Short communication

Effect of structure and acidity of acid modified clay materials on synthesis of octahydro-2H-chromen-4-ol from vanillin and isopulegol

Maria N. Timofeeva [a,b,c,*], Valentina N. Panchenko [a,b], Antonio Gil [d,**], Sergey V. Zakusin [e,f], Victoria V. Krupskaya [e,f], Konstantin P. Volcho [g], Miguel A. Vicente [h]

[a] Boreskov Institute of Catalysis SB RAS, Prospekt Akad. Lavrentieva 5, 630090 Novosibirsk, Russian Federation
[b] Novosibirsk State University, St. Pirogova 2, 630090 Novosibirsk, Russian Federation
[c] Novosibirsk State Technical University, Prospekt K. Marksa 20, 630092 Novosibirsk, Russian Federation
[d] Department of Applied Chemistry, Public University of Navarra, 31006 Pamplona, Spain
[e] Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS, Pr. Staromonetny 35, 119017 Moscow, Russian Federation
[f] Moscow State University, Leninskie Gory 1, 119991 Moscow, Russian Federation
[g] Novosibirsk Institute of Organic Chemistry SB RAS, Prospekt Akad. Lavrentieva 9, 630090 Novosibirsk, Russian Federation
[h] Department of Inorganic Chemistry, University of Salamanca, Salamanca, Spain

ABSTRACT

The Prins cyclization of $(-)$-isopulegol with vanillin to form octahydro-2H-chromen-4-ol was studied in the presence of natural layered aluminosilicates modified by 0.5 mol/dm^3 HCl, such as montmorillonite, kaolin, and metakaolin obtained by the calcination of kaolin at 650 °C. According to infrared spectroscopy using pyridine as probe molecule, the amount and strength of Brønsted acid sites depend on the type of clay and decrease in the following order HCl-montmorillonite > HCl-kaolin > HCl-metakaolin. The difference in Brønsted acidity and textural properties of clays affected the reaction rate and the selectivity towards octahydro-2H-chromen-4-ol.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The acid catalyzed Prins cyclization reaction of $(-)$-isopulegol with aldehydes containing electron–donating and electron–withdrawing substituents is widely used for the synthesis of a variety of octahydro-2H-chromen-4-ols which possess biological activity [1,2]. Recently, acid-activated natural clays were suggested as catalysts for such type of reaction. Thus, octahydro-2H-chromen-4-ols with good yields were synthesized from $(-)$-isopulegol and various types of aldehydes in the presence of montmorillonites K10 [3] and KSF [4] modified by H$_2$SO$_4$. In our previous work [5], we also demonstrated the possibility of application of two montmorillonites from beds located in Mukhortala (Buryatia, Russia) and Tagansk (Kazakhstan) modified by 0.125–3.0 mol/dm^3 HCl for the Prins

cyclization of $(-)$-isopulegol (I) with vanillin (II) to form octahydro-2H-chromen-4-ol (III) (Reaction 1).

$$(1)$$
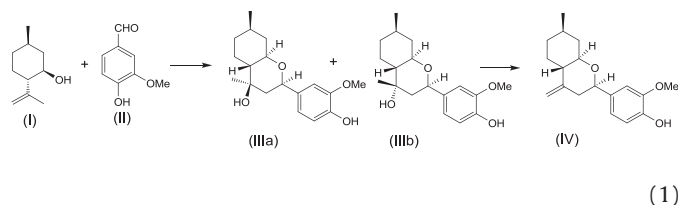
It was found that the textural properties of the acid-activated montmorillonites depended on the HCl concentration. Increasing the HCl concentration led to an increase in microporosity, i.e. the change in the size of the crystallites and the character of their interaction. Moreover, the acid activation led to the change in the chemical composition of montmorillonites that affected the amount of Brønsted acid sites (BAS). The amount of the BAS of montmorillonites samples rose with increasing HCl concentration up to 1.0 mol/dm^3, i.e., up to this HCl concentration, the higher HCl concentration, the larger amount of BAS. The reaction rate rose with the increasing of the amount of BAS.

However, the yield of (III) decreased with the increasing of BAS due to the formation of (IV), produced by dehydration of (III). Therefore, we demonstrated that the amount of BAS and the microporosity of the acid-activated montmorillonites were key factors for the control of the reaction rate and the selectivity towards (III).

