
CATALYSIS IN CHEMICAL
AND PETROCHEMICAL INDUSTRY

Effect of the Nature of Supports and the Degree of Palladium Dispersion on the Catalyst Activity and Selectivity in the Sunflower Oil Hydrogenation Reaction

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Received August 1, 2022; revised September 27, 2022; accepted September 28, 2022

Abstract—Results of studying the Pd/C and Pd/O powder catalysts synthesized by the deposition of 0.5 and 1.0 wt % Pd on carbon materials (Sibunit 159k, thermal carbon black T-900, Vulcan XC-72R) and oxide supports (Ox: γ -Al₂O₃, Cr₂O₃, Ga₂O₃, TiO₂, Ta₂O₅, and V₂O₅, diatomaceous earth FW-70) and their catalytic properties in the partial hydrogenation of sunflower oil were described. Using a Parr fixed-bed reactor, comparative tests of the catalysts in the kinetic mode conducted to determine their activity (SCA, V_0) and *trans*-isomerization selectivity parameters (S_{tr}). The effect of the average particle size of supported palladium (d_{CO}) on these parameters in a wide range of d_{CO} values was discussed.

Keywords: sunflower oil, partial hydrogenation, palladium catalysts, effect of support

DOI: 10.1134/S2070050423040098

INTRODUCTION

The hydrogenation of the $-C=C$ bonds of triglycerides of unsaturated fatty acids contained in vegetable oils, which is aimed at modifying their physicochemical properties, such as melting point, miscibility, viscosity, and surface tension, is a commonly used process for converting liquid oils to solid fats. Typically, the partial hydrogenation process is run in the presence of nickel catalysts at temperatures of 190–230°C [1–5]. This choice is mostly attributed to the availability and low price of the catalysts and the chemical inertness of Ni with respect to oil. It should be noted that these catalysts are not sufficiently active at temperatures below 180°C. In addition, during the production of hydrogenated fats as sunflower oil (SFO) hydrogenation products, a significant amount of *trans* fatty acid (TFA) isomers exhibiting carcinogenic effects are formed. Their content in the fatty acid composition varies in a range of 15–30% [6]. At the same time, the technological processes of hydrogenation include energy-intensive stages of purification of products from toxic nickel compounds [7].

Catalysts based on noble metals that contain a low amount of the active component and are supported on an oxide [8–12] or carbon substrate [13–15] are considered to be promising systems to replace Ni, because

they provide a decrease in the reaction temperature and an increase in the purity of hydrogenation products. The published orders of activity—Rh > Pd > Pt > Ru > Ni [6], Pd > Pt > Ru [16], Pd > Rh > Pt ≳ Ir > Ru ≳ Os [17], and Pd > Pt > Ni > Co > Cu [8]—suggest that palladium and platinum catalysts are significantly superior to Ni systems in this parameter.

The physical and taste characteristics of the resulting oil are determined by the content of both unsaturated fatty acids, in particular, TFAs, and the products of their complete hydrogenation, which are classified as components harmful to health. Therefore, for a comparative assessment of the activity of catalysts and their important characteristics, such as *trans*-isomerization selectivity (S_{tr}) [5, 13, 18] or oleic acid selectivity (S_1) [13, 19], the reference samples and the catalytic testing conditions should be chosen carefully. In particular, in studying the effect of the degree of dispersion of supported catalysts on their catalytic properties in vegetable oil hydrogenation reactions, a set of analyzed samples should differ, if possible, only in the particle size of the supported metal, while the textural characteristics of the support and the testing conditions should be selected such as to avoid diffusion

restrictions during the reaction. Neglect of these conditions can lead to ambiguous results.

The mechanism of the heterogeneous hydrogenation of polyunsaturated fatty acids does not allow avoiding the C=C bond *cis*–*trans* isomerization stage [20, 21]. However, by changing the reaction conditions and the nature of the catalyst, it is possible to affect the TFA content in the product composition. Thus, it was experimentally shown that, under conditions of their liquid-phase hydrogenation, a decrease in the reaction temperature, an increase in the hydrogen pressure and the stirring speed, and a decrease in the substrate load on the catalyst lead to a decrease in the TFA content [1, 7, 9, 22–24]; that is, conditions that contribute to an increase in the hydrogen concentration on the catalyst surface will provide a decrease in the content of *trans*-isomers in the partial hydrogenation products [10, 13, 22–26].

According to [27], the TFA selectivity in the presence of noble metals decreases in the following order: Pd > Rh > Ru > Ir > Pt. A slightly different order was found in [6]: Rh > Pd > Ru > (Ni) > Pt. However, in both cases, the *trans*-isomerization ability of Pd is superior to that of Pt. However, Pd-containing catalysts are proposed as an alternative to the Ni-containing systems currently used in industry due to their cost, which is lower than that of other noble metals, and relative safety for human health. Currently, activities are underway to elucidate the dependence of the catalytic properties of various palladium catalysts in the hydrogenation of vegetable oils [6, 10, 13, 14, 24, 28, 29] or their ethyl esters [11, 16] on the process mode, the chemical composition of the active component precursor, the particle size of supported Pd, and the nature and porosity of the supports.

In this paper, which describes a continuation of research in this direction, results of studying the activity and selectivity of Pd catalysts in the partial hydrogenation of SFO as a function of the nature of the support and the degree of supported metal dispersion are discussed. A distinctive feature of this study is that oxide and carbon materials with low specific surface areas or mesoporous supports containing no micropores are chosen as the supports. This choice makes it possible to minimize the intradiffusion restrictions during SFO hydrogenation and expect that the revealed differences in the catalytic properties of supported palladium will be determined only by the chemical composition of the support and/or the particle size distribution of the supported metal, rather than by a change in the accessibility of the active site of the Pd.

EXPERIMENTAL

Reagents and Materials

The supports for catalysts and their precursors were powdered oxides supplied as reagents and the following commercially available metal oxides and carbon

materials: reagent grade γ -Al₂O₃, Cr₂O₃, Ga₂O₃, TiO₂, Ta₂O₅, and V₂O₅ (Reakhim); diatomaceous earth FW-70 (Celatom); commercial furnace carbon black Vulcan XC-72R; thermal carbon black T-900 (Omsk Carbon Black Plant, Russia); and Sibunit 159k (Center of New Chemical Technologies, Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Omsk, Russia).

Samples of α -Al₂O₃ (7 and 10.6 m²/g) and ru-TiO₂ (rutile, 2 m²/g) were prepared by calcining γ -Al₂O₃ (Reakhim) in air at 1200°C for 6 h; the an-TiO₂ (anatase) sample was prepared at 900°C for 5 h. Zirconia (ZrO₂, 14 m²/g) was synthesized by the precipitation of zirconyl nitrate with an aqueous solution of ammonia (high-purity grade, Reakhim) and the calcination of the resulting hydroxide in air at 900°C for 4 h. The following reagents were used to synthesize the catalysts: reagent grade H₂PdCl₄; special purity grade HCl, Na₂CO₃, and NH₄OH; and high-purity grade NaOOCH.

