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Catalytic oxidation of α-pinene with *tert*-butyl hydroperoxide in the presence of Fe-pillared montmorillonite*

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The reaction of α-pinene with *tert*-butyl hydroperoxide can proceed *via* allylic oxidation or α-pinene isomerization, depending on the structural features of the catalysts based on Fe-pillared montmorillonite.

Key words: α-pinene, allylic oxidation, Fe-pillared montmorillonite, mechanochemical activation, terpenoids, *tert*-butyl hydroperoxide, ^{27}Al NMR spectroscopy.

In spite of diversity of available methods for allylic oxidation of olefins, only few oxidation systems give α,β-unsaturated alcohols or carbonyl compounds in appropriate yields. Oxidation systems based on the lead(IV), selenium(IV), and chromium(VI) compounds turned out to be good in laboratory practice.[1] The main disadvantage of these methods is the use of considerable excess of oxidizing reagents and, as a consequence, a lot of hazardous Pb-, Se-, and Cr-containing waste. This fact stimulated the development of catalytic methods for the allylic oxidation of olefins,[2] among which a special role belongs to the methods of heterogeneous catalytic oxidation using aluminosilicates[3] or aluminophosphates[4] modified by transition metals as catalysts.

Among a wide series of natural and synthetic aluminosilicates, minerals of the smectite group, including montmorillonite, are of highest interest for researchers due to their accessibility, low cost, and a possibility of purposeful control of the chemical properties and porous structure of these minerals by the intercalation into the interlayer space of ions or polynuclear metal hydroxocomplexes and other modifying agents.

As a rule, the catalytic properties of aluminosilicates are based on the Lewis and Brönsted acidic sites. Natural Na-montomorillonite is rarely used as a catalyst for transformations of organic substrates because of its low thermal stability and fairly low catalytic activity. The catalytic activity and sorption properties of montmorillonite can substantially be enhanced by its activation with mineral acids. Such a treatment removes octahedrally coordinated ions (Al, Fe) and isomorphously substituted tetrahedrally coordinated ions from the montmorillonite structure[5] and, as a consequence, increases the number of acidic sites. Another method for the modification of layered aluminosilicates is the exchange of interlayer cations for cations of other metals, which increases the total number of acidic sites and also changes the ratio of the Lewis and Brönsted sites. Acid-activated and M^{n+}-modified montmorillonites have been used successfully as catalysts in olefin isomerization[6] and dimerization,[7] addition of water, halogen chlorides, alcohols, and thiols at the double bond of olefins,[8] acylation[9] and alkylation[10] of alcohols, hydrolysis of acetals and ketals,[11] rearrangements of alkylphenyl esters,[12] Diels—Alder[13] and Friedel—Krafts[14] reactions, *etc.* As a rule, the conversion and selectivity of the processes are much lower in the presence of mineral or Lewis acids.

One more method for the modification of layered aluminosilicates, in particular, montmorillonite, is the substitution of interlayer cations for metal polyhydroxocomplexes. Intercalated polyhydroxocomplexes undergo complete or partial dehydroxylation upon the thermal treatment, resulting in the formation of stable clusters of metal oxides in the interlayer space. They act as supports ("pillars") that fix aluminosilicate layers at certain distances. This favors a considerable increase in the thermal stability of the modified mineral and also provides possibilities for its use as a catalyst for transformations of large molecules. Thus modified layered aluminosilicates are named "pillar-clays." [15—17] Pillaring of aluminosilicates creates microporous structures and results in the formation of additional acidic sites and an increase in the sur-

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face area in both aluminosilicate layers of the initial clay and due to modifying agents themselves.[18]

In addition to reactions typical of montmorillonite, which are caused by the presence of acidic sites,[19] a possibility of oxidative transformations of organic substrates was shown for this type of zeolite-like materials. For instance, Cr-"pillared" montmorillonte exhibits high catalytic activity in the oxidation of alcohols to carbonyl compounds,[20] benzylic oxidation of alkylbenzenes,[21] and allylic oxidation of olefins.[3]

In modified aluminosilicates, layers can be arranged according to two variants: (1) regular structures packed in parallel and forming micropores and (2) chaotically arranged short "wreckage" of layers forming mesopores (so-called delaminated aluminosilicates with the "house of cards" structure).[22,23] The latter manifest higher adsorption ability and catalytic activity compared to the modified aluminosilicates with the structure packed in parallel. However, the formation of these structures requires special conditions of synthesis. We believe that the use of mechanochemical activation would be efficient for the preparation of modified aluminosilicates with the "house of cards" structure.

