m; d = 0.25 mm; film thickness 0.25 μm; ion source temperature: 260 °C; interface temperature: 280 °C; scanning mode 10 up to 800 m/z; scanning rate: 1666; electron-impact ionization. Quantitative identification was carried out with the use of neat reference substances.

Characterization

The catalyst specific surface area, porosity and pore size distribution were determined by nitrogen low-temperature adsorption with Beckman Coulter SA 3100 (Coulter Corporation, USA) analyser. Prior to the analysis, the samples were outgassed in Beckmann Coulter SA-PREP apparatus for sample preparation at 120 °C in vacuum for 1 h.

XPS data were obtained using Mg Kα (hν = 1253.6 eV) radiation with an ES-2403 spectrometer modified with an analyser PHOIBOS 100 produced by SPECS (Germany). All the data were acquired at an X-ray power of 200 W and an energy step of 0.1 eV. The samples were allowed to outgas for 180 min before analysis. The data analysis was performed by CasaXPS.

Pd nanoparticles sizes were evaluated by TEM using a JEOL JEM1010 scanning transmission electron microscope operating at 80 kV. The polymer samples were embedded in an epoxy resin and microtomed in cross-sections. Images of the resulting thin sections (ca. 50 nm thick) were collected with the Gatan digital camera and analysed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

The CO pulse chemisorption was performed using AutoChem 2900 Apparatus (Micromeritics). About 100 mg of catalyst was loaded in a U-tube and the following programme was used: He-flow 25 °C – H$_2$ flow at 25 °C 5 °C/min – 60 °C (20 min) – He-flow 60 °C (30 min) – 25 °C. CO pulses were injected onto the catalyst after 5 min interval until the Pd surface was saturated. The stoichiometry for CO adsorption on Pd was 2 [44]. The following gas composition was used: 10 vol% CO in He (AGA).

Parameter estimation methodology is described in Section 'Kinetic regularities'.

Results and discussion

Catalyst characterization

In XPS spectra (Fig. S1a and b; Table S1) the main elements were carbon, oxygen and palladium. We have also observed in trace amounts nitrogen, silicon, aluminium and sulphur, which can be