In this work, the effects of textural properties and Brønsted acidity on the catalytic performance in Reaction (1) of acid-activated clays with different structures, such as the montmorillonite from Mukhortala (Buryatia, Russia), the kaolin from Kampanovsk (Krasnoyarsk, Russia), and a metakaolin obtained by its calcination are investigated. Special attention will be paid to the relation between the structure of the clays and the distribution of the products of the reaction, particularly the selectivity of isomers IIIa and IIIb.

2. Experimental

2.1. Materials

(−)-Isopulegol and vanillin were purchased from Acros Organic. Tridecane and toluene were purchased from Aldrich. The montmorillonite was a calcium-rich natural sample from the bed located in Mukhortala (Buryatia, Russia, hereafter denoted as M). Kaolin was a natural sample from the bed located in Kampanovsk (Krasnoyarsk, Russia, hereafter denoted K). Metakaolin was prepared by the calcination of kaolin in air at 650 °C for 4 h, and denoted MK. Chemical composition and textural properties of these clays are shown in Table 1.

For the preparation of the acid activated clays, 5 g of M, K or MK was suspended in 150 cm^3 of aqueous solutions of 0.5 mol/dm^3 of HCl and the mixture was stirred at room temperature for 7 days. Then, the solid was separated, washed with water, and dried at room temperature. The designation of the samples and their chemical compositions are presented in Table 1.

2.2. Instrumental measurements

The porous structure of the materials was studied from nitrogen (Air Liquide, 99.999%) adsorption at −196 °C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). All samples (0.2 g) were degassed for 24 h at 200 °C at a pressure lower than 0.133 Pa. The specific surface area (S_{BET}) was calculated from the adsorption data over the relative pressure range between 0.05 and 0.20. The total pore volume (V_Σ) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume (V_μ) and the external specific surface area (S_{ext}) were calculated using the t-plot method, and the pore diameter applying the BJH method.

The chemical analyses of the solids were carried out by means of inductively coupled plasma–atomic emission spectrometry (ICP-AES).

The X-ray diffraction patterns from random samples were collected on a X-ray diffractometer (Ultima-IV, Rigaku), acquired as part of the Moscow State University Development Programe, using Cu-K$_\alpha$ radiation ($\lambda = 1.54056$ Å), rapid detector D/Tex-Ultra, scan range 3.6–65° 2θ, scan speed 5°/min, step 0.02° 2θ, maximum intensity ~25,000 counts.

The Brønsted surface acidity of samples (strength and amount of BAS) was studied by IR spectroscopy using pyridine as probe molecule. The analysis method is described in [5]. IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer in the range between 400 and 6000 cm^{-1} with a resolution of 4 cm^{-1}.

2.3. Catalytic tests

The reaction of vanillin with (−)-isopulegol was carried out at 35 and 50 °C in a glass vial (15 cm^3) equipped with a magnetic stirrer. Before the reaction, all materials were treated at 150 °C for 2 h to remove residual water in the samples. The standard procedure was as follows: 0.65 mmol of vanillin in 4 cm^3 of toluene was added to 100 mg of catalyst and 48 mg (0.26 mmol) of tridecane (internal standard). Then, 0.65 mmol of (−)-isopulegol was introduced into the reactor. At various time intervals, aliquots were taken from the reaction mixture and analyzed after separation by centrifugation of the catalysts. The products were analyzed using a gas chromatograph (Agilent 7820) with a flame ionization detector on a capillary column (HP-5).

Compounds (IIIa–b) and (IV) were isolated using column chromatography. Their structure was confirmed by NMR (Bruker AV-400, CDCl$_3$) and HR-MS (DFS-Thermo-Scientific spectrometer) [5].

3. Results and discussion

3.1. Characterization of acid-treated clays

The chemical composition of the acid-activated montmorillonite, kaolin, and metakaolin is shown in Table 1. As can be seen from these data, acid modification of clays leads to a small increase of the molar ratio Si/Al due to the beginning of the leaching of Al from the framework of the clay. These data are in accord to the results obtained from IR spectroscopy.