Kinetic tests were conducted using refined deodorized SFO Sloboda (EFKO, Russia) and H₂, He, and N₂ gases supplied in cylinders. Commercial catalysts Pricat 9908 (Johnson Matthey) and Nysosel 210 (BASF) with a Ni content of about 50 wt % were chosen as the reference samples.

Catalysts and Methods of Their Preparation

In this study, three sets of catalysts were synthesized: samples in which 0.5 or 1.0 wt % Pd was supported on carbon supports (designated as 0.5%Pd/C and 1.0%Pd/C), samples in which 1.0 wt % Pd with different degrees of dispersion was supported on Al₂O₃ (designated as 1.0%Pd/Al₂O₃), and samples in which 0.5 wt % Pd was supported on the surface of the above oxides with a low specific surface area (designated as 0.5%Pd/Ox).

The 0.5%Pd/C and 1.0%Pd/C set catalysts were synthesized by supporting palladium oxides on the surface of carbon by the hydrolysis of Pd²⁺ chloride complexes in the presence of a reducing agent [30, 31]. To synthesize 0.5%Pd/C catalysts (C denotes carbon supports with a low specific surface area), a calculated amount of a 0.1 M H₂PdCl₄ solution was added dropwise to a vigorously stirred suspension of the powder support in an aqueous solution of Na₂CO₃ at 20°C for 8–10 min; the suspension was further aged under the same conditions for 30 min to provide the complete precipitation of palladium hydroxide. For the 0.5%Pd catalysts, the $\chi = \text{Na}_2\text{CO}_3 : \text{H}_2\text{PdCl}_4$ molar ratio was 4. Palladium deposition completeness was controlled from the absence of Pd(II) ions in mother solution aliquots after a qualitative reaction with KJ or NaBH₄. Subsequent reduction was run at 75°C by introducing excess sodium formate (NaOOCH : H₂PdCl₄ = 1.5 mol/mol) into the suspension. The catalyst was separated on a filter, washed with distilled water until

Table 1. Textural and substructural characteristics of inorganic supports and degree of metal dispersion in the 0.5%Pd/C and 0.5%Pd/Ox catalysts

Support	Textural characteristics			XRD	Average particle size of Pd, nm	
	S_{BET} , m ² /g	V_{Σ} , cm ³ /g	$D_{\text{av, BET}}$, nm	CSR size*, nm	d_{CO} , CO titration	d_s , TEM
Sibunit 159k	11.6	0.031	10.7	L_c 3.1	3.3	2.3
T-900 (thermal carbon black)	8	0.022	11.0	L_c 2.3; L_a 1.8; d_{002} 3.53	2.5	2.0
α -Al ₂ O ₃ (from γ -Al ₂ O ₃)	10.6	0.025	9.4	82	1.9	2.2
Diatomaceous earth FW-70 (SiO ₂)	1.73	0.003	8.7	Amorphous	7.7	8.4
ZrO ₂ (monoclinic)	19.3	0.07	13.4	30	1.4	1.6
ZrO ₂	—	—	—	—	3.2	—
β -Ga ₂ O ₃	17.5	0.103	23.9	20	2.6	1.8
TiO ₂ (rutile)	2.0	0.0025	5.5	>200	8.3	2.6
Ta ₂ O ₅	6.8	0.025	15.0	41	2.6	1.7
α -Cr ₂ O ₃	2.5	0.007	11.3	142	3.5	2.8
V ₂ O ₅	3.5	0.012	15.6	138	3.6	2.0
In ₂ O ₃	3.9	0.027	28.4	—	6.0	—

* CSR is coherent scattering region. Values are calculated from XRD data. L_a is the average CSR size in a direction parallel to the graphite-like layers; L_c is the average size in a perpendicular direction; and d_{002} is the interplanar distance.

the absence of chloride ions (reaction with AgNO₃), and dried in air at 65°C for 10–12 h. Immediately before use, the catalyst samples were held in a hydrogen stream at 150°C for 30 min; after cooling, H₂ was replaced with He and passivated by air pulses in a helium stream. To synthesize 1.0%Pd/C catalysts (C denotes carbon supports with a developed surface, namely, carbon black Vulcan XC-72R), the above procedure was used. The difference was that Na₂CO₃ was introduced into the suspension immediately before the reduction of Pd(II) ions with sodium formate, rather than at the first stage of the synthesis. A Na₂CO₃ solution was added drop by drop for 10 min; the resulting mixture was stirred at 20°C for 20 min. Reduction was run at 20°C for 30 min with the subsequent increase in temperature to 60°C and stirring of the suspension for 15 min. The molar ratio of the reagents was Pd : Na₂CO₃ : HCOONa = 1 : 3.5 : 1.5.

The 1.0%Pd/Al₂O₃ and 0.5%Pd/Ox set catalysts were synthesized in accordance with the same procedure as that used for the 0.5%Pd/C samples, yet at a molar ratio of the reagents of Pd : Na₂CO₃ : HCOONa = 1 : 4 : 1.5 and Pd : Na₂CO₃ : HCOONa = 1 : 10 : 1.5, respectively. The supports for synthesizing 1.0%Pd/Al₂O₃ were Al₂O₃ samples prepared by calcining alumina (Puralox SCCA-150/200) in air at 1000°C for 4 h and subsequent cooling. The heating rate of the samples to a given temperature was 10°C/min. The 0.5%Pd/Ox catalysts were synthesized in accordance with the basic procedure at a molar ratio of the

reagents of Pd : Na₂CO₃ : HCOONa = 1 : 10 : 1.5. The textural and substructural characteristics of inorganic supports and the degree of dispersion of the metal in the 0.5%Pd/Ox catalysts are shown in Table 1.

Physicochemical Methods of Studying the Catalysts

The textural characteristics of the supports and catalysts were determined by the low-temperature adsorption of N₂ at 77 K using an ASAP-2400 automated volumetric adsorption unit (Micromeritics Instrument Corp., Norcross, GA, United States). Before analysis, the samples were held at a pressure of 1×10^{-3} mmHg and a temperature of 150°C for 4 h. Specific surface area (S_{BET} , m²/g) was calculated according to analysis of the adsorption branch (BJH cum. ads.) of the isotherm in a relative pressure range of 0.05–0.20; total pore volume (V_{Σ} , cm³/g) was calculated according to N₂ adsorption capacity at $p/p_0 = 0.98$. Volumes of pores with sizes of 17–3000 Å were calculated from the adsorption (V_{ads}) and desorption hysteresis branches (V_{des}) of the capillary condensation of nitrogen. Average pore diameter (D_{av}) was calculated as $D_{\text{av}} (\text{Å}) = 4V_{\Sigma} \times 10^4 / S_{\text{BET}}$.