In the present work, we considered structural features of Fe-pillared montmorillonite Fe-PILC and its mechanochemically activated analog Fe-PILC/MA and studied their catalytic properties in the allylic oxidation of model α-pinene (**1**) with *tert*-butyl hydroperoxide.

Experimental

(1*R*)-(+)-α-Pinene was purchased from Aldrich. *tert*-Butyl hydroperoxide was synthesized by a known procedure.[24] Alumina (TU 6-09-3916-75) and silica gel KSK with a particle size of 0.070—0.140 mm were used to prepare Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2. Methylene chloride was distilled above P_2O_5.

Reaction mixtures were analyzed by GC-MS on a Hewlett Packard G1081A instrument consisting of an HP 5890 (series II) gas chromatograph and an HP MSD 5971 mass-selective detector (energy of ionizing electrons 70 eV; HP5 column (5% diphenyl + 95% dimethylsiloxane) 30 m × 0.25 mm × 0.25 μm; helium as carrier gas, 1 mL min^{-1}; temperature-programming for the columns: 2 min at 50 °C, heating rate 10 °C min^{-1}, 5 min at 280 °C; temperature of the ion source 173 °C; data were collected with a rate of 1.2 scan s^{-1} in a mass region of 30—650 amu). Reaction products were identified by comparison of the mass spectra and retention times with the corresponding parameters of reference compounds. The contents of components in the mixture were calculated from the surface areas of the peaks ignoring correction coefficients.

Natural Na-montmorillonite (monomineral fraction, Taganskoe deposit, Kazakhstan) was used. The chemical composition of Na-montmorillonite (in weight fractions) is as follows: SiO_2, 66.0%; Al_2O_3, 24.9%; MgO, 3.5%; Na_2O, 1.8%; Fe_2O_3, 0.9%; CaO, 0.7%; K, Ti, and Mn oxides, 2.2%. Both standard montmorillonite (samples of Fe-PILC) and montmorillonite mechanochemically activated (MA) in a planetary mill for 15 min (Fe-PILC/MA samples) were used for the preparation of catalyst samples.

A complex of physicochemical methods was used to characterize montmorillonite and samples of the montmorillonite-based catalyst: X-ray diffraction analysis, DTA, ^{27}Al NMR spectroscopy, IR spectroscopy, electron microscopy (EM), chemical analysis, and specific surface (S_{sp}) measurement.

X-ray diffraction studies were carried out on a DRON diffractometer using monochromatic Cu-Kα radiation; DTA was conducted on a Q-1500 D derivatograph with a heating rate of 10 °C min^{-1}. ^{27}Al NMR spectra with sample rotation at a magic angle were recorded on a Bruker MSL-400 impulse spectrometer (rotation frequency of the sample 104.2 MHz), and chemical shifts were measured relatively to the $Al(H_2O)_6{}^{3+}$ aquacomplex as external standard, the measurement accuracy being ±2 ppm. IR spectra were obtained on a BOMEM MB-102 FTIR spectrometer in a range of 250—4000 cm^{-1}, and samples (1.5 mg) were prepared by molding with KBr (700 mg). EM studies were performed on a JEM-2010 electron microscope with a working point resolution of 0.19 nm. Chemical analyses of samples were carried out by atomic adsorption spectrometry on an AAS-3 spectrometer.

Synthesis of Fe-pillared montmorillonite. A hydrolyzed aqueous solution of $FeCl_3$ ($OH^-/Fe^{3+} = 2$) was added to a 1% suspension of montmorillonite in water followed by storage for 24 h. The solid phase was separated from the solution, washed, dried in air at 110 °C, and calcined for 4 h at 500 °C.

Samples of Fe-PILC with an iron weight fractions of 6 and 20% (Fe-PILC$^{(6\%)}$ and Fe-PILC$^{(20\%)}$, respectively) and Fe-PILC/MA with an iron weight fraction of 6% were tested as catalysts for α-pinene oxidation.

