

Catalysts Based on Fiberglass Support: IV. Platinum Catalysts Based on Fiberglass Support in Oxidation of Hydrocarbons (Propane and *n*-Butane) and Sulfur Dioxide

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Abstract—Platinum catalysts (0.003–0.52% Pt) based on leached sodium silicate and boron silicate fiberglass supports are studied in the complete oxidation of hydrocarbons (*n*-butane and propane) and high-temperature SO₂ oxidation. It was shown that platinum localized in the bulk of the glass matrix show a higher activity and thermal stability than metal particles supported on the outer surface of fiberglass. The experimental results for hydrocarbon oxidation on platinum-containing fiberglass gauzes at short contact times are discussed.

INTRODUCTION

The use of fiberglass materials in the complete oxidation of hydrocarbons is of great scientific and practical interest in connection with exhaust gas cleaning. It is not only important to develop highly active compositions but also to find an optimal design of catalysts based on them with optimal performance characteristics: high strength, stability, and good gas-dynamic properties. Catalysts based on fiberglass woven materials are very promising for these purposes. It has been shown recently that catalysts based on fiberglass woven materials are very active in many chemical processes, including hydrocarbon oxidation, even when the concentration of active elements (Pt, Pd, Ag, Cr, Co, etc.) is very low [1–4]. Earlier, we studied physicochemical properties of fiberglass supports and the conditions for catalyst preparation on the state and localization of active platinum and palladium particles [5–7].

The presence of well-developed technology for the preparation of fiberglass materials with different weaves, density, permeability, and layer thickness enables their potential use as catalysts for hydrocarbon oxidation at short contact times. It was shown in a series of experimental studies (see [8] and references therein) that these regimes allow high rates of reactant conversions and provide the required selectivity to target products. In practice, this enables the partial oxidation of hydrocarbons in smaller reactor volumes and catalysts with smaller catalyst loading.

In this work, we studied fiberglass-supported platinum catalysts in the complete oxidation of hydrocarbons and in the high-temperature oxidation of SO₂ to SO₃. We also present experimental data on the tests of

these catalysts in propane oxidation at short contact times.

CATALYST PREPARATION AND TESTING

Commercially available fiberglass woven materials made of 7–10-μm fibers were used. These materials were made of two types of glass: sodium silicate (type T) and aluminoboronsilicate (type E). Fiberglass fabric was leached before use with a 5–5.5% solution of HNO₃ to extract non-silica components. Earlier, we described in detail the properties of fiberglass woven materials [5, 6]. These properties depend on the initial composition of materials and leaching conditions. The SV sample used in this work was prepared by the almost complete leaching of the sodium silicate fiberglass fabric. It contained ~98.5% SiO₂ and had a specific surface area (S_{sp}) of 1.2 m²/g. The aluminoboron silicate glass support (sample EB) contained ~70% SiO₂ and had a specific surface area of 20 m²/g. A lower concentration of SiO₂ in the EV sample was due to the low (~30%) extent of non-silica component extraction, which was chosen to provide the acceptable strength of the support because it was shown in [6] that the strength of support is very low and they can even be destroyed at high (>50%) extents of boron silicate fiberglass leaching.

For comparison, we also used silica gel as a supporting material (sample A with S_{sp} = 10 m²/g and a grain size of 0.2–0.5 mm).

Platinum was introduced into a fiberglass matrix using three methods [7]. Method 1 consisted of fiberglass impregnation with the solutions of H₂PtCl₆ and [Pt(NH₃)₄]Cl₂ at room temperature. Then, fiberglass was separated from the impregnation solution, dried at

110°C, calcined in air at 300°C for 2 h and reduced in hydrogen at 300°C for 2 h. The total concentration of metal ranged between 0.03 and 0.52 wt %. Method 2 entailed the impregnation of fiberglass by platinum ammoniate at an elevated temperature. Then, the samples were washed with deionized water to remove metal compounds weakly bound to the support, dried, and calcined as in method 1. Method 3 was analogous to method 2 with the exception that cesium cations were intercalated into the fiberglass matrix beforehand. These cations played the role of “spacers” in the microcavities of fiberglass and simplified platinum intercalation into fiberglass. The presence of a washing stage enabled the low concentration of platinum (0.003–0.03 wt %) in the catalysts prepared by methods 2 and 3.