The total weight content of platinum in the catalysts was determined by X-ray fluorescence analysis (VRA-30 instrument).

The particle size and particle size distribution of supported palladium were studied by transmission

electron microscopy (TEM) on a JEM-2010 instrument at an accelerating voltage of 200 kV and a lattice resolution of 1.4 Å. The catalysts were compared by d_s (surface mean diameter of the particles), which were calculated from the particle size distribution histograms using formula (1):

$$d_s = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}, \quad (1)$$

where n_i is the number of particles with diameter d_i in the i th column of the histogram.

The adsorption properties of supported platinum with respect to CO were studied by pulsed titration at 20°C in a flow unit in a hydrogen stream as described in [32]. The degree of dispersion of palladium particles (D_{CO}) was calculated as the molar ratio of adsorbed CO to Pd in a titrated weighed portion of the catalyst ($D_{CO} = CO : Pd$); their average size (d_{CO}) was calculated as d_{CO} (nm) = 1.08/ D_{CO} .

The content of solid triglycerides (STGs) of acids at different temperatures (10, 15, 20, 25, 30, and 35°C) in the oil hydrogenation products was recorded using a Chromatec Proton 20M nuclear magnetic resonance (NMR) analyzer by the pulsed NMR method [33]. The obtained data were further used to plot the temperature profile of the melting of the sample, i.e., the temperature dependence of the weight content of solid fat in the sample.

Catalytic Testing and Product Analysis Procedures

The partial hydrogenation of the Sloboda SFO was run in a fixed-bed mode in a 300-cm³ 4848 Mini Parr reactor at temperature T of 180°C, a suspension stirring speed ω of 1200 rpm, and a hydrogen pressure P of 5 atm. To this end, a weighed portion of a catalyst carefully ground in an agate mortar and 50 g of oil were loaded into the reactor; the system was purged with nitrogen, and the reaction mixture was heated. Upon the achievement of a desired temperature, nitrogen was displaced from the reactor with hydrogen, a required pressure was set, and the stirrer was turned on to start the reaction. During oil hydrogenation, the hydrogen consumption rate was controlled. The test was terminated after the absorption of the calculated amount of H₂ required for the formation of a product with an iodine value (IV) of 71–75.

The content of fatty acids in the composition of the feed oil and hydrogenation products (hydrogenated fats) was determined by gas chromatography. Fatty acid triglycerides were preconverted into their methyl esters. The resulting mixture was analyzed on a Khromos GC-1000 chromatograph equipped with a flame ionization detector. To separate the products, a BPX70 capillary column (SGE, Australia, 60 m × 0.2 mm × 0.25 μm) was used with temperature pro-

gramming of 120 to 245°C at a rate of 3°C/min. The carrier gas (He) was fed at a rate of 68.5 cm³/min. The volume of the injected sample was 0.2 μL.

To assess catalytic activity, a hydrogen absorption curve as a function of reaction time was plotted. Reaction rate W (cm³/min) was found as slope α of the initial region of the absorption straight line. To calculate catalyst activity per unit mass of metal (V_0) and specific catalytic activity (SCA or TOF), formulas (2) and (3) were used:

$$V_0 (\text{mol N}_2 / (\text{g}_{Pd} \text{ s})) = W (\text{cm}^3 \text{ N}_2 / \text{min}) / (24.055 \times 10^3 m_{Pd} (\text{g}) 60 \text{ s}); \quad (2)$$

$$\text{SCA} (\text{s}^{-1}) = (M_{Pd} (\text{g/mol}) V_0) / D_{CO}, \quad (3)$$

where m_{Pd} is the weight of palladium in the catalyst sample in grams and $M_{Pd} = 106.4$ is the molecular weight of Pd.

RESULTS AND DISCUSSION

0.5%Pd/C and 0.5%Pd/Ox Catalysts

Some characteristics of the supports and the degree of palladium dispersion in these catalysts are shown in Table 1. It is evident that the supports are mesoporous metal and silicon oxides with a small pore volume and low specific surface areas and Sibunit 159k and T-900 carbon materials with a low specific surface area.

Catalyst activity was determined from the saturation rate of the C=C bonds of triglycerides of fatty acids contained in the SFO. The results of individual tests in the form of time dependences of the absorbed hydrogen volume are shown in Fig. 1. The inset shows the initial linear portion of the curves that was used to calculate reaction rates W (cm³/min) as their slope α to the abscissa axis.

Conditions providing the kinetic reaction mode were chosen. Thus, according to Fig. 2, for 0.5%Pd/ZrO₂, which is the most active sample in the set of Pd/Ox catalysts, a linear dependence of the reaction rate on the catalyst weight is observed in a weighed portion range of 5–50 mg; this fact indicates the absence of external diffusion restrictions. According to the intercept on the abscissa axis, it can be found that, during the reaction, no more than 9.4×10^{-8} mol of Pd is poisoned by impurities contained in the feed SFO; therefore, in the comparative analysis of the catalysts, the contribution of these impurities can be ignored. The heat pretreatment in a hydrogen stream aimed at stabilizing the active component in a state close to the reaction state did not lead to significant changes in the hydrogenation kinetic curves. Therefore, changes in the state of the active component, which can occur due to the effect of high temperatures and poisons during the reaction, are either absent or occur at the very beginning of the reaction and then do not affect the kinetics of the process. It should be

