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Method of Immobilization of Titanium Silicalite, Catalyst of Hydrocarbon Oxidation, in Polymer Matrix

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Abstract

A principally new method of immobilization was developed for titanium silicalite (TS-1), the catalyst of liquid-phase hydrocarbon oxidation. The method involves encapsulation of catalyst particles in a polymer matrix. A series of catalysts was synthesized using different types of polymer matrices for practical implementation in oxidation processes. The optimal composition of the components of catalytic system and the type of polymer matrix for practical use in liquid-phase oxidation of the hydrocarbons of C₆–C₉ fraction were established, with the use of 30 % aqueous hydrogen peroxide solution as the oxidizer and methanol as a solvent.

Key words: titanium silicalite, immobilization, polymer matrix, liquid-phase oxidation of hydrocarbons

INTRODUCTION

Titanium-containing zeolite called titanium silicalite (TS-1) exhibits high catalytic activity in the oxidation of a large number of various organic substances. In particular, titanium silicalite is widely used in the processes of hydroxylation of aromatic compounds, oxidation of alkanes and thioethers, epoxidation of olefins and in other important processes of organic synthesis [1–3]. At present, industrial introduction of titanium silicalite in the processes of liquid-phase oxidation of hydrocarbons is hindered because titanium silicalite powder is fine, so additional stages (such as settling, filtering, centrifuging *etc.*) are to be added in order to remove the catalyst from the reaction mixture [4].

For the industrial use of titanium silicalite in the reactors with high productivity with the steady catalyst layer, it is necessary to form the catalyst into larger catalytic particles – spheres, rings, granules *etc.*

There is a small amount of data in the literature describing the methods of shaping titanium silicalite into larger particles. Among the mentioned methods, noteworthy are pressing of titanium silicalite powder, deposition on various supports, and extrusion of the mixtures of titanium silicalite with various organic and inorganic binders.

The major disadvantage of the catalysts obtained by pressing titanium silicalite powder is their extremely low mechanical strength, which causes rapid destruction of the catalytic system under the process conditions [5]. Titanium silicalite shaping by the deposition on supports is also conjugated with a number of difficulties among which we are to mention complexity of choosing the suitable support: on the one hand, it must be chemically inert to the components of reaction mixture, on the other hand, it must be able to form the system that would be stable against washing titanium silicalite out. The authors of [6] proposed to use the titanium silicalite supporting substrates con-

taining hydroxyl groups on their surface to interact with the hydroxyl groups of the zeolite. The authors of [7] propose to use aluminium oxide or silica gel as a support, and polyatomic alcohols as binding components. However, these supports have a clear shortcoming: acid properties, which causes an increase in the selectivity of the side process – decomposition of hydrogen peroxide – under the conditions of alkane oxidation.

The most promising method is extrusion of the mixtures of titanium silicalite with various organic and inorganic binders. In the majority of cases, the shaping mixture is composed of powdered titanium silicalite (active component), inorganic binder (matrix) and organic additives. Inorganic binders are various modifications of aluminium and silicon oxides, aluminium hydroxide, as well as their mixtures, zeolites and minerals of natural and artificial origin [8, 9].

We prepared the samples of moulded titanium silicalite with inorganic binders based on aluminium and silicon oxides, and aluminium hydroxide. Catalyst samples were tested in the oxidation of *n*-nonane by a 30 % solution of hydrogen peroxide in methanol in a laboratory set-up of continuous action. The data are presented in Table 1.

The studies carried out by us showed that inorganic binders based on aluminium and silicon oxides or aluminium hydroxide are unsuitable for the preparation of moulded titanium silicalite as the catalyst of *n*-alkane C₆–C₉ oxidation by hydrogen peroxide. In all experiments (see Table 1) we observed almost complete ineff-

icient decomposition of hydrogen peroxide and very low yield of the target products of oxidation. The reactivity of *n*-alkanes is low, so the rate of their oxidation on titanium centres of titanium silicalite (active component) is lower than the rate of hydrogen peroxide decomposition on the acid centres of the inorganic binder, which results in the inefficient almost complete decomposition of hydrogen peroxide [10].

In our opinion, among the methods of titanium silicalite shaping the most promising one is immobilization of the active component on polymer supports. For example, a method described in [11] involves encapsulation of titanium silicalite in polymeric matrix, which may be polystyrene and its co-polymers, fluorinated polyolefins in the presence of organic solvent (cyclohexane, tetrahydrofuran). The tests of the resulting catalyst in the oxidation of *n*-pentane with a 30 % aqueous solution of hydrogen peroxide with the formation of secondary alcohols and ketones showed that the degree of *n*-pentane transformation was 40 %. This method has an essential advantage: the support is inert towards the components of the reaction mixture. The major disadvantages of this method of obtaining encapsulated titanium silicalite include the multistage manufacturing process, the use of a large number of auxiliary substances (solvents) and relatively low activity of the resulting catalyst. In this connection, the development of new methods of titanium silicalite immobilization on polymer supports is urgent.

