

Isomerisation of α -pinene using modified montmorillonite clays

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Abstract

Liquid phase catalytic isomerisation of α -pinene with natural Indian Montmorillonite modified by sulphuric acid treatment and cation exchange was studied. More than 96% α -pinene conversion is observed for acid treated clays with camphene selectivity ranging from 39 to 49%. For acid treated clays prepared by treating with low normality acid (1–4N), limonene is the main product whereas clay samples prepared with high normality (5–9N) acid, α -terpinene is a main product among monocyclic terpenes. Ce^{3+} , Fe^{3+} , La^{3+} , Ag^+ , exchanged clays showed higher than 90% conversion for α -pinene with 39–49% selectivity for camphene. However, Li^+ , Ca^{2+} , Mg^{2+} exchanged clay showed poor conversion (4–12%) for α -pinene. Observed conversions and selectivities have been explained in terms of surface acidity, structural and textural features of the modified clays determined by using X-ray diffraction and N_2 adsorption at 77 K. Correlation of α -pinene conversion with cyclohexanol dehydration showed that α -pinene conversion is a Bronsted acid catalyzed reaction.

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1. Introduction

Monoterpenes like α -pinene are economically important compounds that are widely used in pharmaceuticals, cosmetics, flavor and fragrance industries. α -Pinene, one of the important monoterpene is present to the extent of 85% in essential oils like pine oil, turpentine oil. α -Pinene is highly acid sensitive and undergoes isomerisation reaction due to the formation of a carbocation, which rearranges through two routes, one leading to bicyclic and tricyclic products and another to opening of bicyclic ring to monocyclic products. Some of the isomerised products are industrially valuable chemicals. For example, camphene is used as an intermediate in camphor synthesis, which finds use in fragrance and pharmaceuticals industry. Therefore, it is desired to maximize selective isomerisation of α -pinene to such desired isomers.

Solid acids like clays and zeolites due to their unique characteristics namely tunable surface acidity, shape selectivity and eco-friendly nature have potential to be tailor-made for selective isomerisation of α -pinene to a desired compound.

As a result, efforts are being directed and varieties of solid acids have been studied for α -pinene isomerisation. For example, Yamamoto et al. [1] studied α -pinene isomerisation using mesoporous silicious, FSM-16 and have shown maximum conversion of 77.8% with 41% selectivity for camphene and limonene each, when FSM-16 is pretreated at 673 K. Silica supported rare earth oxides have also been studied for isomerisation of α -pinene [2]. The conversion was observed to be dependent on the nature of the rare earth metal loaded on silica. La, Pr, Yb and Y were observed to show 15–30% conversion at 323–353 K with 50–70% selectivity towards limonene. Selectivity for camphene was observed to be 17–21% only. It is interesting to note that both the above studies were primarily carried out to characterize acid–basic characteristics of the solids using α -pinene isomerisation. Lopez et al. [3] have studied isomerisation of α -pinene with microporous zeolites, mordenite and Y in liquid phase at 120 °C. Limonene and camphene were reported to be the main products with mordenite giving the maximum yield of 68% for limonene and camphene with selectivity higher than 54%. From their study, it is also shown that solids with wider pore diameters yield undesired products. The comparative study of α -pinene isomerisation over dealuminated Y, mordenite and SAPO-5 in gas and liquid phase showed that liquid phase reaction leads to higher selectivity (30–42%) towards camphene whereas in

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gas phase the selectivity for camphene was 27–33% only. Furthermore, deactivation of the catalyst was also found to be higher in gas phase reaction. Cruz Costa et al. [4] studied α -pinene isomerisation in both gas and liquid phase using Zr and Sn phosphates. The reaction showed both ionic and radical rearrangement as seen from α -pyronene and limonene formed during this reaction. Findik and Gunduz [5] studied liquid phase isomerisation of α -pinene with clays, activated carbon, Halloysite, TiO₂ and natural zeolite, clinoptilolite at 155 °C and reported selectivity towards camphene up to 43%. α -Pinene conversion was shown to be first order reaction with respect to camphene and limonene. From kinetic study on clinoptilolite it was shown [6] that, initially camphene and limonene were main products and only at relatively high conversions, other secondary products were formed. Stefanis et al. [7] has compared α -pinene isomerisation using mesoporous alumina-pillared clays, tin phosphate and mid pore zeolite USY, ZSM, H-mordenite. The study showed that in pillared clays, the reaction of α -pinene essentially depends on pore acidities rather than diffusion of molecules in channels. They have rationalized the product formed with zeolites in terms of carbocation intermediate cascade. Severino et al. [8] used TiO₂ based catalysts to study the influence of preparation variables and to determine the reaction kinetics, they also studied α -pinene conversion with zeolite to correlate with amount of extra lattice aluminium. Volzone et al. [9] has reported 50% conversion of α -pinene at 100 °C with selectivity of camphene and limonene as 52–54 and 32–46%, respectively, using Argentine montmorillonite and US Saponite. Catalytic activity was correlated with textural properties and surface acidity of clays. Grzona et al. [10] studied the effect of Bronsted acidity of the sulphated zirconia on isomerisation of α -pinene. Tetragonal zirconium oxide was shown to be catalytically active for α -pinene isomerisation while monoclinic ZrO₂ showed no activity. The catalyst concentration of 1% was reported to be the optimum for obtaining high activity while keeping the selectivity towards camphene.