Fig. 1 shows the IR spectra of natural and acid-modified clays in the region 500–1800 cm^{-1}. In the region of low wavenumbers in the spectrum of M, there are several characteristic bands of this mineral at 845 cm^{-1} (AlMgOH and ν_s (O–Si–O)), 882 cm^{-1} (AlFeOH), 628 cm^{-1} δ (Si–O), 926 cm^{-1} (a deformation vibration of Al$_2$OH) and a broad band in the region of 950–1250 cm^{-1} (the stretching vibrations of silica–oxygen tetrahedra ν_{as} (Si–O–Si (Al))) [6,7]. The activation of M by 0.5 mol/dm^3 HCl leads to the reduction in the intensity of the bands at 845 and 882 cm^{-1} that can indicate the leaching of Mg^{2+} and Fe^{3+} cations. According to analytical data leaching of Mg^{2+} and Fe^{3+} cations from M was 85.7 and 12.5%, respectively. Moreover the shape of the broad band in the region of 950–1250 cm^{-1}, related to the Si–O–Si (Al) bonds, and the decrease in the intensity of the band at 793 cm^{-1}, assigned to opal CT/A also point the change of the chemical composition of M after acid modification.

In the IR spectrum of kaolin several bands can be revealed at 913, 876, 797, 750, and 699 cm^{-1}, assigned to the Al$_2$OH, AlMgOH, and Si–O–Al vibrations of the clay sheet (Fig. 1) [8–10]. The strong bands in the region of 1000–1120 cm^{-1} can characterize Si–O stretching in untreated kaolinite. After activation of kaolin by 0.5 mol/dm^3 HCl, the band at 786 cm^{-1} disappears, which accords with the leaching of Al

Table 1
Chemical composition and textural properties of montmorillonite (M), kaolin (K), and metakaolin (MK), and these clays modified by 0.5 mol/dm^3 HCl.

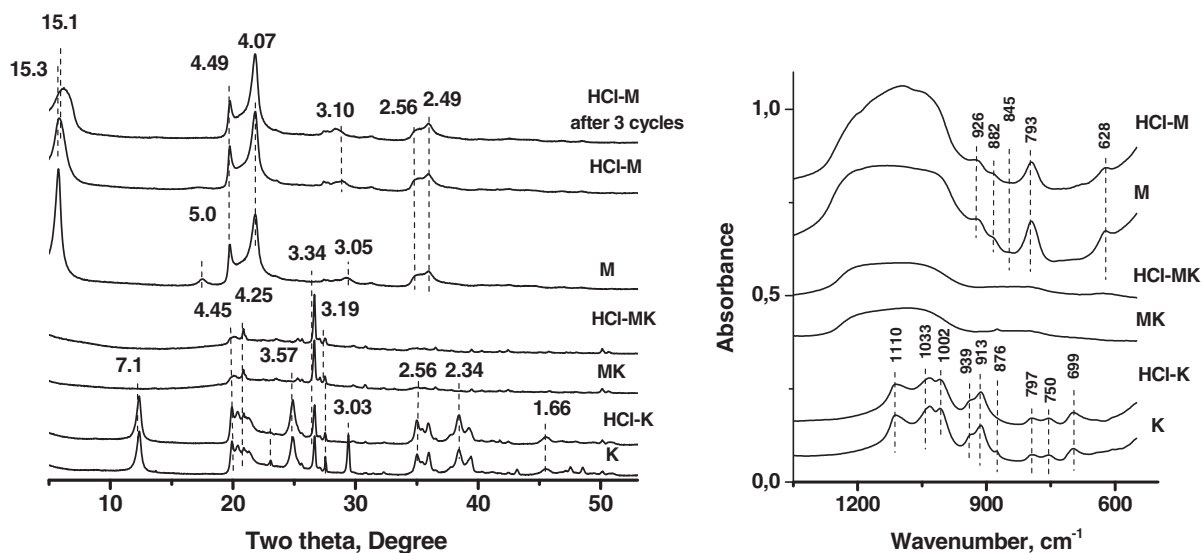|	Chemical composition, (wt.%)				Textural properties						
	Si	Al	Na	Si/Al (mol/mol)	S_{BET} (m^2/g)	S_{ext} (m^2/g)	S_{ext}/S_{BET} (%)	V_Σ (cm^3/g)	V_μ (cm^3/g)	V_μ/V_Σ (%)	d_{pore} (nm)
M	28.5	7.2	0.1	4.0	105	97	92.4	0.224	0.003	1.3	9.0
HCl-M	33.2	8.1	0.1	4.2	111	95	85.6	0.271	0.006	2.2	7.4
K	15.2	17.1	0.02	0.92	19	19	100	0.062	0	0	–
HCl-K	19.1	17.6	0.03	1.13	23	22	95.7	0.092	0	0	–
MK	21.1	18.9	0.04	1.08	17	17	100	0.061	0	0	–
HCl-MK	24.7	19.0	0.05	1.25	30	23	76.7	0.090	0.003	3.3	–

Fig. 1. XRD patterns and IR spectra of natural clays, clays modified by 0.5 mol/dm³ HCl and HCl-MM after 3 catalytic cycles.

from the structure of solid. The intensity of bands in the region of 1000–1120 cm⁻¹ slightly decreases, that also points out the change of the chemical composition of kaolin after acid modification.