Synthesis of Fe_2O_3. A precipitate obtained by the precipitation of a 0.5 *M* solution of $FeCl_3$ (10 mL) with a 1 *M* solution of NaOH (15 mL) was separated from the solution, washed with water to the negative reaction to Cl^- ions, dried at 110 °C, and calcined for 4 h at 500 °C.

Synthesis Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2. A 0.5 *M* solution of $FeCl_3$ (2 mL) was poured to a suspension of Al_2O_3 (1.0 g) in water (10 mL), and a 1 *M* solution of NaOH (3 mL) was added dropwise with stirring. The suspension was stirred for 5 h. The solid phase was separated from the mother liquor, washed with water to the negative reaction to Cl^- ions, dried at 110 °C, and calcined for 4 h at 500 °C. The synthesis of Fe_2O_3/SiO_2 was similar.

Oxidation of α-pinene in the presence of Fe-containing catalysts (general procedure). A catalyst ($3.67 \cdot 10^{-2}$ mmol Fe (2.5 mol.% with respect to α-pinene)), α-pinene (0.2 g, 1.47 mmol), *tert*-butyl hydroperoxide (0.3 mL, 2.99 mmol), and dichloromethane (2 mL) were placed in a flat-bottom 10-mL flask equipped with a reflux condenser and a tube filled with calcium chloride. The reaction mixture was vigorously stirred for 50 or 80 h at 40 °C. The catalyst was filtered off and washed with 4 mL of dichloromethane. The filtrate was analyzed by GC-MS.

Results and Discussion

Let us consider specific features of Fe-pillared montmorillonite samples, depending on the properties of the starting materials, *viz.*, Na-montmorillonite and mechanochemically activated Na-montmorillonite.

According to the EM data, Na-montmorillonite consists of large layered sheets with the thickness to 100 nm. They are dispersed during mechanochemical activation, and the order of layer packing is violated. Mechanochemically activated Na-montmorillonite consists of aggregates from 20 to 500 nm in size, which in turn consist of 10-nm blocks.

According to the X-ray diffraction data, mechanochemical activation distorts bonds between aluminosilicate layers of the mineral, which results in their shift and turn; however, the ordering in the layer is retained as a whole. This is confirmed by the almost complete disappearance of the most intense line d_{001} in the X-ray diffraction patterns (the first basal reflection), which equals 1.425 nm for the starting sample. The intensity decrease and broadening of other lines occur simultaneously (d_{hkl} = 0.447, 0.309, 0.254 nm); however, their set remains the same as that of the starting sample.

The DTA data (Fig. 1) indicate the existence of several endothermic peaks of Na-montmorillonite: at 150 °C (the loss of molecular water is 16.25 wt.%), 540, 680 and 850 °C (the loss of constitution water from the structure is 4.5 wt.%). The DTA curve of the mechanochemically activated sample exhibits virtually smoothened endothermal peaks, and the total weight loss remains almost unchanged compared to the starting sample, being 22 wt.%. Thus, dehydroxylation occurs during mechanochemical activation but water is not removed from the system and remains therein in the molecular form.

A comparison of the IR spectra of the starting and mechanochemically activated Na-montmorillonites (Fig. 2) shows that the activation results in structural changes in the mineral. For instance, the absorption band at 3630 cm^{-1} corresponding to stretching vibrations of the OH groups (2 Al—OH) disappears transforming into a shoulder at 3630 cm^{-1}, the shoulder at 1114 cm^{-1} shifts to 1120 cm^{-1}, and the absorption bands at 842, 795, and 697 cm^{-1} disappear. However, a broad band appears at 705 cm^{-1} and the relative intensities and contours of the bands at 524 and 470 cm^{-1} change. An analysis of the IR spectra indicates disordering of the structure of mechanochemically activated montmorillonite related to the cleavage of the Al—O bonds and, possibly, Si—O—Al bonds (see Ref. 25).

