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OBTAINING PALLADIUM NANOPARTICLES AND THEIR APPLICATION AS CATALYST IN HYDROGENETION OF VEGETABLE OIL

Abstract. Palladium nanoparticles are obtained by reduction of palladium chloride with sodium borohydride. The obtained palladium particles are characterized by intense optical absorption in the region of λ=350 nm, which indicates the formation of particles with a size of 10-50 nm. Palladium nanoparticles are immobilized on activated carbon to increase the contact surface. The catalytic activity of the obtained catalyst has been studied in the hydrogenation reaction of vegetable oil at convection and microwave heating. It has been found that at the content of 1 % of the oil mass catalyst, a higher melting product is formed (38^{0}C. Decrease of temperature and duration reduction of the process results in low melting margarines of MLF and MLB grades). The use of microwave technology (power 700 W) reduces significantly the duration of the process (up to 30 minutes) to form a product with the melting point of 34^{0}C.

Key words: palladium nanoparticles, reduction, hydrogenation of vegetable oil, margarine, microwave activation.

Introduction. The colloids and clusters of platinum group metals exhibit high catalytic activity and selective capacity in relation to many reactions [1, 2]. In the work [3], it is reported that colloidal particles of platinum group metals synthesized by different methods differ markedly in their reaction and catalytic activity.

In the present work, obtaining of stable solutions of palladium nanoparticles, as well as the catalytic properties of immobilized Pd nanoparticles on activated carbon in the hydrogenation reaction of vegetable oil in margarine under the conditions of convection heating and microwave activation is described.

Depending on the melting point, consistency and appearance, margarines are divided into the following grades: hard (MH, MHC, MHF), soft (MS) and liquid (MLF, MLB). MH grade is used in bread, confectionery and culinary production and in home cooking. MHF - for the preparation of creams, fillings in flour confectionery goods, souffle, sweets and other sugary and flour confectionery goods (the melting temperature of MH and MHF grades should be 25-38^{0}C). MHC (the melting point is 36-44^{0}C) is used in the production of puff pastry. MS grade (the melting point is 25-36^{0}C) is directly used in food consumption, as well as in home cooking and in food industry. MLF grade is used for frying and cooking baked goods in home cooking, public catering network and industrial processing; and MLB is used for the mass production of bakery and baked confectionery products, as well as when frying products in the public catering network (the melting points of the grades MLF and MLB is not standardized) [4].

Experiment

UV spectra were recorded on a Shimadzu UV-1800 spectrometer (Japan). The melting point was determined on a PTP(M) device (Russia). Micrographs of the catalyst surface with 100-, 500- and 1000-fold increase were taken with a scanning electron microscope JSM-6510 LV of JEOL (Japan). The hydrogen generator GVCH-12M1 (Russia) was used to obtain hydrogen.

Obtaining of palladium nanoparticles supported on activated carbon. Prior to carrying out the reaction, solution of sodium borohydride and palladium chloride was prepared (2 drops of hydrochloric acid are added to the solution to dissolve the salt in water). At room temperature, to the reaction vessel containing 100 ml of $1{\cdot}10^{-3}$ mol/L of solution of palladium chloride, with constant stirring dropwise 100 ml of $1{\cdot}10^{-3}$ mol/L of solution of sodium borohydride is added. At the same time, colouration of the solution into whity brown is observed.

In order to prevent the agglutination process of nanoparticles into larger agglomerates, 2g of powdered pharmaceutical activated carbon is added to the reaction mixture and the solution is stirred for 6 hours. Then, the solution is filtered and the resulting solid mass is dried in a drying oven at a temperature of 110^0C for an hour.

Hydrogenation of vegetable oil.

a) 50 g of cottonseed oil is loaded and 0.5 g of catalyst (the palladium content in the catalyst is 0.53%) is added to a three-necked flask equipped with a stirrer, thermometer and hydrogen inlet tube. The process is carried out at 220-230^0C for 6 hours at a hydrogen flow rate of 0.2 l/min.

b) Mixture of 50 g of vegetable oil, 0.5 g of catalyst with constant hydrogen bubbling is irradiated with microwaves for 30 minutes.