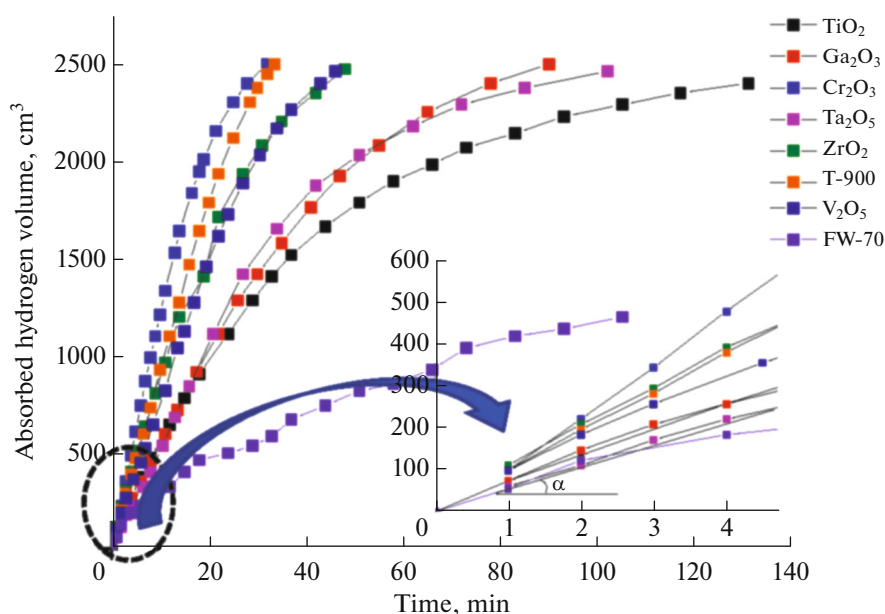


Fig. 1. Hydrogen absorption curves for SFO hydrogenation using 10 mg of 0.5%Pd/Ox catalysts. Conditions: $T = 180^{\circ}\text{C}$, $P_{\text{H}_2} = 5$ bars, $\omega = 1200$ rpm, and oil weight of 50 g.

noted that the further attrition of the weighed portions of the catalyst did not lead to an increase in their activity. For the most active catalyst, i.e., 0.5%Pd/Sibunit 159k, a significant decrease in activity is observed in the case of a 30-mg weighed portion. Therefore, it is reasonable to expect that, in the case of using weighed portions of the catalysts discussed in this study of ≤ 20 mg, their activity is measured in the kinetic mode of the reaction.

The results of calculating the initial hydrogenation rates from the hydrogen absorption curves are summarized in Table 2 and graphically represented in Fig. 3. It is evident that, for this set of samples, the reaction rate (V_0) tends to decrease with a decrease in the degree of dispersion of the metal; the effect is attributed to a decrease in the content of surface palladium atoms. At the same time, no clear dependence of SCA on the type of oxide support or the average particle size of Pd was observed. However, the carbon-supported catalyst was found to be significantly more active than all the Pd/Ox catalysts. It can be assumed that the hydrophobic surface of carbon is better “wetted” by triglycerides than the surface of an oxide support. Under partial SFO hydrogenation conditions, no dependence of the activity of supported palladium on the cation charge or acid–base properties of the oxide support is observed. Thus, catalysts containing 0.5% Pd with an identical degree of dispersion on the surface of Ga_2O_3 and Ta_2O_5 are characterized by an identical activity. However, it was shown earlier that a 0.5%Pd/ Ta_2O_5 catalyst is inactive in the hydrogenation of maleic acid in aqueous solutions and the hydrogenation of cyclohexene in an alcoholic solution

[31]. Special attention should be given to this fact, because it shows the effect of the solvation of the catalyst surface and substrate molecules on the functioning of the catalyst.

This study describes a limited list of oxide-supported palladium catalysts; therefore, the effect of the degree of dispersion of Pd/Ox samples on their catalytic properties in SFO hydrogenation cannot be assessed. The results of studies on this issue are conflicting. Thus, the authors [11] showed that the SFO hydrogenation reaction in the presence of Pd/Ox catalysts (where Ox = SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , MgO , ZnO , CeO_2 , or CeZrO_2) is structurally insensi-

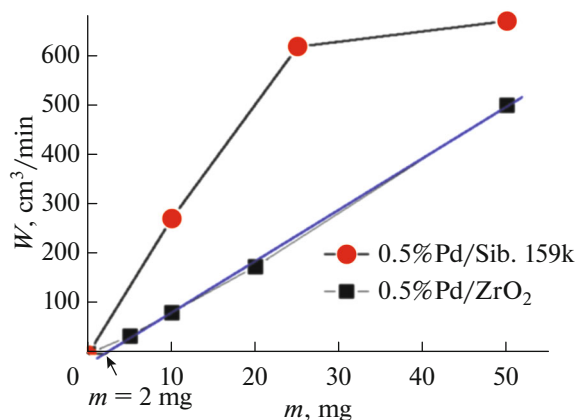


Fig. 2. Vegetable oil hydrogenation rate in the presence of the 0.5%Pd/C and 0.5%Pd/ ZrO_2 samples versus catalyst portion mass.

Table 2. Hydrogen absorption rate in SFO hydrogenation in the presence of catalysts containing 0.5% Pd on various supports (conditions: $T = 180^\circ\text{C}$; $P_{\text{H}_2} = 5 \text{ bar}$; $\omega = 1200 \text{ rpm}$; oil weight, 50 g)

Support	CO : Pd	d_{CO} (Pd), nm	W , $\text{cm}^3 \text{H}_2/\text{min}$	V_0 , $\text{mol H}_2/(\text{g}_{\text{Pd}} \text{ s})$	SCA, s^{-1}
Sibunit 159k	0.33	3.3	273	3.78	1220
Carbon black T-900	0.44	2.5	88.6	1.23	297
$\alpha\text{-Al}_2\text{O}_3$	0.57	1.9	83.3	1.15	215
Diatomaceous earth FW-70 (SiO_2)	0.14	7.7	23.0	0.32	242
ZrO_2	0.63	1.7	83.5	1.16	195
ZrO_2	0.34	3.2	123	1.70	532
Ga_2O_3	0.41	2.6	48.8	0.68	175
TiO_2	0.13	8.3	48.8	0.68	553
Ta_2O_5	0.41	2.6	48.8	0.68	175
Cr_2O_3	0.30	3.6	120	1.66	590
V_2O_5	0.30	3.6	73.6	1.02	362
In_2O_3	0.18	6.0	31.7	0.44	259

tive to the Pd particle size in a particle size range of 1.7–7.8 nm (degree of dispersion of 55–12%). On the other hand, the authors [12], in a comparative analysis of two sets of Pd/ SiO_2 samples with the different degrees of Pd dispersion of 2.7–4.0 and 6.1–7.8 nm, respectively, found that the catalysts with the coarse particles exhibit higher activity (SCA), oleic acid selectivity (S_1), and *trans*-isomerization selectivity (S_{tr}) in the partial hydrogenation of soybean oil esterification products. It should be noted that the latter results were obtained at low catalyst loads using supports that significantly differed in textural characteristics.

The reaction products were studied by gas chromatography. The results are shown in Table 3. It is evident that all catalysts exhibit *trans*-isomerization activity; therefore, 36–42 wt % of C18:1t fatty acids are detected in the products (see Table 3, Fig. 4). The fatty

acid composition of the reaction products does not depend on the catalyst activity, support nature, and metal particle size. Apparently, the support nature does not change the selectivity of supported palladium; that is, it does not change the ratio between the hydrogenation and isomerization rates.