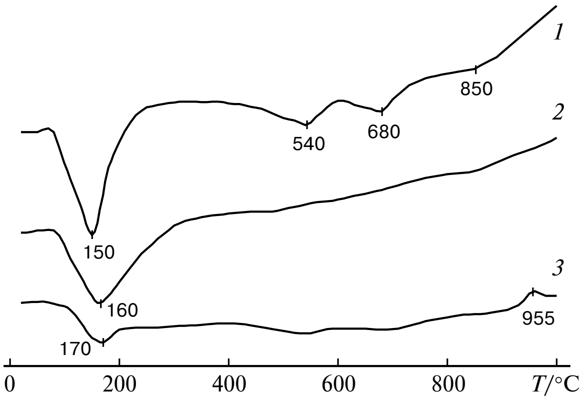


Fig. 1. DTA curves of air-dried Na-montmorillonite (*1*), mechanochemically activated Na-montmorillonite (*2*), and Fe-pillared montmorillonite (*3*).

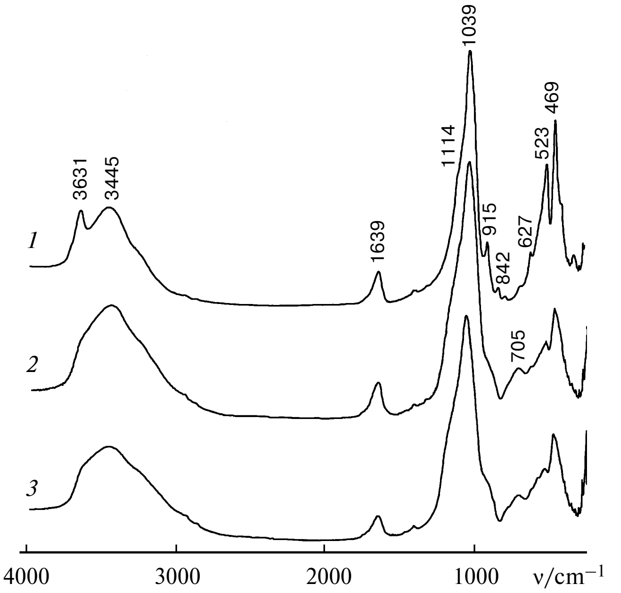


Fig. 2. IR spectra of Na-montmorillonite (*1*), mechanochemically activated Na-montmorillonite (*2*), and Fe-pillared mechanochemically activated montmorillonite (*3*).

The decrease in symmetry of the environment of Al is indicated by the ^{27}Al NMR spectroscopic data. In Na-montmorillonite, Al exists predominantly in octahedral positions of AlO_6 (δ 4). A specific feature of mechanochemically activated Na-montmorillonite, whose NMR spectrum is presented in Fig. 3, is the presence of pentacoordinated aluminum in its structure (δ ~30) along with the tetra- and hexacoordinated (δ 51 and 4, respectively) aluminum atoms. According to the estimates, the content of pentacoordinated Al can be at most 15%, and if the considerable quadrupole broadening of the ^{27}Al line in the AlO_4 tetrahedra is taken into account, its content decreases to ~5%.

Considering the aforesaid, we can assert that the mechanochemical activation of Na-montmorillonite is accompanied by the disordering of its structure: the interlayer bonds are violated and distortions occur in the structure of the aluminosilicate layers but the two-dimensional ordering in the layer is retained as a whole, *i.e.*, montmorillonite with the delaminated structure of the "house of cards" type is formed.[23]

The intercalation of polynuclear iron(III) hydroxocomplexes (PHC) into Na-montmorillonite results in

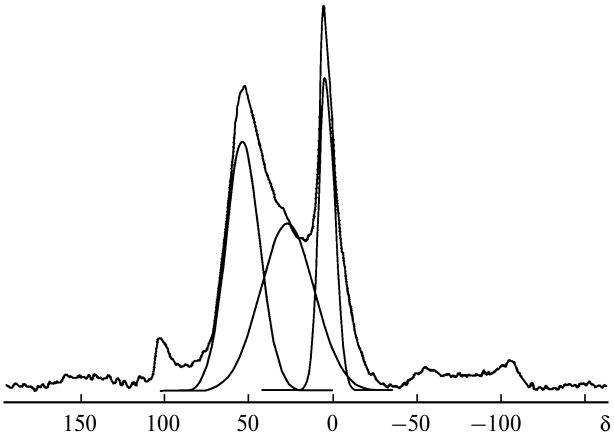


Fig. 3. ^{27}Al NMR spectra of mechanochemically activated Na-montmorillonite with spectral line resolution into components corresponding to tetra- (δ 51), penta- (δ ~30), and hexacoordinated (δ 4) aluminum.