Results and discussion

Synthesis of palladium dispersions has been carried out by reduction of palladium chloride with sodium borohydride [5].

The reduction reaction of palladium proceeds according to the following scheme:

$$2NaBH_4 + PdCl_2 + 6H_2O \rightarrow 2NaCl + 2H_3BO_3 + 7H_2 + Pd$$

The obtained palladium particles are characterized by intense optical absorption in the region of λ=350 nm (figure 1).

It is known [6] that a solution containing palladium nanoparticles with a particle size of 10 nm absorbs ultraviolet radiation in the region of 230 nm. With increase of the size of particles, the absorption bands shift into the visible region, for example, with an increase in the diameter of particles to 50 nm, a broad absorption band with a maximum of about 450 nm is observed. The obtained absorption spectrum data of palladium particles indicate the formation of particles with the sizes of 10-50 nm.

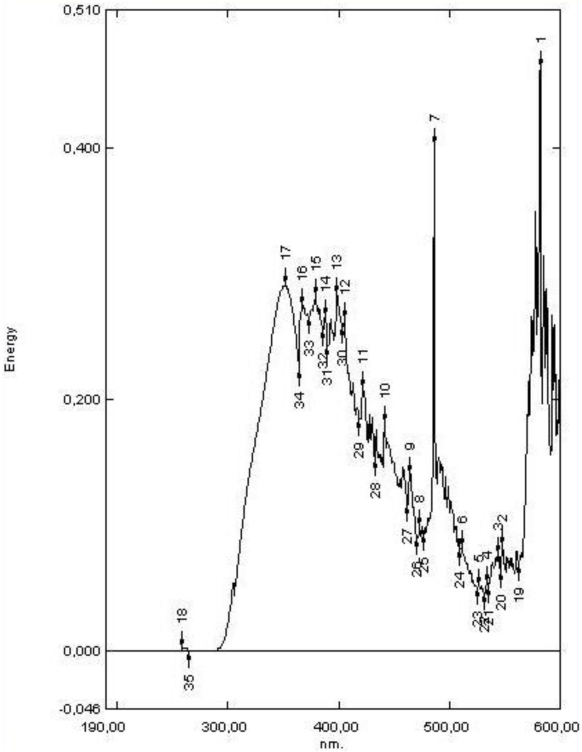
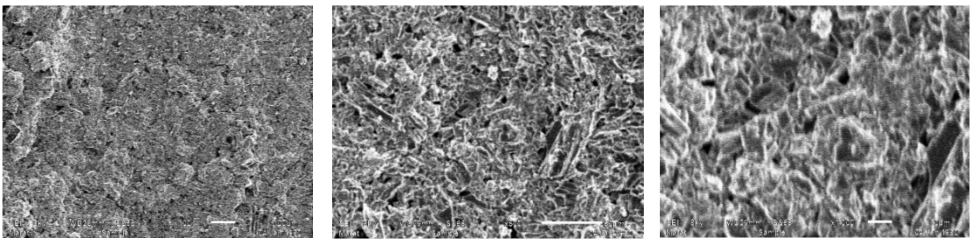


Figure 1 – Spectrum of the UV and visible region of the obtained palladium nanoparticles

The work [5] describes that palladium nanoparticles obtained by this method coagulate easily to form a precipitate. In order to prevent the agglutination process of nanoparticles into larger agglomerates, powdered pharmaceutical activated carbon was added to the reaction mixture. Micrographs of the obtained catalyst surface, taken with a scanning electron microscope JSM-6510 LV of JEOL (Japan) are shown in figure 2. Palladium nanoparticles (white dots) are fairly evenly distributed on the surface of activated carbon.

In addition to preventing the agglutination of nanoparticles, the contact surface of the catalyst increases.



100-fold increase   500-fold increase   1000-fold increase

Figure 2 – Micrographs of palladium nanoparticles immobilized on activated carbon

The hydrogenation process of vegetable oil has been carried out according to the known method [7]. The hydrogenation results on the obtained catalyst under various conditions are given in table.