Taking into account known literature and experimental data and evaluation of the outlooks for the development of the methods of titanium silicalite shaping, we developed a new method of catalyst immobilization using polymeric matrices based on polypropylene of different grades, polyethylene, polystyrene, polymethylmetacrylate and other compounds that are chemically neutral under the process conditions.

EXPERIMENTAL

Preparation, immobilization and physicochemical methods to investigate encapsulated titanium silicalite

The active component of the catalytic system DP-2 is titanium silicalite powder. It was

TABLE 1

Effect of the type of inorganic binder on the parameters of *n*-nonane oxidation by hydrogen peroxide. Temperature 60 °C, *n*-nonane/hydrogen peroxide ratio = 4.9 : 1 (by mass), degree of hydrogen peroxide conversion 98 %, titanium silicalite (TS-1) content in all samples 50 mass %, load on catalyst 12.6 L/(h · kg_{cat})

Binder types	Selectivity, %	Total yield of nonanols and nonanones, %
γ-Al ₂ O ₃	90–92	8–10
γ-Al ₂ O ₃ + SiO ₂	87–91	9–13
Al(OH) ₃	94–96	4–6

obtained according to the procedure described in [12]. Its titanium content calculated for TiO_2 was 3.16 %.

Encapsulated titanium silicalite DP-2 was obtained in a laboratory one-screw extruder with screw diameter 18 mm, which is intended for compounding small amounts of polymers with fillers and additives; it is equipped with powder dosing unit. The laboratory set-up includes several units: charging unit intended for charging the polymer into the extruder through the dosing unit; extruder itself, intended for the formation of polymer melt and for component mixing (powdered titanium silicalite and the polymer) through the melt; discharging unit at the outlet of the extruder: catalytic system in the discharging unit passes through the molding head providing the formation of granules, spheres, rings or other necessary shapes of the required size. Dispersing unit is not present in the laboratory set-up because the particles of dried powdered titanium silicalite are weakly prone to agglomeration.

Extrusion temperature was chosen within the range 160–180 °C depending on the melting point of the polymer used. Extrusion pressure was 30–40 bar, mass expenditure rate of the dispersed phase was 0.02 g/min, titanium silicalite content in the polymer was 30 to 60 mass %. The major requirements to the extruded material include homogeneous distribution of dispersed phase over the dispersion medium, high catalytic activity in the process of *n*-nonane oxidation by a 30 % aqueous solution of hydrogen peroxide.

Evaluation of the homogeneity of the average size of TS-1 particles and the distribution of titanium silicalite particles in a polymer matrix was carried out by means of thin films with an Axioskop 40A Pol optical polarization microscope (Carl Zeiss, Germany).

Determination of the specific surface of moulded titanium silicalite DP-2 samples was carried out according to the procedure described in [13, 14] from benzene adsorption using the dynamic method.

The strength of the granules of immobilized titanium silicalite was determined with the help of a Testometric winTest™ Analysis M350-10AT (UK).

Changes of the structure of catalytic system as a result of the action of reaction medi-

um was evaluated with the help of IR spectroscopy in the air at room temperature using a Perkin–Elmer 221 spectrometer; the spectra were recorded in KBr tablets within the range 400–4000 cm^{-1} .

Sample testing procedure and analysis of reaction mixture

Catalytic activity and performance characteristics of the catalysts, namely, the stability of granules to the action of the medium, were evaluated from the results of catalytic tests that were carried out in the laboratory set-up composed of the vessel with initial reagents, heat exchangers, pump, glass reactor filled with the catalyst. The model system was *n*-nonane. Immobilized DP-2 was used in the form of granules 1 × 1 × 1 mm in size.