some disordering of the montmorillonite structure: the lines in the X-ray diffraction patterns of the air-dried sample (especially d_{001}) are broadened but the set of lines corresponds to the starting montmorillonite. It should be mentioned that the line with d_{hkl} = 0.254 nm becomes more intense with the total decrease in intensities. The data of complex thermal analysis (see Fig. 1, curve *3*) also show that the introduction of the Fe^{III} PHC into Na-montmorillonite results in structural disordering of the system, which follows from the considerable smoothening of the endothermic peaks, disappearance of the endotherm at 850 °C, and appearance of an exotherm at 955 °C corresponding, most likely, to the formation of high-temperature oxide phases.

After the thermal treatment at 500 °C, the lines in the X-ray diffraction pattern of Fe-pillared montmorillonite (Fe-PILC$^{(20\%)}$) become more distinct. A line with d_{hkl} = 0.272 nm appears in addition to the lines corresponding to Fe-pillared montmorillonite (d_{hkl} = 1.53, 0.444, 0.316, and 0.251 nm). It is known that the lines with d_{104} = 0.2701 nm and d_{110} = 0.2519 nm are the most intense in the set of lines for hematite α-Fe$_2$O$_3$. The incorporation of the Fe^{III} PHC into the interlayer space of the aluminosilicate is confirmed by the fact that the thermal treatment at 500 °C of the starting montmorillonite results in a decrease in the first basal reflection d_{001} from 1.425 to 0.955 nm, while for Fe-pillared montmorillonite d_{001} remains virtually unchanged and equal to 1.53 nm.

Thus, we can speak about the formation of "pillars" of Fe^{III} oxide in the interlayer space of montmorillonite and layer-pillared structure formation. An increase in S_{sp} from 47 m^2 g^{-1} (Na-montmorillonite) to 144 m^2 g^{-1} (Fe-PILC$^{(20\%)}$) indicates the formation of parallel slit-like micropores.**23**

Under the same synthesis conditions, a considerably less amount of the Fe^{III} PHC can be introduced into mechanochemically activated Na-montmorillonite than into the starting Na-montmorillonite (6 and 20 wt.%, respectively). Evidently, this is related to a considerable disordering of the montmorillonite structure during the activation. According to the X-ray diffraction data, a Fe-PILC/MA sample is poorly crystallized, and weakly intense lines are presented in the X-ray diffraction patterns. As a whole, the X-ray diffraction patterns of Fe-PILC/MA do not virtually differ from the those of mechanochemically activated Na-montmorillonite.

According to the IR spectroscopic data, the intercalation of the Fe^{III} PHC into mechanochemically activated montmorillonite does not result in the appearance of new bands or disappearance of already present absorption bands; however, the relative intensities of the latter are redistributed to some extent (see Fig. 2). The construction of the differential spectrum makes it possible to conclude about the intercalation of Fe into the montmorillonite structure.

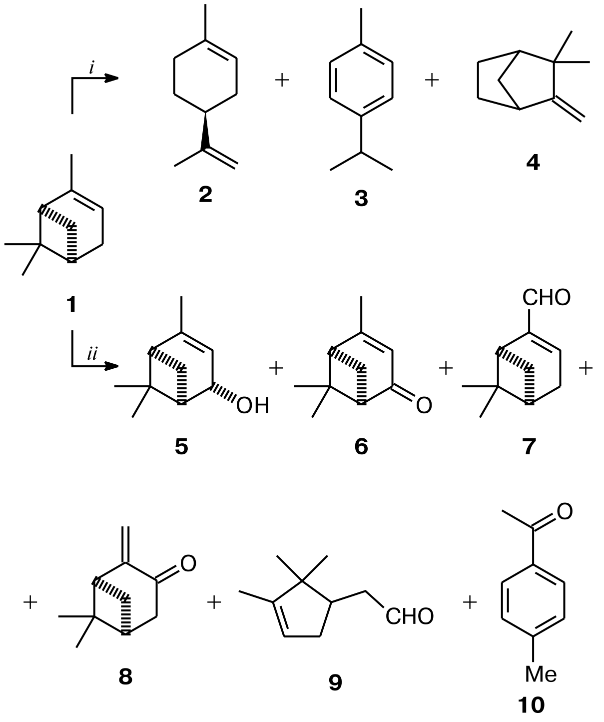
Thus, based on the above data, we can conclude that in the case of Fe-PILC a layer-pillared structure with Fe$_2$O$_3$-pillars and developed micropores is formed, while Fe-PILC/MA is characterized by the "house of cards" structure containing fragments of the layer-pillared structure with Fe$_2$O$_3$-pillars and meso- and macropores.