The catalytic properties of supported metals in the complete oxidation of hydrocarbons were studied by two methods:

1. Reaction rate (w) measurements in the complete oxidation of *n*-butane in a flow-circulation setup at 400°C and at a constant conversion x of 60%. The concentration of *n*-butane was 0.2 vol %. The flow rate of the *n*-butane–air mixture was 10 l/h; the circulation rate was 1000 l/h. The catalyst loading ranged from 0.5 to 2 g. The concentrations of *n*-butane and reaction products were determined by chromatography. In all cases, the products of *n*-butane oxidation were CO₂ and H₂O.

2. Propane oxidation was studied in a flow-type reactor at short contact times of the flow with a fiberglass catalyst. Samples tested in these experiments contained 0.2% Pt and were prepared using method 1 and leached sodium silicate fiberglass. The catalytic element was gauze with a square cell of ~2.5 mm. The thickness of filaments was 1 mm. The size of holes was 1.5 mm. That is, there were 16 holes per 1 cm². Filaments of ~1 mm were spun of 7-μm fibers. This catalytic element was loaded in the cross-section of a flow-type vertical tubular reactor with a diameter of 25 mm.

A flow of the gaseous mixture containing 2–4% propane in air was supplied from the bottom onto the gauze element with a flow rate of 5–10 cm/s. The contact time was 10–20 ms. The temperature in the reactor was controlled with an external heater. In the experiments, we measured the propane conversion at 10–20-ms contact times by analyzing gases at the inlet and outlet by chromatography. Temperatures of gas heating were measured using a thermocouple placed in the flow above the catalytic element near the fiberglass material.

The catalytic properties in the reaction of sulfur dioxide oxidation were studied in a flow-type reactor at 700°C. A concentrated gaseous mixture (20 vol % SO₂, 20 vol % O₂, and 60 vol % N₂) was used as a feed gas. The catalyst loading was 1–2 g. The contact time was varied from 0.3 to 2 s by changing the feed flow rate. The conversion of SO₂ was used as an activity measure. This parameter remained constant for at least 8 h. In several cases, we carried out stability tests for 48 h. The concentration of SO₂ before and after the reactor was determined by the Reich iodometric method using an electronic device for the automatic detection of titration time. Temperature was changed and controlled accurate to ±0.5°C using a microprocessor temperature controller. To prevent product condensation, the reaction contour was placed in a thermostated compartment.

RESULTS AND DISCUSSION

1. The Complete Oxidation of *n*-Butane

Table 1 shows the results of testing platinum catalysts supported on leached aluminoboron silicate and sodium silicate fiberglass material. For comparison, platinum supported on silica gel was used. Table 1 shows that the activity of fiberglass-supported platinum catalysts per gram of the catalyst was 2–2.5 times higher than for the sample based on silica gel. It is important to note that there was no correlation between

Table 1. The effect of composition and preparation conditions of platinum catalysts on the rate of the complete oxidation of *n*-butane on 1 g of the catalyst (w_{Cat}) and on 1 g of platinum (w_{Pt})

Sample	Impregnation method	Support	Pt, %	D_{Pt} , Å	$w_{\text{Cat}} \times 10^2$, cm ³ (g Cat) ⁻¹ s ⁻¹	w_{Pt} , cm ³ (g Pt) ⁻¹ s ⁻¹
1-A-0.32 Pt	1	SiO ₂ A	0.320	200–250	3.6	11
1-EV-0.4 Pt	1	EV	0.400	80–100	8.9	22
1-EV-0.52 Pt	1	EV	0.520	80–100	9.4	18
1-SV-0.22 Pt	1	SV	0.220	60–80	6.5	29
1-SV-0.15 Pt	1	SV	0.150	30–40	7.4	50
1-SV-0.09 Pt	1	SV	0.090	20	9.0	100
1-SV-0.04 Pt	1	SV	0.040	20	6.9	170
1-SV-0.03 Pt	1	SV	0.030	20	10.9	360
T-1	2	SV	0.010	~10	9.3	930
T-18	3	SV	0.003Pt 0.310Cs	~10	4.9	1600