It should be noted that the published data on studying the effect of support nature on the *trans*-isomerization ability of palladium catalysts are ambiguous. Thus, researchers from Turkey compared two commercial samples (5%Pd/C and 10%Pd/ Al_2O_3) in soybean oil hydrogenation and did not find any dependence of S_{tr} on the type of the support. A similar result in the case of SFO hydrogenation was obtained by the authors [11] in a comparative analysis of catalysts in which Pd was supported on SiO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, TiO_2 , MgO , ZnO , CeO_2 , and CeZrO_2 . At the same time, the authors [35], studying the hydrogenation of canola (variety of rapeseed) oil in the presence of 5%Pd/C, 5%Pd/ Al_2O_3 and 5%Pd/ BaSO_4 catalysts, found that the formation of *trans*-isomers depends on the type of the substrate.

1.0%Pd/C Catalysts

Under varied synthesis conditions, a set of 1.0%Pd/C samples with average particle sizes of supported Pd of 2–12 nm was synthesized. Commercial mesoporous carbon black Vulcan XC-72R ($S_{\text{BET}} = 252 \text{ m}^2/\text{g}$, $V_\Sigma = 0.63 \text{ cm}^3/\text{g}$, $D_{\text{av}} = 10 \text{ nm}$) was used as a carbon support. A decrease in the degree of dispersion was provided by increasing pH to 9–11 and/or increasing the temperature to 80°C during the contact between the precursor the support. The degree of metal dispersion in the resulting catalysts was controlled using the facts that reductive sorption signifi-

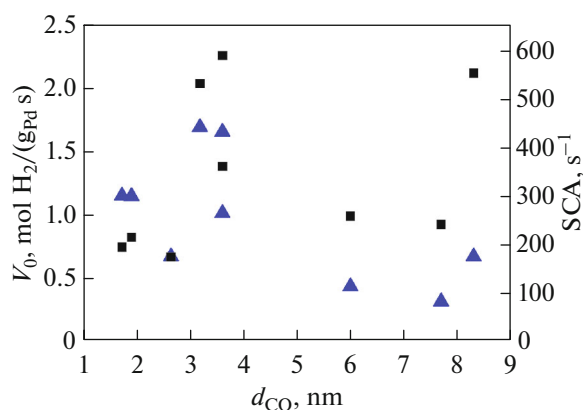


Fig. 3. (▲) Vegetable oil hydrogenation rate and (■) palladium SCA in the presence of the 0.5%Pd/Ox samples (10 mg) versus average particle size of the supported metal.

Table 3. Composition of SFO partial hydrogenation reaction products in the case of the 0.5%Pd/C, 0.5%Pd/ α -Al₂O₃, and 0.5%Pd/Ox catalysts (10 mg)

Support	IV	C14:0	C16:0	C18:0	C18:1c	C18:1t	C18:2c	C18:2t
Feed oil	202.1	0.08	7.34	3.71	25.60	0	61.33	0.93
Sibunit 159k	74.2	0.07	7.57	9.13	37.82	41.16	1.35	1.88
T-900	75.8	0.08	7.59	8.73	39.65	39.71	1.35	2.65
α -Al ₂ O ₃	74.6	0.08	7.53	9.22	36.41	42.02	1.37	2.39
ZrO ₂ ($d_s = 1.7$ nm)	74.1	0.08	7.60	11.20	36.36	38.53	2.03	3.21
ZrO ₂ ($d_s = 3.2$ nm)	73.8	0.07	7.48	9.57	36.51	42.26	0.96	2.17
V ₂ O ₅	76.7	0.07	7.50	7.45	43.16	36.63	1.34	2.95
Ga ₂ O ₃	75.5	0.08	7.52	8.57	38.42	40.40	1.43	2.62
TiO ₂	76.5	0.07	7.49	9.41	39.89	36.16	2.26	3.75
Ta ₂ O ₅	75.8	0.09	7.64	8.03	39.61	39.64	1.22	2.82
Cr ₂ O ₃	74.8	0.08	7.55	8.35	40.25	39.59	1.16	2.05

cantly contributes to the formation of large metal particles on the carbon surface [36, 37] and the additional introduction of chloride ions into the suspension can inhibit the reduction of the metal. To this end, hydrochloric acid or sodium chloride was introduced into a suspension of carbon in water; it is evident from the data of Table 4 that this procedure provided the formation of catalysts with smaller palladium particle sizes.

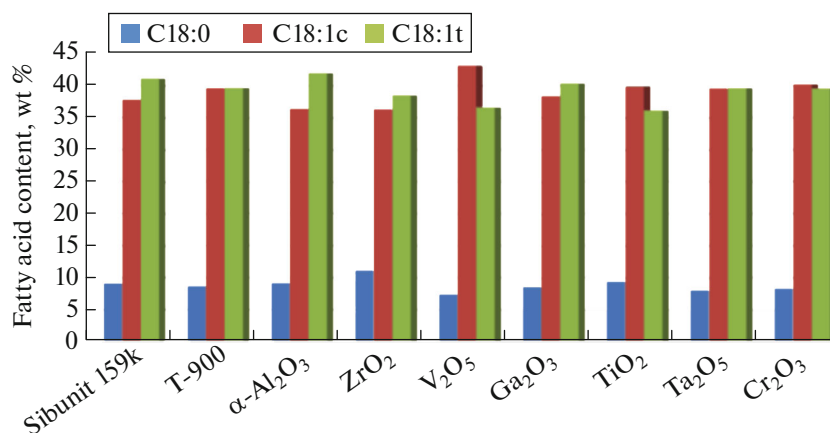
Experimental dependences of the SCA of these catalysts and the vegetable oil hydrogenation rates (V_0) on the average particle size of palladium, which were calculated by formulas (3) and (2), are shown in Fig. 5.

The results suggest that, in a range of 2–12 nm, the SCA increases with an increase in the average particle size of palladium. At the same time, an increase in the SCA does not compensate for the decrease in activity (V_0) of the catalysts due to an increase in the average particle size.

Table 4. Effect of chloride ions in the reaction mixture composition on the degree of dispersion of 1%Pd/Vulcan XC-72R catalysts

Molar ratio of reagents		Degree of dispersion	
H ₂ PdCl ₄ : HCl	H ₂ PdCl ₄ : NaCl	CO : Pd	d_{CO} , nm
–	–	0.38	2.8
1 : 16	–	0.50	2.2
–	1 : 16	0.48	2.3
1 : 16	1 : 16	0.50	2.2
–	1 : 46	0.51	2.1

It is evident from the results of analysis for the SFO hydrogenation products (Table 5) that the hydrogenated fats obtained using catalysts with different degrees of dispersion of the metal are characterized by a similar fatty acid composition. This finding is confirmed by the STG content curves recorded using an

**Fig. 4.** Content of fatty acid residues in the SFO partial hydrogenation products in the presence of 0.5%Pd/support samples.