The catalytic activities of Fe-PILC$^{(6\%)}$, Fe-PILC$^{(20\%)}$, and Fe-PILC/MA$^{(6\%)}$, as well as several other Fe-containing catalysts, were tested in the allylic oxidation of α-pinene (**1**) with *tert*-butyl hydroperoxide (Scheme 1). The experimental results are presented in Table 1.

The catalytic process performed in the presence of Fe-PILC$^{(6\%)}$ is characterized by the high conversion of the starting substrate **1**; however, the products of its allylic oxidation are absent in the mixture of the reaction products (see Table 1, entry *1*). When this catalyst is used, the main components of the reaction mixture are limonene (**2**) (a product of α-isomerization) and *p*-cymene (**3**) (an oxidative dehydrogenation product). In addition, the mixture contains camphene (**4**) and products of α-pinene fragmentation. A similar result was obtained for the use of the catalyst with a higher iron content: Fe-PILC$^{(20\%)}$ (see Table 1, entry *2*).

On the contrary, when Fe-PILC/MA$^{(6\%)}$ is used as the catalyst, a relatively low conversion of olefin **1** and a high selectivity of the oxidation process are observed (see Table 1, entry *3*). Along with allylic oxidation products **5**—**8**, the mixture contains α-campholene aldehyde (**9**) that appears due to the rearrangement of epoxypinane on the acidic sites of aluminosilicate**26** (no epoxypinane itself was found in the mixture). With an increase in the reaction duration (see Table 1, entry *4*) the conversion of α-pinene increases but the amount of allylic oxidation products does not increase. Among non-identified products, the main fraction belongs to compounds with the molecular weight 164, 166, and 168 corresponding to sub-

Scheme 1



Reagents and conditions: *i*. Fe-PILC, Bu^tO_2H, CH_2Cl_2, 40 °C; *ii*. Fe-PILC/MA, Bu^tO_2H, CH_2Cl_2, 40 °C.

stances with two oxygen-containing functions. In addition, the product of oxidative destructurization, *viz.*, *p*-methylacetophenone (**10**), appears in the reaction mixture.

An increase in the oxidant amount made it possible to achieve the 100% conversion of α-pinene, and the content of verbenone (**6**) in the mixture exceeded 80% according to the GLC data (see Table 1, entry *5*). As for the prolong reaction duration, the mixture contains non-identified products with the molecular weight corresponding to products of deeper oxidation.

Thus, it follows from the obtained experimental data, that the reaction direction (isomerization or oxidation) depends on structural properties of the Fe-pillared montmorillonite used.

A possibility of the oxidation process for catalysis by Fe-pillared montmorillonite is determined, first of all, by accessibility of Fe_2O_3-pillars for substrate molecules. It is most likely that the oxidation occurs on these pillars. This requirement is fulfilled only under conditions of free diffusion of molecules of the substrate and reaction products in the interlayer space of Fe-pillared montmorillonite. If the catalyst pore size caused by both the distance between the aluminosilicate layers and the distance between the Fe_2O_3-pillars is smaller than the kinetic diameter of a diffusing molecule, then free diffusion in the interlayer space is impossible. As a result, the reaction will occur only on sterically accessible acidic sites of the aluminosilicate surface that provide isomerization, disproportionation, and other processes to occur. A similar situation takes place, most likely, when the reaction is performed in the presence of Fe-PILC. Taking into account the predominant formation of limonene, we can say that

Table 1. Results of oxidation of α-pinene (**1**) using Fe-containing catalysts[a]