the apparent reaction rate per unit catalyst weight and the concentration of metal in the catalyst. Samples with different concentrations of platinum and different preparation procedures had activities per unit platinum weight differing by two orders of magnitude. Samples prepared by methods 2 and 3 had the maximal values of w_{Pt} ($930\text{--}1600 \text{ cm}^3 (\text{g Pt})^{-1} \text{ s}^{-1}$). Possible reasons for this effect may be the difference in platinum dispersion and the nature of its interaction with the glass matrix.

It was shown in our previous work [7] that the dispersion of platinum particles and their localization are determined by the concentration and the method of platinum introduction into fiberglass material. In the samples prepared using standard impregnation (method 1) and containing 0.15–0.52 wt %, most of the active component is localized on the outer surfaces of fibers. According to the electron microscopic data, the average size of metal particles increases with an increase in the platinum concentration from $30\text{--}40 \text{ \AA}$ for 1-SV-0.15 Pt to $80\text{--}100 \text{ \AA}$ for samples 1-EV-0.4 Pt and 1-EV-0.52 Pt. In the case of platinum supported by method 1 on silica gel (sample 1-A-0.32 Pt), the average size of platinum species reached $200\text{--}250 \text{ \AA}$. Using these data, it is easy to estimate the specific surface area of platinum, which decreases from $0.1 \text{ m}^2/\text{g}$ (samples 1-SV-0.15 Pt and 1-EV-0.4 Pt) to $0.04 \text{ m}^2/\text{g}$ (sample 1-A-0.32 Pt). The ratio of the reaction rate w_{Cat} to the surface area of the catalyst is constant for all five samples with an increased concentration of platinum (0.15–0.52%): $w/S = 0.75 \pm 0.15 \text{ cm}^3 (\text{m Pt})^{-2} \text{ s}^{-1}$. This value corresponds to the turnover frequency of $2 \pm 0.4 \text{ s}^{-1}$, which is typical of most palladium and platinum catalysts supported on SiO_2 and Al_2O_3 for the complete oxidation of hydrocarbons [9]. These data suggest that the catalysts based on leached boron and sodium silicate fiberglass and prepared using method 1 have activities similar to usual supported catalysts.

Much higher turnover frequencies ($8\text{--}15 \text{ s}^{-1}$) are observed in the case of catalysts with low concentrations of platinum prepared under the conditions of activated impregnation (sample T-1, 0.01% Pt) and with the preliminary intercalation of Cs^+ (sample T-18, 0.003% Pt).

The state of platinum in these samples was studied in detail earlier [7] using high-resolution electron microscopy and XPS coupled with the method of ionic etching. It was found that platinum was absent from the outer surface of samples obtained by methods 2 and 3. All the platinum is localized in the fiberglass bulk and penetrates to a depth of 100 \AA . These particles are so highly dispersed that they cannot be observed by transmission electron microscopy. Clusters with a size of 10 \AA appear on high-resolution images only after thermal treatment by electron beam when the coalescence of even smaller platinum particles existing in these microcavities becomes possible probably as a result of the partial sintering of microcavities of fiberglass. According to XPS data, these platinum microparticles are not neutral. They have a positive charge and are

chemically bound to the support. XPS data show that the state of platinum does not change during the reaction.

As we pointed out earlier [7], the stabilization of highly dispersed platinum states becomes possible for several reasons. First, the introduction of the active component is due to the chemical interaction (exchange) of platinum ions with hydroxyl-group protons on the fiberglass surface. Second, these ions are positioned in the interlayer space of support with a pseudolamellar intercalation structure [5], which efficiently prevents platinum aggregation. We assume that platinum microparticles localized in the glass matrix bulk are in the metastable state, which stipulates their high activity.