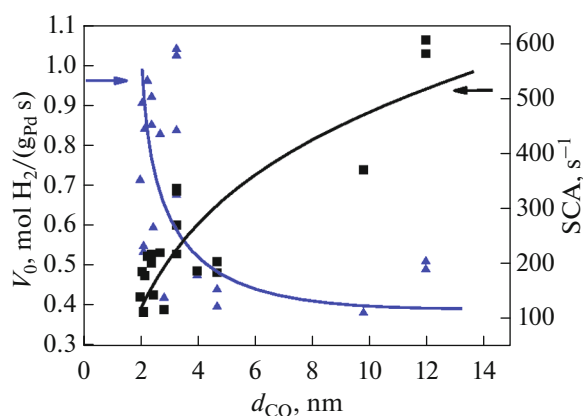


Fig. 5. Vegetable oil hydrogenation rate (V_0) and palladium SCA for the 1.0% Pd/C catalyst samples (10 mg) versus average particle size of the supported metal.

NMR-analyzer, which are similar in shape and position (Fig. 6).

Data on the fatty acid composition of the produced hydrogenated fats were used to study the effect of medium-sized palladium particles on the content of TFA isomers. It is evident (Fig. 7) that, with allowance for the relative analysis error of 5%, the TFA content in the composition of SFO hydrogenation products does not depend on the degree of dispersion of the supported metal.

Returning to Fig. 4, it should be noted that the supporting of palladium on Vulcan XC-72R did not provide the formation of 1% Pd/C catalysts with a narrow and monomodal distribution of the active component with an average size d_{CO} of less than 1.8 nm (i.e., in the small particle size region of interest, where an increase in catalytic activity is observed).

1.0% Pd/Al₂O₃ Catalysts

To study the size effect in the SFO hydrogenation reaction, primarily in the region of small particle sizes of supported palladium, the 1.0% Pd/Al₂O₃ were used. To select a support for synthesizing the catalysts, alumina Puralox SCCA-150/200 was calcined in air at

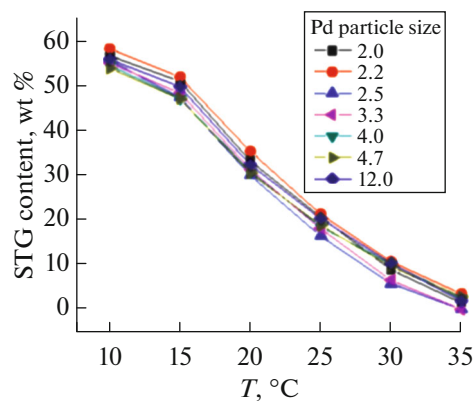


Fig. 6. Temperature profile of melting of reaction products in the case of the 1% Pd/C catalysts.

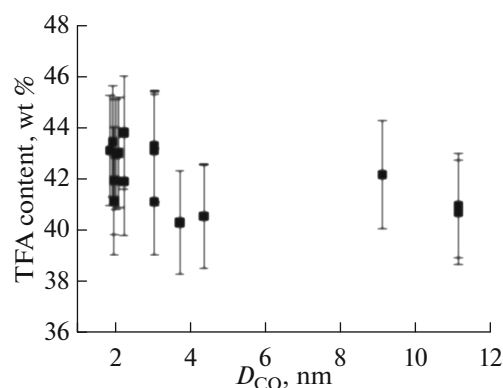


Fig. 7. TFA isomer content in the reaction product versus average particle size of the supported metal for the 1% Pd/C catalysts.

800, 1000, and 1100°C. The textural characteristics of the synthesized materials are shown in Table 6. It should be emphasized that all these supports do not contain micropores, in which the diffusion of large triglyceride molecules can be significantly slowed down. For the synthesis of the 1.0% Pd/Al₂O₃, Al₂O₃ calcined at 1000°C and characterized by high V_{Σ} and D_{av} values and a developed specific surface area was chosen.

Table 5. Reaction product composition in the case of the 1% Pd/C catalysts

Pd particle size, nm	IV	C14:0	C16:0	C18:0	C18:1c	C18:1t	C18:2c	C18:2t
2.0	73.1	0.09	7.1	10.1	36.9	41.6	1.7	1.4
2.2	72.3	0.09	7.0	10.8	36.8	41.3	1.4	1.5
2.5	72.8	0.07	6.9	10.7	37.4	39.8	1.6	1.9
3.3	73.7	0.08	7.4	9.3	37.1	41.6	1.7	1.6
4.0	73.9	0.10	7.0	10.4	37.7	37.9	2.6	2.4
4.7	73.3	0.08	7.5	10.8	37.9	37.8	2.0	2.6
12.0	74.4	0.09	7.4	10.3	37.1	38.5	3.0	2.3

Table 6. Textural characteristics of Puralox SCCA-150/200 and Al₂O₃ supports

Al ₂ O ₃ precursor	$T_{\text{calc}}, ^\circ\text{C}$	Calcination time, h	Textural properties			
			$S_{\text{BET}}, \text{m}^2/\text{g}$	$V_{\Sigma}, \text{cm}^3/\text{g}$	$V_{\text{micro}}, \text{cm}^3/\text{g}$	$D_{\text{av, BET}}, \text{\AA}$
Puralox SCCA-150/200	—	—	200	0.48	0.00	96.0
—	800	4	168	0.46	0.00	109
—	1000	4	104	0.37	0.00	143
—	1100	6	13.8	0.06	0.00	188

Table 7. Synthesis conditions and physicochemical characteristics of the 1.0%Pd/Al₂O₃ catalysts

Parameter	Catalyst number							
	1	2	3(2*)	4(2*)	5	6	7(6*)	8(6*)
	<u>Palladium hydroxide precipitation stage</u>							
Temperature, $^\circ\text{C}$	35	35	35	35	65	99	99	99
	<u>Liquid phase reduction stage</u>							
Reducing agent	—	—	—	—	NaOOCH	NaOOCH	NaOOCH	NaOOCH
Temperature, $^\circ\text{C}$	—	—	—	—	65	99	99	99
	<u>Additional stage of heat treatment in H₂</u>							
Temperature, $^\circ\text{C}$	—	150	250	450	150	150	450	600
Calcination time, h	—	0.5	1.0	6.0	0.5	0.5	6.0	2.0
	<u>Characteristics of catalysts</u>							
CO/Pd	1.00	0.82	0.62	0.44	0.53	0.40	0.35	0.25
$d_{\text{CO Pd}}, \text{nm}$	1.1	1.4	1.7	2.4	2.0	2.7	3.1	4.3
$d_{\text{S Pd}}, \text{nm}$	—	1.5	1.7	2.2	—	2.5	—	—
See Fig. 7	—	A**	B**	C**	—	D**	—	—

* The number of the modified sample is given in parentheses.