Entry	Catalyst	*t*/h	Conversion of α-pinene (%)	Composition of reaction products based on reacted α-pinene[b] (%)											
				I				II			III		IV[c]	V[d]	VI
				5	**6**	**7**	**8**	**9**	**3**	**10**	**2**	**4**			
1	Fe-PILC$^{(6\%)}$	50	84.9	—	—	—	—	—	19.4	—	39.9	4.6	6.0	6.8	23.3
2	Fe-PILC$^{(20\%)}$	50	74.2	—	—	—	—	—	11.2	—	36.7	4.9	11.3	19.7	16.2
3	Fe-PILC/MA$^{(6\%)}$	50	53.4	12.4	54.9	—	4.9	7.0	7.7	—	—	—	—	—	13.1
4	Fe-PILC/MA$^{(6\%)}$	80	75.8	7.3	36.9	4.3	—	6.5	4.7	10.0	—	—	—	—	30.3
5[e]	Fe-PILC/MA$^{(6\%)}$	50	100	—	84.2	—	—	—	3.6	—	—	—	—	2.7	9.5
6	Fe_2O_3	80	81.2	12.0	27.5	7.2	3.9	9.0	—	6.2	—	—	—	—	34.2
7	Fe_2O_3/Al_2O_3	80	76.5	21.2	35.0	3.0	2.7	6.3	—	—	—	—	4.2	—	27.6
8	Fe_2O_3/SiO_2	80	63.9	5.6	19.9	3.9	4.1	7.7	6.1	—	—	—	31.4	—	21.3
9[e]	Fe_2O_3	50	100	—	58.6	—	—	—	—	—	—	—	—	25.9	15.5
10	Montmorillonite	50	64.6	—	2.0	—	—	2.3	13.0	9.8	27.0	9.0	9.1	15.0	12.8

[a] Standard conditions for the reaction: catalyst ($3.67 \cdot 10^{-2}$ mmol of Fe), 0.2 g (1.47 mmol) of α-pinene, 0.3 mL (2.98 mmol) of Bu^tO_2H, 2 mL of CH_2Cl_2, argon atmosphere, 40 °C.

[b] I, allylic oxidation products; II, other oxidation products; III, isomerization products; IV, other products; V, fragmentation products; VI, non-identified products (GLC data).

[c] For entries *1*, *2*, and *10*, α-terpineol; for entry *7*, verbenene; for entry *8*, verbenene and menthatrienes.

[d] Toluene, 1-methylcyclohexene, and 1-methyl-4-methylenecyclohexane.

[e] The amount of Bu^tO_2H was increased by 5 times.

the amount of the Brönsted acidic sites prevails over the Lewis sites.[27]

In the case of the catalyst based on Fe-pillared mechanochemically activated montmorillonite, meso- and macropores formed in its structure provide free diffusion of the substrate to the Fe_2O_3-pillars and, therefore, the oxidation process occurs when Fe-PILC/MA is used.

To determine the role of iron oxide composing Fe-pillared montmorillonite in the oxidation process, we carried out a series of experiments using Fe_2O_3 and Fe_2O_3 supported on the surface of alumina and silica gel (Fe_2O_3/Al_2O_3 and Fe_2O_3/SiO_2, respectively) as catalysts. The results of these experiments are presented in Table 1 (entries *6—9*). An analysis of the data obtained for α-pinene oxidation in the presence of these catalysts shows similar behavior of Fe_2O_3, Fe_2O_3/Al_2O_3, Fe_2O_3/SiO_2, and Fe-PILC/MA. This fact can confirm that the catalytic oxidation process on Fe-PILC/MA is based on catalysis by iron oxide particles, which fix clay layers.

In the presence of the initial Na-montmorillonite, the main directions of the reaction are isomerization, fragmentation, and hydration of α-pinene (see Table 1, entry *10*). A similar result was obtained for a sample of Na-montmorillonite calcined for 4 h at 500 °C. The action of high temperatures on montmorillonite results in the removal of interlayer water and irreversible collapse of clay layers induced by this removal. The short interlayer distance (d_{001} = 0.955 nm) prevents organic molecules to insert and, hence, only acidic sites on the surface layers of aluminosilicate remain accessible.

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