The strongly change in the shape of spectrum of kaolin (Fig. 1) after the calcination at 650 °C for 4 h can indicate the degradation of its layer structure. The broad band in the region of 1000–1120 cm⁻¹ and the band at 786 cm⁻¹ remain in the spectrum of metakaolin, but its acid modification leads to the disappearance of the band at 786 cm⁻¹ and to a slight change of the shape of the broad band.

The X-ray diffraction patterns of the samples are shown in Fig. 1. Montmorillonite is a 2:1 hydrous aluminosilicate with the octahedral sheet located between two tetrahedral sheets, with a global negative layer charge balanced by interlayer cations. XRD pattern shows has high intensity for the (001) reflection with a $d_{(001)}$ value of 15.3 Å, a broad diffraction (020) band with a spacing of 4.49 Å, several small basal reflections $d_{(003)}$ at 5.0 Å, $d_{(004)}$ at 3.79 Å, $d_{(005)}$ at 3.05 Å, $d_{(006)}$ at 2.50 Å, the non-basal (060) reflection at 1.49 Å, and a few small non-basal reflections. Basal spacing $d_{(001)}$ of 15.3 Å accords with the predominance of calcium and magnesium cations in the interlayer space of the montmorillonite. Quantitative analysis detects the presence of 30% microcrystalline opal CT/A as interstitial impurity, characterized by the diffraction peaks at 4.07, 3.10, 2.49 Å, and others [11]. A shift of the (001) reflection from 15.3 to 15.1 Å observed during treatment of 0.5 mol/dm³ HCl occurs as a result of the leaching of interlayer cations and the partial protonation of the interlayer space. At the same time, the decrease of the intensity of (001) reflection relative to the intensity of the (020) diffraction effect indicates the decreasing of the structure ordering caused by the partial leaching of the octahedral cations.

Kaolin is an 1:1 hydrous aluminosilicate with interbedded octahedral and tetrahedral sheets and characterized by a neutral structure with interlayer distance of $d_{(001)}$ 7.15 Å (Fig. 1). Natural Kampanovsk kaolin has a good structural ordering with several strong basal reflections $d_{(001)}$ at 7.15 Å, $d_{(002)}$ at 3.59 Å and $d_{(003)}$ at 2.38 Å, and several strong non-basal reflections at 4.45, 4.35, 4.17, 3.85, 2.56, 2.49, 2.34, 2.28, 1.99, 1.69, 1.67, 1.66, 1.62, 1.49 Å, and others. As admixtures, 4% quartz (d = 3.343, 2.458, 2.128, 1.817, 1.541 Å), 6% calcite (3.85, 3.033, 2.093, 1.912, 1.875, 1.603, 1.524 Å, etc.), 3% illite ($d_{(001)}$ 10.0, $d_{(002)}$ 5.0 Å), and a possible 7% illite–smectite mixed-layered mineral (IS MLM) with $d_{(001)}$ 11.0 Å, were detected.

Acid activation of kaolin by 0.5 mol/dm³ HCl leads to the complete disappearance of calcite and IS MLM reflections, indicating the dissolution of these minerals. The absence of visible changes in the kaolin XRD patterns during acid treatment is in accord with the high stability of

kaolin structure in acid conditions, kaolin is very inert under these conditions.

The structure of kaolin is very sensitive to the temperature treatment. Calcination of kaolin at 550–950 °C produces the amorphization of the structure, the phase thus formed is called metakaolin [12]. It has been reported that such transformation occurs with the loss of structural water with a reorganization of the structure; only a small part of AlO_6 octahedra is maintained, the rest are transformed into much more reactive tetra- and penta-coordinated units [13]. In the present case, heating at 650 °C for 4 h leads to an almost complete destruction of the structure, so that XRD patterns reflect amorphous substance by the "halo" in the range of 15–35° 2θ (Fig. 1). A residual presence of diffuse reflections, especially at 7.2, 4.4, and 2.57 Å, indicates that the destruction of the kaolinite structure is incomplete. Calcite and illite (IS MLM) remained in the sample after calcination at 650 °C, but they disappeared after the acid treatment, as observed in the activation of raw kaolin.