** Designation of catalysts in Fig. 7.

Tests on optimizing the 1%Pd/Al₂O₃ synthesis procedure described in Experimental showed that, by changing the duration and temperature of the procedure, it is possible to reliably vary the average particle size of Pd in the final catalysts in a range of 1–4 nm, i.e., in the range of manifestation of size effects in the catalytic reaction. The variable synthesis parameters in optimizing the procedure and the respective degrees of dispersion of the synthesized samples are shown in Table 7.

Transmission electron microscopy microphotos and particle size distribution histograms of supported palladium for some catalysts are shown in Fig. 8.

Comparative analysis of the hydrogen absorption curves in SFO hydrogenation using the 1.0%Pd/C, 1.0%Pd/Al₂O₃, Pricat, and Nysosel samples (Fig. 9) shows that the palladium catalysts are significantly superior to the nickel-containing Pricat and Nysosel catalysts in activity (V_0).

The experimental dependences of SCA and V_0 on the average particle size of palladium for the

1.0%Pd/Al₂O₃ catalysts are shown in Fig. 9. It is evident that, with an increase in the particle size, the SCA increases; this pattern is consistent with the dependence recorded for the 1.0%Pd/C catalysts. These relationships determined for the 1.0%Pd/Al₂O₃ and 1.0%Pd/C catalysts are in agreement with the results obtained by the authors [38, 39], who implemented the hydrogenation process under supercritical conditions. This effect is apparently attributed to the fact that the molecules of fatty acid triglycerides are fairly large (≈ 3 nm); this feature hinders their sorption on small palladium particles. With a further increase in the particle size of supported palladium, it is reasonable to expect a steady state mode of the SCA.

The dependence of catalytic activity (V_0) on the average particle size passes through a maximum, which is achieved at $d_{\text{CO}} = 1.4$ nm (see Fig. 10). A decrease in the catalytic activity in a region of $d_{\text{CO}} > 2$ nm was found for the Pd/C catalysts as well (see Fig. 4).

Analysis of the fatty acid composition of hydrogenated fats (Table 8) shows that it is approximately

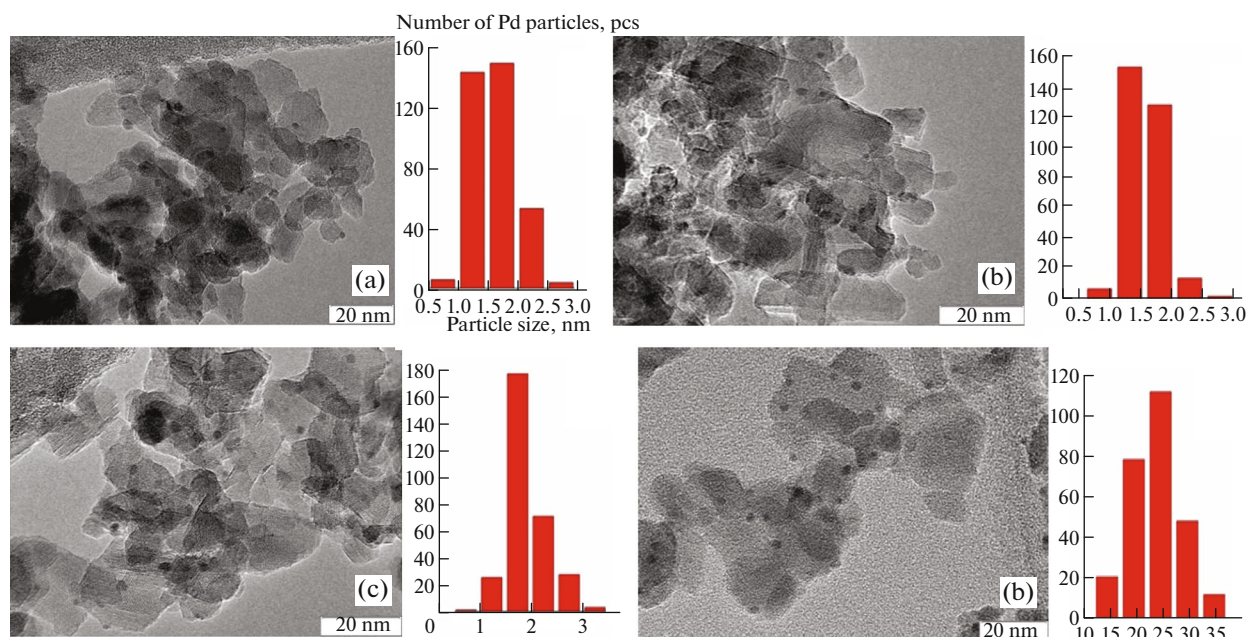


Fig. 8. Microphotos and Pd particle size distribution histograms for the 1%Pd/Al₂O₃ catalysts.

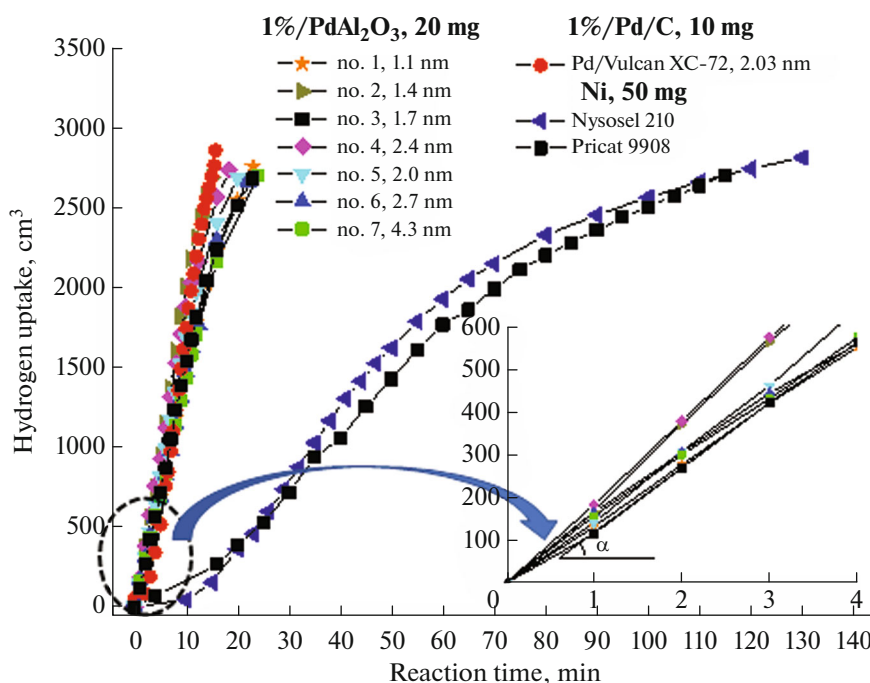


Fig. 9. Hydrogen absorption curves for SFO hydrogenation using the 1.0%Pd/C, 1.0%Pd/Al₂O₃, Pricat, and Nysosel catalysts. The inset shows the initial linear portion of the curves. Conditions: $T = 180^\circ\text{C}$, $P_{\text{H}_2} = 5 \text{ bar}$, $W = 1200 \text{ rpm}$, and oil weight of 50 g.

identical for all hydrogenation products. This finding is confirmed by the shape of the curves of STG content, which represent coinciding temperature profiles of melting of the reaction products (Fig. 11).