The hydrogenation results of vegetable oil

No.	Hydro-genation duration, h	Process temperature, °C	Wt% of the catalyst from oil weight	The content of palladium nanoparticles in the catalyst, %	Wt% of palladium particles from oil weight	The melting point of a product, °C
1	6	220-230	0,1	0.053	$5{,}3 \cdot 10^{-4}$	8
2	6	220-230	0,5	0.265	$2{,}65 \cdot 10^{-3}$	10
3	6	220-230	1,0	0.53	$5{,}3 \cdot 10^{-3}$	38
4	6	200	1,0	0.53	$5{,}3 \cdot 10^{-3}$	15
5	5	220-230	1,0	0.53	$5{,}3 \cdot 10^{-3}$	9
6	0.5	MW radiation, 700 W	1,0	0.53	$5{,}3 \cdot 10^{-3}$	34

As the catalyst content is increased from 0.1 to 1 %, a higher melting product (38^0C) corresponding to the margarine of MHC grade is formed. Decrease of temperature and duration reduction of the process results in low melting margarines of MLF and MLB grades. The use of microwave technology (power 700 W) leads to a significant duration reduction of the process up to 30 minutes, while a product with the melting point of 34^0C, which meets the standards of MH, MHF AND MS grades, has been obtained.

Conclusions. Thus, hydrogenation catalyst of vegetable oil in which palladium nanoparticles are immobilized on activated carbon is obtained. The parameters of the hydrogenation process of vegetable oil, which allow obtaining various margarine grades are established.

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Резюме

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ПАЛЛАДИЙДІҢ НАНОБӨЛШЕКТЕРІН АЛУ ЖӘНЕ ОЛАРДЫ
ӨСІМДІК МАЙЫН ГИДРЛЕУ КАТАЛИЗАТОРЫ РЕТІНДЕ ПАЙДАЛАНУ

Хлорлы палладийді натрий боргидридімен тотықсыздандыру арқылы палладийдің нанобөлшектері алынды. Алынған палладий бөлшектері λ=350 нм аумағында қарқынды оптикалық жұтылумен сипатталады, ол 10-50 нм өлшемді бөлшектердің түзілгендігін дәлелдейді. Жанасу бетін жоғарылату үшін палладийдің нанобөлшектері белсендірілген көмірге иммобилизацияланды. Алынған катализатордың каталитикалық белсенділігі өсімдік майын конвекциялық және микротолқындық қыздыру жағдайында зерттелді. Май массасынан катализатор мөлшері 1% болғанда жоғары температурада балқитын өнім түзіледі (38^{o}С. Температураны төмендеткенде және үрдіс ұзақтығын қысқартқанда МЖК және МЖП маркалы төмен температурада балқитын маргариндер түзіледі). Микротолқындық технологияны қолдану (қуаты 700 Вт) кезінде үрдіс ұзақтығы айтарлықтай қысқарып (30 мин-ке дейін), балқу температурасы 34^{0}С-ге тең өнім түзіледі.

Түйін сөздер: палладийдің нанобөлшектері, тотықсыздандыру, өсімдік майын гидрлеу, маргарин, микротолқындық активация.

Резюме

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ПОЛУЧЕНИЕ НАНОЧАСТИЦ ПАЛЛАДИЯ И ИХ ПРИМЕНЕНИЕ
В КАЧЕСТВЕ КАТАЛИЗАТОРА ГИДРИРОВАНИЯ РАСТИТЕЛЬНОГО МАСЛА

Восстановлением хлористого палладия борогидридом натрия получены наночастицы палладия, которые характеризуются интенсивным оптическим поглощением в области λ=350 нм, что свительствует об образовании частиц размером 10-50 нм. Для увеличения контактной поверхности наночастицы палладия иммобилизованы на активированный уголь. Каталитическая активность полученного катализатора исследована в реакции гидрирования растительного масла при конвекционном и микроволновом нагреве. Найдено, что при содержании 1 % от катализатора массы масла образуется более высокоплавкий продукт (38^{o}С. Понижение температуры и сокращение продолжительности процесса приводит к низкоплавким маргаринам марок МЖК и МЖП). Использование микроволновой технологии (мощность 700 Вт) значительно сокращает продолжительность процесса (до 30 мин) с образованием продукта с т.пл. 34^{0}С.

Ключевые слова: наночастицы палладия, восстановление, гидрирование растительного масла, маргарин, микроволновая активация.