The textural properties of the solids are shown in Table 1. Montmorillonite has a relatively large specific surface area value, 105 m²/g, which slightly increases after acid activation, up to 111 m²/g. Montmorillonite is relatively resistant to acid treatments, although its Mg^{2+} cations are easily dissolved, Al^{3+} are dissolved only under strong acid conditions [14]. So, in spite of the long time of treatment, 0.5 mol/dm³ HCl at room temperature causes a slight alteration of the structure of the clay (in fact, the Si/Al only increases from 4.0 to 4.2). The rest of the textural properties also showed slight increases. It may be considered that acid treatment progresses with the dissolution of octahedral cations and the consequent formation of high-surface amorphous silica, but the formation of silica may be negligible under these conditions. So, the most significant effect in the solid should be the change of its original compensating cations by protons.

Raw kaolin has low specific surface area, 19 m²/g, which remains practically constant after calcination to form metakaolin (17 m²/g). After acid treatment, the specific surface area slightly increases. Kaolin is very inert under dilute acid conditions [15], as already shown by previous characterization techniques, so the slight increase in surface area may be due to the cleaning of the surface by elimination of the soluble admixtures, particularly calcite. In the case of MK, the increase in the specific surface area is larger, reaching 30 m²/g, which, besides to the dissolution of calcite, may be ascribed to the dissolution of small amounts of Al^{3+} from the structure. As previously, the amount of silica formed may be negligible. Due to the absence of exchangeable cations in K and MK, only small amounts of protons may be exchanged in the edges of the particles.

3.2. Catalytic properties of clays modified by 0.5 mol/dm³ HCl

Montmorillonite, kaolin and metakaolin modified by 0.5 mol/dm³ HCl were used as catalyst for the Prins cyclization reaction (Reaction 1) of (−)-isopulegol (I) with vanillin (II) to octahydro-2H-chromen-4-ol (isomers IIIa and IIIb). All samples were activated at 150 °C for 2 h for the removal of the water adsorbed onto the solids. Molar ratio of (I)/(II) was 1.0/1.0. The original solids, not treated with HCl, were inactive in this reaction. In the case of acid-treated montmorillonite, the reaction proceeded at 35 °C, reaching a high conversion of (II) (75.8%) after 2 h of reaction. However, in the cases of acid-treated kaolin and metakaolin, the conversion was very low at this temperature, and it was necessary to carry out the reaction at 50 °C to obtain a significant conversion of (II), 23% for both catalysts, for the same time of reaction (Table 2). The conversion of (II) after 2 h of reaction decreases in the following order (Table 2):

HCl-M ≫ HCl-K > HCl-MK.

The main products of the reaction were the isomers (IIIa–b). Selectivity towards (III) decreases in the order (Table 2):

HCl-MK > HCl-K > HCl-M.

The low selectivity towards (III) in the presence of acid-treated montmorillonite is related with the dehydration of isomers (III) to (IV). The differences in conversion of (II) and selectivity towards (III) may be likely related to the differences in the amount and strength of Brønsted acid sites (BAS). According to IR spectroscopy using pyridine as probe molecule, acid modification of the clays led to changes in their surface acidity (Table 2). The amount and strength of BAS depend on the type of clay and decrease in the order:

HCl-M > HCl-K > HCl-MK

that is, the same order observed for the catalytic performance. The evolution of the number of acid sites may be likely related to the incorporation of protons to the solids, being higher in montmorillonite by the substitution of exchangeable cations and by the larger extend of acid activation.

Another reason of the change of the catalytic properties may be the difference in structural and textural properties of natural clays. As the difference in the amount of BAS between HCl-M and HCl-K is small (Table 2), the high activity of HCl-M may b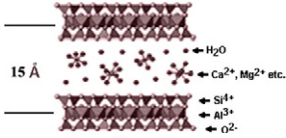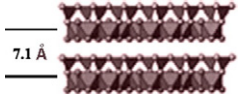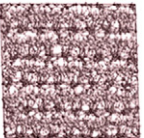e related to the larger specific surface area in HCl-M compared to HCl-K (Table 1). At the same time the difference in activity between HCl-K and HCl-MK is significant in spite of the close specific surface area. This phenomenon is likely related to the difference in the amount of accessible active sites. According to experimental data (Table 1) the acid activation leads to the decrease in the external surface area. The ratio of S_{ext}/S_{BET} for HCl-K is larger compared to that for HCl-MK. Therefore, the accessibility of the active sites in HCl-MK should be lower than that in HCl-K. This assumption is in accord to the difference of the rate constants based on the specific surface area (k_S) (Table 2).