Experiments were carried out at a temperature of 60 °C, the mass ratio of *n*-nonane/solvent (methanol) equal to 0.064 : 1, mass ratio of *n*-nonane/hydrogen peroxide equal to 4.6 : 1. This mass ratio of *n*-nonane/solvent (methanol) was chosen in order to obtain a homogeneous mixture because initially the reaction mixture contains 3.7 mass % water. In addition, small amounts of reaction water (0.2 mass %) are formed during the process. Experiments were carried out in the isothermal mode under the conditions close to ideal displacement in the kinetic region. The load on the catalyst was 12.6 L/(h · kg_{cat}). The reactor is a glass tube conventionally divided into three zones: the central part of the tube is filled with catalyst granules, while the lower and upper parts are filled with Fenske rings. Temperature mode in the reactor is maintained due to heat carrier supplied to the jacket. Heat carrier is water heated to the temperature of 60 °C. The reaction mass is fed by the pump from the vessel of initial components (equipped with a mixer and a jacketed) into heat exchanger where it is heated to the synthesis temperature. Then the heated reaction mixture enters the reactor with immobile catalyst layer. A mixture of reaction products and unreacted initial substances is cooled in heat exchanger and enters the receiving vessel.

Oxidation products were identified by means of gas chromatography/mass spectrometry with a Shimadzu GCMS QP-2010 instrument

with BP1 column. Analysis of the components of reaction mixture was carried out by means of gas liquid chromatography with a Khromos GKh-1000 instrument with metal column (3 m × 3 mm), Reoplex 4000 on Chromaton N-AW was used as the immobile phase. Flame ionisation detector was used. Nitrogen was used as carrier gas; flow rate through the column was 15 mL/min. Temperatures of evaporator and thermostat were maintained at 250 and 90 °C, respectively. Hydrogen peroxide was determined by means of iodometric titration.

It was shown that the major products of liquid-phase oxidation of *n*-nonane by a 30 % aqueous solution of hydrogen peroxide on shaped titanium silicalite are the corresponding secondary alcohols (nonanol-2, nonanol-3, nonanol-4) and ketones (nonanon-2, nonanon-3, nonanon-4). Oxygen formed as a result of hydrogen peroxide decomposition was detected as a side product.

RESULTS AND DISCUSSION

In our search for the simplest method of obtaining a catalytic system composed of a polymeric composite material in which the dispersed phase is titanium silicalite powder, we preferred to choose extrusion. This process is able to ensure rather homogeneous distribution of the dispersed phase in the continuous phase of the catalytic system due to mixing “in melt” and the formation of the granules of required size and shape due to different design of molding head.

From the viewpoint of efficiency and simplicity of molding method, the most interesting polymers are polyolefins – polyethylene and polypropylene, and their copolymers. To obtain moulded titanium silicalite, we used polypropylene of different grades, differing by molecular mass, specific surface, density and the melt molding index. To prepare the samples of the catalytic system, we used titanium silicalite as the active component. The average size of its particles was (250 ± 2) nm. Its content in the samples varied from 30 to 60 % and provided the formation of a composite material with the high degree of homogeneity of the distribution of active component particles within the matrix, on the

one hand, and optimisation of reactor operation on the other hand.

It was established during optimisation of catalyst composition that the specific surface of the catalytic system and mechanical strength of the samples increase with an increase in the content of powdered titanium silicalite TS-1 in the polymer matrix from 30 to 40–42 mass %. With further increase in TS-1 content in the polymer composition above 50 mass %, specific surface increases but mechanical strength decreases substantially. It is likely that the extremal dependence of mechanical strength on the concentration of dispersed filler is due to a decrease in the thickness of the polymer layer between TS-1 particles or its complete absence, which results in the formation of defect regions with low mechanical strength. The dependences obtained for the catalytic system DP-2-1 are presented in Fig. 1.

The following system was used for designation of the samples of the catalytic system DP-2 differing by the type of polymeric matrix and by the concentration of the active component (TS-1): the first digit after the common title DP-2 defines the type of polymeric matrix (1 – polypropylene Caplen, Technical Conditions TU 2211-015-00203521-95; 2 – polypropylene 22015-16, State Standard GOST 26996-86; 3 – polypropylene Balen 225-01030-16, TU 224-020-002035-21-96). The second digit after the designation of the type of polymeric matrix depicts the concentration of the active component in the catalytic system (30 or 50 %).

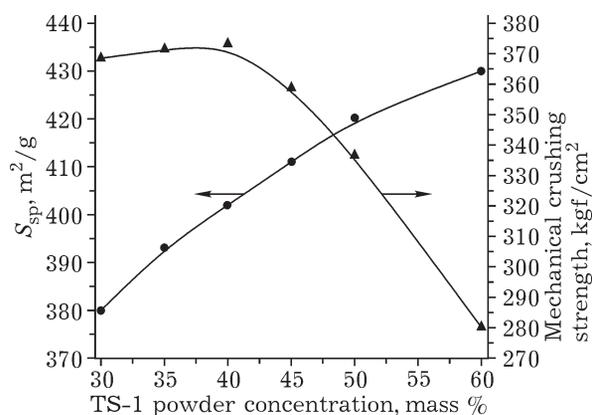


Fig. 1. Dependence of catalyst parameters on the concentration of the dispersed phase (titanium silicalite TS-1 powder).