The localization of active platinum particles in fine microcavities of fiberglass makes the transport of reactant molecules to these particles difficult. Unfortunately, it is hard to distinguish the rates of diffusion and the catalytic reaction. Moreover, the mechanism of diffusion is unclear because the pseudolamellar structure of the matrix is rather labile at elevated temperatures.

On the other hand, the molecular characteristics of active entities (structure, size, etc.) are unknown. If we hypothesize that the transport of reactive molecules is fast and each platinum ion (active site) participates in the reaction, then the turnover frequency is $\sim 16 \text{ s}^{-1}$ for sample T-18 according to data of Table 1. This is an order of magnitude higher than in the case of samples with an increased concentration of platinum. Since platinum clusters with a size of $5\text{--}10 \text{ \AA}$, rather than isolated platinum atoms, are the participants of the reaction, the turnover frequency will be another order of magnitude higher. In other words, the catalytic reaction may occur at millisecond contact times (i.e., they are very fast).

Although the above estimates are conditional, we assume that the presence of nonequilibrium, energetically oversaturated structures in the platinum–glass system is the reason for the high rate of the reaction.

The activity of catalysts with the low concentrations of platinum prepared by method 1 (samples 1-SV-0.09 Pt, 1-SV-0.04 Pt, and 1-SV-0.03 Pt) is mediocre. Indeed, according to electron microscopy and XPS, the concentration of metallic platinum on the outer surface of fiberglass is much lower than in, say, sample 1-SV-0.22 Pt. In other words, the portion of highly active platinum (ions or clusters) that is not blocked by platinum on the outer surface of fibers is higher than in the case of samples with the high concentrations of platinum, where the low-active platinum (mesoparticles) dominates. In addition to a special catalytic function, platinum bound to the support matrix is probably responsible for some stabilization of surface metallic platinum and some strengthening in the chemical affinity of platinum fragments and silicate support.

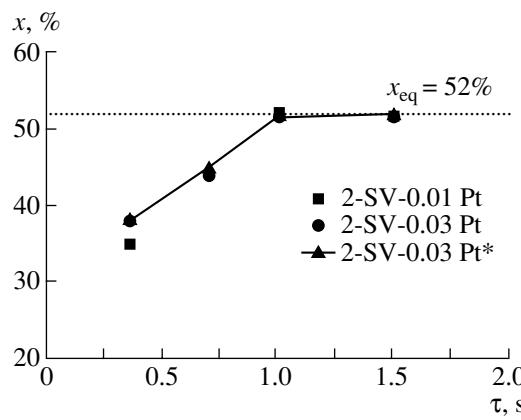


Fig. 1. Effect of contact time τ on the conversion of SO_2 on different catalysts.

2. SO_2 Oxidation to SO_3

Platinum is the most active catalyst in sulfur dioxide oxidation. It is known that, before the 1940s, the oxidation of SO_2 in industry was carried out over platinum grids, which were later replaced by vanadium catalysts, which are cheaper and less susceptible to poisons. However, an interest in the practical use of platinum catalysts has recently appeared [10]. The main challenge is to increase the extent of platinum use by choosing appropriate support materials that provide a high dispersion of active metal, high thermal stability, resistance to sulfatization, and optimal geometric forms with good aerodynamic characteristics. For these purposes, multichannel ceramic monoliths with a supported layer of highly dispersed materials (alumina, silica, zirconia, etc.) were proposed, on which active platinum compounds were deposited [10, 11].