The effect of the degree of Pd dispersion on the *trans*-isomerization ability of the Pd/Al₂O₃ catalysts

(Fig. 12) is similar to the earlier recorded for the Pd/C catalysts (see Fig. 7). No effect of the particle size of the supported metal on the TFA content in the reaction product composition is observed.

The *trans*-isomerization ability of the 1.0%Pd/Al₂O₃ catalysts is graphically represented in the form of a

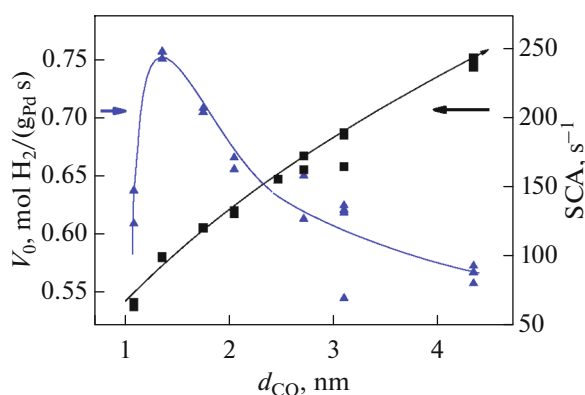


Fig. 10. SCA and V_0 of the 1.0%Pd/ γ -Al₂O₃ catalysts versus average particle size of the supported metal.

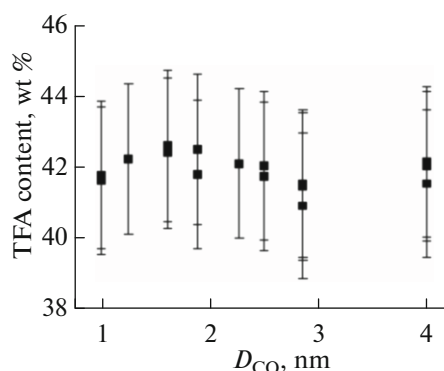


Fig. 12. TFA content in the reaction product composition versus average particle size of the supported metal for the 1%Pd/Al₂O₃ catalysts.

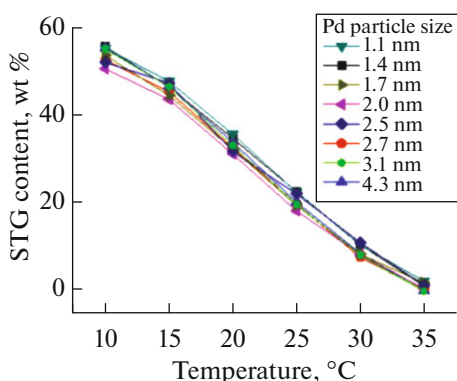


Fig. 11. Temperature profile for the melting of reaction products reaction products in the case of using the 1%Pd/Al₂O₃ catalysts.

dependence of the TFA content on the degree of palladium dispersion in Fig. 11. The similar TFA content values in the SFO partial hydrogenation products for the catalysts of this set and for the Pd/C samples (see Fig. 7) suggest that the particle size of the supported metal does not affect the TFA content in the reaction product composition.

CONCLUSIONS

A comparative analysis of the activity and selectivity of a set of supported Pd catalysts in the partial hydrogenation of SFO in the kinetic reaction mode as a function of the nature of the support and the degree of dispersion of the supported metal has been conducted. Studies of the effect of the degree of dispersion of 1.0%Pd/Al₂O₃ and 1.0%Pd/C catalysts on their catalytic properties has shown that, with an increase in the average particle size of Pd (d_{CO}), the SCA value increases, while the catalytic activity (V_0) in a region of $d_{CO} > 2$ nm is reduced with a decrease in the degree of dispersion. At the same time, in the presence of Pd/Al₂O₃ catalysts in the region of smaller sizes of $d_{CO} < 2$ nm, the curve of V_0 has a volcano shape with a maximum at $d_{CO} = 1.4$ nm. For the set of 0.5%Pd/C and 0.5%Pd/Ox catalysts, no clear dependence of V_0 or SCA on the type of the support or the average particle size of Pd has been revealed. However, it has been found that the carbon-supported catalyst is significantly more active than all other described oxide systems. It can be assumed that the hydrophobic surface of carbon is better wetted by triglycerides than the surface of an oxide support.

Table 8. Reaction product composition in the case of using the 1%Pd/Al₂O₃ catalysts

Pd particle size, nm	IV	C14:0	C16:0	C18:0	C18:1c	C18:1t	C18:2c	C18:2t
1.1	72.7	0.09	7.3	11.6	35.2	39.8	2.1	2.5
1.4	74.1	0.07	7.4	10.3	36.8	39.2	2.5	2.4
1.7	73.1	0.09	7.4	10.6	35.9	40.6	2.1	2.0
2.0	73.1	0.09	7.4	10.3	37.2	39.8	1.7	2.2
2.5	71.7	0.09	7.4	11.3	35.1	41.7	1.3	1.9
2.7	73	0.08	7.4	10.6	37.0	39.7	1.9	2.1
3.1	73.4	0.08	7.4	10.3	37.5	39.3	1.7	2.4
4.3	73.1	0.10	7.4	10.7	36.7	39.6	1.9	2.3

Under reaction conditions, all palladium catalysts exhibit *trans*-isomerization activity, while increasing the content of C18:1t fatty acids in the product to 36–42 wt %. In this case, the composition and ratio of the resulting fatty acids do not depend either on the catalyst activity or on the support nature or on the metal particle size. This finding is confirmed by the curves of the temperature profile for the melting of reaction products, which are similar in shape and position. Apparently, the nature of the support does not change the selectivity of the catalyst; that is, it does not change the ratio between hydrogenation and isomerization rates by changing the state of palladium particles.

FUNDING

This work was supported by the Ministry of Science and Higher Education of the Russian Federation under a state task to Borekov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (project no. AAAA-A21-121011390055-8).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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