TABLE 2

Composition and characteristics of immobilized titanium silicalite (DP-2)

Samples	Melt index, g/10 min	Concentration of volatiles, mass %	Tensile yield strength, MPa	Relative elongation at yield stress, %	Crushing strength, kgf/cm ²	Specific surface, m ² /g
DP-2-1-30	2.9–3.5	0.09	34	10	368.5	380
DP-2-1-50	2.9–3.5	0.09	34	10	336.6	420
DP-2-2-30	1.1–2.0	0.09–0.20	22–25	300	433.4	300
DP-2-2-50	1.1–2.0	0.09–0.20	22–25	300	411.6	340
DP-2-3-30	2.4–3.7	0.09	34	10	302.0	350
DP-2-3-50	2.4–3.7	0.09	34	10	287.2	380

The highest values of crushing strength are observed for samples DP-2-2-30 and DP-2-2-50, while the lowest ones are observed for DP-2-3-50 and DP-2-3-30 (Table 2). Mechanical strength of DP-2-1 samples exhibits intermediate values.

To estimate the homogeneity of the distribution of titanium silicalite powder in the polymer matrix, we used the optical microscopy of thin films. The results obtained for samples DP-2-1-30 and DP-2-1-50 are shown in Fig. 2. One can see that catalytic system DP-2-1-30 with the 30 mass % content of dispersed filler has nonuniform structure, unlike for the system DP-2-1-50 with the 50 mass % content of dispersed filler. In general, it may be concluded that the catalytic system DP-2 relates to statistical composite systems. The lower is mass concentration of dispersed filler, the longer is the distance to transfer the introduced titanium silicalite particles for their uniform distribution. It is likely that the dependence of homogeneity

of the distribution of dispersed filler particles on the amount of filler (for other conditions kept identical) is similar to the dependence of mechanical density on the same parameter.

The characteristics of the obtained samples of DP-2 catalyst are presented in Table 2.

Relying on the data shown in Figs. 1 and 2, we chose the systems with titanium silicalite TS-1 50 % to study their catalytic properties. The time within which the catalyst achieves the static regime is approximately the same for all polymeric matrices: 23.3 h. The major parameters of the process (the degree of hydrogen peroxide transformation, selectivity of the formation of target products) were estimated after the catalyst operation reached the steady regime.

The maximal average degree of hydrogen peroxide transformation (33.5 %) is observed when DP-2-3-50 catalyst is used. The catalysts DP-2-2-50 and DP-2-1-50 provide the average degree of hydrogen peroxide transformation 32.6 and 31.6 %, respectively.

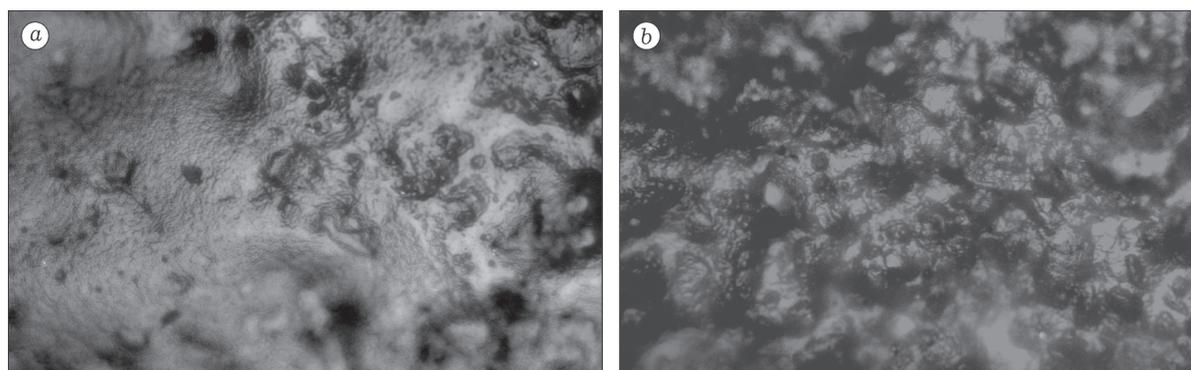


Fig. 2. Photomicrographs of DP-2-1 catalyst section: a – nonhomogeneous structure of DP-2-1-30 sample; b – homogeneous structure of DP-2-1-50 sample.