We thought that it would be interesting to test platinum catalysts supported on leached Na–Si fiberglass fabric in sulfur dioxide oxidation at high temperatures ($>650^\circ\text{C}$), which are typical of the oxidation of concentrated sulfurous gases when conventional vanadium catalysts for sulfuric acid synthesis are thermally unstable. The lamellar structure of leached Na–Si fiberglass is characterized by some lability; that is, silica layers and microcavities can move and merge with an increase in temperature. However, we assume that the low con-

centration of platinum in the catalysts prepared by methods 2 and 3 and its localization in the narrow microcavities of a glass matrix provide high dispersion and a lower susceptibility to platinum sintering with particles on the support surface. The assumption of the high thermal stability of such fiberglass catalysts was tested in the experiments on the high-temperature (700°C) oxidation of SO_2 (20 vol %) on platinum–fiberglass catalysts prepared by method 2 and containing 0.01 and 0.03% Pt (samples 2-SV-0.01 Pt and 2-SV-0.03 Pt) (Table 2).

Under the above conditions for testing, the calculated equilibrium conversion of SO_2 x_{eq} is $\sim 52\%$. The contact time was varied from 0.3 to 2 s by changing the feed flow rate.

As can be seen from Fig. 1, both samples were close in their activities. The equilibrium conversion is achieved at a contact time of 1 s. About the same activities are also typical of shorter contact times (at $\tau = 0.36$ s, $x = 37.0 \pm 0.5\%$). These conversions did not change with an increase in the time-on-stream to 48 h at 700°C . This fact points to the high thermal stability of the catalysts. To confirm this conclusion we subjected the 2-SV-0.03 Pt sample to “accelerated thermal aging” by calcining it in air at 800°C for 10 h to obtain sample 2-SV-0.03 Pt*, which was then tested at 700°C . As can be seen from Fig. 1, thermal aging had no effect on the activity. The XRD study of the 2-SV-0.03 Pt* sample showed that severe thermal treatment did not result in an increase in the size of platinum particles or in the formation of crystalline phases in silica fiberglass support. Note that commercial vanadium catalysts for SO_2 oxidation strongly deactivate under analogous conditions due to their crystallization and the intensive sintering of silica gel support [12].

3. Propane Oxidation on Fiberglass Catalytic Elements at Short Contact Times

Experiments were carried out under the conditions of dynamic heating of the reactor, that is, in the regime of scanning the temperature of the reaction flow. At the initial moment, the external heater (the winding of the reactor walls) was switched on. Then, a temperature change in the process was registered using a thermocouple in the flow immediately after the catalytic gauze. In the preliminary runs, we determined the reference temperature profile obtained in the absence of propane in an oxygen flow. The test runs were carried out under identical thermal and hydrodynamic conditions with the hydrocarbon in an air flow. This difference scheme allowed us to register the light-off temperature of catalytic combustion and to calculate the reaction rate in thermal units by comparing temperature profiles with reference profiles. That is, this difference scheme was close to a calorimetric one (Fig. 2).

It can be seen from Fig. 2 that when some threshold temperature (250 – 320°C depending on the concentra-

Table 2. Properties of catalysts studied in SO_2 oxidation

Sample	Support	Active component	Thermal treatment conditions
2-SV-0.01 Pt	SV	0.01% Pt	300°C , 2 h
2-SV-0.03 Pt	SV	0.03% Pt	300°C , 2 h
2-SV-0.03 Pt*	SV	0.03% Pt	800°C , 10 h

tion of propane in an air flow) is reached, “trigger switching” is observed in the reaction regime: starting from almost zero conversion, the reaction rate increases stepwise despite very short contact times, and almost complete conversion is observed. Note that it was impossible to obtain the exact dependence of the conversion on the temperature and time because the process was too fast for chromatographic analysis. In fact, we only managed to register conversions equal to 0 and 100% before and after the threshold temperature. In terms of traditional combustion theory, our catalytic combustion occurred in a narrow region where the thermal front contracts to the width of catalytic gauze (~1 mm). That is, it is characterized by a greater steepness and localization than in classical combustion processes of a gaseous flame.

In some experiments, we observed the two-step light-off of reaction. Figure 2 shows a sample temperature profile with two consecutive thresholds of trigger switching of the reaction. This phenomenon can be due to two mechanisms differing in their physical nature. Either the temperature profile reflects the dynamics of an autowave process of self-activation with a delay of a traveling wave on the thermal nonuniformity of the catalytic element (the thermophysical mechanism), or the two steps are due to the consecutive inclusion of the active sites of two types, which are activated at low and high temperatures (the kinetic mechanism). Addressing these questions is outside the scope of this work.