It has been reported that the (IIIa)/(IIIb) molar ratio is related to the acidity, geometry, and textural properties of the HCl-M, as the reaction occurs involving a carbocation, which spatial arrangement may be strongly conditioned by the time that the reactants are close to the acidic active sites [5]. In this sense, it may be considered that montmorillonite and kaolin are layered materials, montmorillonite having larger acidity, surface area, and interlayer distance, which favors the reaction between (I) and (II) in the interlayer region, increasing the conversion, and also influences the arrangement of (III), conditioning the isomer ratio. In the case of metakaolin, its amorphous structure, without interlayer region, low external surface area and, therefore, low accessibility of active sites, seems to decrease the time of contact between the reagents and the active sites. Noteworthy, when reaction proceeds on the surface of amorphous HCl-MR molar ratio of (IIIa/IIIb) is higher than that in the interlayer region. This phenomenon may be related with participation of H_2O molecule in reaction mechanism. At the beginning of reaction, H_2O molecule is generated during the condensation and may be adsorbed on the surface. At the end of the reaction intermediate reacts with this adsorbed water molecule with formation of (III). We can assume that in the case of HCl-MK intermediate can react only with H_2O molecule adsorbed on the surface, while in the case of layer materials intermediate can react both with adsorbed molecule and located into interlayer region. Thus, the properties of the catalysts condition their catalytic performance, leading to very different conversions, and also affect the spatial arrangement and configuration of the intermediates of the reaction, conditioning the final isomer ratio.

Stability of the most active HCl-MM catalyst was investigated by using it in various successive catalytic tests. After each catalytic experiment, the catalyst was separated, washed with toluene, dried at room temperature and used in the next run. According to experimental data, HCl-MM can be used repeatedly without significant loss of catalytic activity during at least three catalytic cycles (Fig. 2), due to the stability of the layer structure of montmorillonite, as confirmed by the XRD analysis of the catalyst after reaction (Fig. 1).

Table 2
Structure and catalytic properties of montmorillonite, kaolin, and metakaolin modified by 0.5 mol/dm³ HCl.

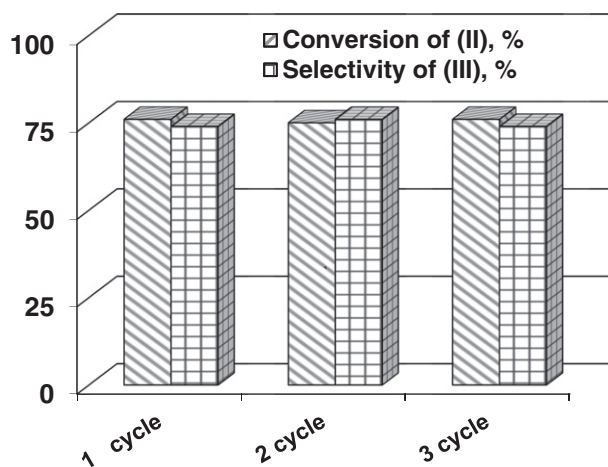|	HCl-M	HCl-K	HCl-MK
Structure			
Acidic properties			
Amount of BAS, μmol/g	14.8	13.5	9.4
Strength of BAS (PA), kJ/mol	1162	1168	1170
Catalytic properties			
Temperature, °C	35	50	50
$k \cdot 10^3$, L/(mol · min)	45.9	14.1	7.9
$k_S \cdot 10^3$, (L · g · m²)/(mol · min)	0.41	0.61	0.26
Conversion of (II), mol.%	75.8	30.2	25.5
Selectivity of (III), mol.%	73.6	76.8	89.8
(IIIa)/(IIIb), mol/mol	5.7	6.2	7.0

Fig. 2. HCl-MM recycling during the Prins cyclization reaction of (−)-isopulegol (I) with vanillin (II) to octahydro-2H-chromen-4-ol. The amount of the reactants was corrected based on reaction conditions.