The sequence of catalytic systems DP-2-2-50–DP-2-3-50–DP-2-1-50 exhibits an increase in the average selectivity of alcohol formation (from 31.7 to 52.3 %) and ketones (from 11.7 to 20.8 %). The changes of major process characteristics with time depending on the type of polymeric matrix are presented in Table 3.

It was established that the best process characteristics are observed when polypropylene Caplen TU 2211-015-00203521-95 is used as the polymeric matrix.

Among the whole sequence of catalysts studied, DP-2-1-50 sample has the best relation between oxidation process parameters and performance characteristics, namely, the stability of granules to the action of reaction medium. During the catalytic tests of DP-2-1-50 for

200 h we did not observe a decrease in its catalytic activity and changes of other characteristics of the catalytic system – mechanical strength and specific surface.

One of the necessary criteria of polymeric matrices is the absence of the interaction of tetra-coordinated titanium of TS-1 lattice with the matrix during operation, as well as the stability of the matrix to process conditions. It follows from Fig. 3, where we show the IR spectra of fresh DP-2-1-50 catalytic sample and the sample that had worked for 200 h, that the positions of characteristic peaks and their intensities do not change during operation (the peaks characteristic of titanium silicalite in the IR region are the bands at 960 and 540 cm^{-1} ,

TABLE 3
Results of the tests of catalytic systems

System types	Time, h	Degree of hydrogen peroxide transformation, %	Selectivity of formation, %	
			Alcohols	Ketones
DP-2-1-50	23.3	32.2	48.2	24.5
	27.8	31.4	49.7	23.6
	30.8	31.9	50.1	22.8
	36.3	31.9	51.7	21.7
	40.3	31.9	54.2	18.2
	45.3	31.1	54.6	18.2
	47.8	31.2	54.9	18.6
	50.0	31.2	54.8	18.5
	Average		31.6	52.3
DP-2-2-50	23.3	32.9	29.7	12.2
	27.8	32.8	30.8	11.3
	30.8	32.7	31.5	11.6
	36.3	32.6	32.0	11.8
	40.3	32.9	32.4	11.3
	45.3	32.2	32.5	11.7
	47.8	32.1	32.8	11.7
	50.0	32.6	32.1	12.0
	Average		32.6	31.7
DP-2-3-50	23.3	33.7	33.7	18.5
	27.8	33.8	34.8	17.1
	30.8	33.4	34.4	16.9
	36.3	33.1	34.5	14.1
	40.3	33.8	34.6	14.2
	45.3	33.6	34.6	14.0
	47.8	33.4	34.4	15.0
	50.0	33.2	34.3	14.8
	Average		33.5	34.4

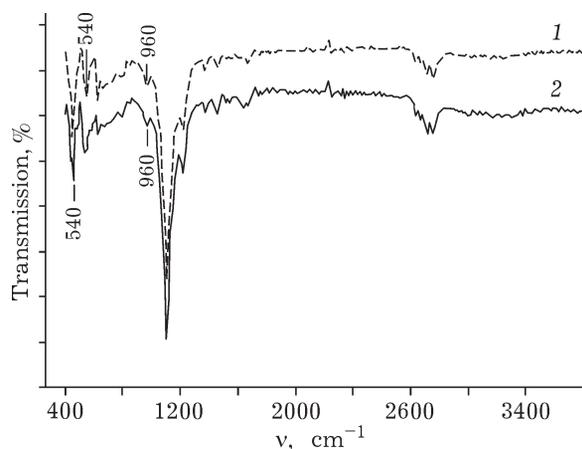


Fig. 3. IR spectra of DP-2-1 samples: 1 – freshly prepared, 2 – after operation for 200 h.

corresponding to tetra-coordinated titanium of the lattice of titanium silicalite).

On the basis of the data obtained using physicochemical methods of analysis and catalytic tests, DP-2-1-50 can be recommended as a catalyst of liquid-phase oxidation of C_6 – C_9 hydrocarbons.

CONCLUSION

Investigations of moulded titanium silicalite DP-2 provide evidence of the possibility to use it for oxidation of n -alkanes. The most promising catalyst that promotes selective formation of alcohols and ketones is titanium silicalite im-

mobilized on the polymeric support – polypropylene Caplen TU 2211-015-00203521–95.

It was established that the catalytic system DP-2-1-50 composed of titanium silicalite immobilized on polypropylene Caplen TU 2211-015-00203521–95 provides the average total selectivity of n -nonane transformation into corresponding alcohols and ketones at a level of 73.1 %.

The possibility of long-term operation of the developed catalytic system in hydrocarbon oxidation processes was confirmed.

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