The cited high rate of the reaction at short contact times ($\tau \sim 10^{-2}$ s) on a single gauze is very surprising because the same sample (1-SV-0.22 Pt) did not show a high activity toward *n*-butane oxidation under the flow-circulation conditions (400°C).

Indeed, in the flow-circulation setup, a conversion of 60% is achieved at ~2 orders of magnitude higher contact times. Because fiberglass woven catalysts prepared by simple impregnation (e.g., 1-SV-0.22 Pt) are close to the samples of platinum supported on Al_2O_3 and SiO_2 , the rate constant can be estimated from the first-order rate law [9]: $k \sim 5 \text{ s}^{-1}$. Based on this value, we can estimate the propane conversion x assuming that the reaction mixture passes through the two-dimensional catalytic element in the regime of a plug flow. Then, $x = 1 - \exp(-V_{\text{Cat}}k/v)$, where $v = 25 \text{ cm}^3/\text{s}$ is the flow rate, $V_{\text{Cat}} = 0.2 \text{ cm}^3$ is the catalyst volume calculated from the geometry of the fiberglass woven catalyst. After substituting the numerical values in the expression for x , we obtain that the propane conversion is only several percent. The apparent propane conversion close to 100% is possible if k is increased by two or three orders of magnitude. Taking into account that the reaction is limited by external diffusion [13] when not all of the surface platinum atoms are accessible to the gaseous reactants, the true value of k should be even higher.

In other words, it is difficult to explain the complete conversion of propane at millisecond contact times in the flow-circulation setup in the framework of the

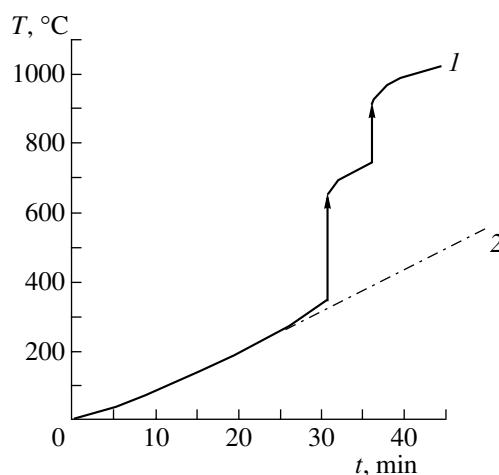


Fig. 2. Temperature profile of the light-off of the catalytic combustion of propane (4 vol % in air) on a single gauze of the fiberglass woven catalyst (1-SV-0.22 Pt): (1) process curve and (2) reference curve. The linear flow rate of the reaction flow is $\sim 5 \text{ cm/s}$; the power of a reactor hater is 290 W; the characteristic time of the thermal inertia of the reactor is $\sim 1 \text{ h}$; and the characteristic time of the light-off process is $<1 \text{ s}$.

purely heterogeneous mechanism of the reaction. Taking into account the trigger nature of changes in the conversion when passing through the threshold value, we assume that the reaction occurs via the heterogeneous–homogeneous mechanism at short contact times.

Although experimental data obtained at this stage of our studies are very limited, we can conjecture the main stages of the process. The catalytic surface is an initiating unit of the process. It generates and desorbs reactive species to the gas phase where they participate in fast (possibly branched chain) reactions of final product formation. In other words, the process regime can be called “stopped catalysis.”

Similar ideas relevant to heterogeneous–homogeneous processes of hydrocarbon oxidation on single metallic gauzes at millisecond and shorter contact times were developed in recent papers [14–16].

Obviously, the above hypothesis on the homogeneous propagation of the reaction on fiberglass woven catalysts requires direct registration of active species desorbed from the surface and the presence of the dependence of their nature on the composition and spatial localization of the active component. In the end, this will allow one to find optimal regimes for the process toward valuable products of the partial oxidation of light paraffins.

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