4. Conclusions

Various clays, such as natural montmorillonite, natural kaolin, and metakaolin obtained by calcination of kaolin at 650 °C for 4 h, were chemically activated using 0.5 mol/dm^3 HCl solutions. Textural and physicochemical properties of these materials were investigated by X-ray diffraction, N$_2$ adsorption/desorption, chemical analysis and FT-IR spectroscopy using pyridine as probe molecule. Physicochemical methods point out that acid activation leads to the beginning of leaching of Al from the solids, which favors the change in textural and acidic properties. According to IR spectroscopy results, the amount and strength of Brønsted acid sites depend on the type of clay and decrease in the order:

HCl-M > HCl-K > HCl-MK.

The effect of the structural properties and Brønsted acidity on the catalytic properties of these acid modified natural clays was investigated in the Prins cyclization of (−)-isopulegol with vanillin to form octahydro-2H-chromen-4-ol. It was found that the reaction rate and the selectivity towards octahydro-2H-chromen-4-ol showed the same trend as indicated above, while the molar ratio between its isomers (IIIa)/(IIIb) followed the opposite trend. This confirms the strong dependence of the catalytic behavior on the textural, acidic and structural properties of the catalysts.

References

[1] O.S. Mikhalchenko, K.P. Volcho, N.F. Salakhutdinov, Synthesis of heterocyclic compounds by interaction of aldehydes with monoterpenoids, in: L. Torrioni, E. Pescasseroli (Eds.), New Developments in Aldehydes Research, Nova Science Publishers, New York 2013, pp. 49–80.
[2] N.M. Nasir, K. Ermanis, P.A. Clarke, Org. Biomol. Chem. 12 (2014) 3323–3335.
[3] G. Baishya, B. Sarmah, N. Hazarika, Synlett 24 (2013) 1137–1141.
[4] J.S. Yadav, B.V. Subba Reddy, A.V. Ganesh, G.G.K.S. Narayana Kumar, Tetrahedron Lett. 51 (2010) 2963–2966.
[5] M.N. Timofeeva, K.P. Volcho, O.S. Mikhalchenko, V.N. Panchenko, V.V. Krupskaya, S.V. Tsybulya, A. Gil, M.A. Vicente, N.F. Salakhutdinov, Synthesis of octahydro-2H-chromen-4-ol from vanillin and isopulegol over acid modified montmorillonite clays: effect of acidity on the Prins cyclization, J. Mol. Catal. A Chem. 398 (2015) 26–34.
[6] J.D. Russell, A.R. Fraser, in: M.J. Wilson (Ed.), Clay Mineralogy: Spectroscopic and Chemical Determinative Methods, Chapman &Hall, London 1996, pp. 11–67.
[7] V.C. Farmer, in: H.V. Olphen, J.J. Fripiat (Eds.),Data Handbook for Clay Materials and Other Non-metallic Minerals 1999, pp. 285–337.
[8] S. Kumar, A.K. Panda, R.K. Singh, Preparation and Characterization of Acids and Alkali Treated Kaolin Clay, Bull. Chem. React. Eng. Catal. 8 (2013) 61–69.
[9] H. Suquet, Effects of dry grinding and leaching on the crystal structure of chrysotile, Clay Clay Miner. 37 (1989) 439–445.
[10] G. Jozefaciuk, D.M. Sarzynska, Effect of acid treatment and alkali treatment on nanopore properties of selected minerals, Clay Clay Miner. 54 (2006) 220–229.
[11] B.Y. Lynne, K.A. Campbell, N. Z. J. Sediment. Res. 74 (2004) 561–579.
[12] R.C. Mackenzie, Differential Thermal Analysis, vols. I and II, Academic Press, London, 1970.
[13] J.F. Lambert, W.S. Minman, J.J. Fripiat, Revisiting kaolinite dehydroxylation: a silicon-29 and aluminum-27 MAS NMR study, J. Am. Chem. Soc. 111 (1989) 3517–3522.
[14] C. Pesquera, F. Gonzalez, I. Benito, C. Blanco, S. Mendioroz, J.A. Pajares, Passivation of a montmorillonite by the silica created during acid activation, J. Mater. Chem. 2 (1992) 907–911.
[15] C. Belver, M.A. Bañares Muñoz, M.A. Vicente, Chemical activation of a kaolinite under acid and alkaline conditions, Chem. Mater. 14 (2002) 2033–2043.