Montmorillonite clay after modification has been shown to possess catalytic activity for carbonium ion based organic transformations [11]. Two most widely used techniques for

modification of these clays for controlling surface acidity and texture include acid activation with mineral acid [12] and exchange of the non-framework cations present in the clay interlayer space. In the present paper, we have studied the modification of Indian natural montmorillonite both by acid treatment and cation exchange with variety of cations with an objective to determine their activity for α -pinene conversion and selectivity towards monocyclic or bicyclic compounds. Other clays namely Kaolin, Saponite, Hectorite, Attapulgite were also studied for comparison.

2. Experimental

2.1. Material

Montmorillonite clay used was from Barmer, Rajasthan, India having chemical composition as given in Table 1. Chemical composition of clay was determined using volumetric and gravimetric techniques by previously reported methods [13]. α -Pinene was purchased from Aldrich and all other chemicals used were AR grade. Hectorite, Kaolins both poorly and well crystalline, Attapulgite, Saponite and Ca-montmorillonite were procured from Clay Mineral Society, Source Clay Mineral Repository, University of Missouri, Columbia, USA and were used as such.

2.2. Preparation of catalyst

2.2.1. Acid treated clays

Natural bentonite was up-graded prior to acid treatment by sedimentation taking 1:100 ratio of clay and de-ionized water. Slurry prepared thus was stirred overnight and then allowed to sediment for 8 h. Slurry was then decanted and dried under sunlight. The impurities like silica, grit were removed as a solid residue. Thus dried clay was designated as N₀ and was taken for digestion with sulphuric acid of varied concentration from 1 to 9N at 80 °C under reflux for two hours. Typically, 5 g of clay was taken in 100 ml of acid solution. The acid treated clay was washed thoroughly with distilled water till absence of SO₄²⁻ as tested by BaCl₂ solution followed by drying in an oven at 110 °C. Clays were

Table 1
Chemical composition of acid treated clays (wt.%)

Sample	SiO ₂	R ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
N ₀	56.00	31.00	23.31	7.63	0.058	6.00	3.00	2.06	1.08
N ₁	60.00	29.00	20.84	8.10	0.063	4.72	3.20	1.94	0.98
N ₂	62.00	27.87	20.68	7.13	0.064	4.50	3.02	1.90	0.96
N ₃	65.00	26.49	19.34	7.09	0.059	4.24	2.82	1.86	0.90
N ₄	66.50	26.58	19.58	6.95	0.054	3.84	1.92	1.80	0.82
N ₅	68.00	25.08	18.34	6.68	0.059	3.52	1.84	1.82	0.64
N ₆	69.09	24.56	17.91	6.60	0.054	3.24	1.60	1.62	0.58
N ₇	70.65	22.92	16.51	6.35	0.058	2.98	1.48	1.22	0.44
N ₈	71.12	22.79	16.62	6.12	0.048	2.08	1.02	1.10	0.32
N ₉	72.68	22.24	16.20	5.89	0.056	1.65	0.82	0.84	–

Table 2
Surface area, cation-exchange capacity and surface acidity of acid treated clays

Clay	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)	CEC (meq/100 g)	Acidity by NaOH (meq/100 g)
N ₀	102	0.13	45	82.6	6.7
N ₁	133	0.16	51	56.5	85.4
N ₂	176	0.18	40	70.7	90.3
N ₃	201	0.19	35	79.1	79.4
N ₄	208	0.20	37	70.4	96.8
N ₅	214	0.21	42	98.9	86.5
N ₆	229	0.23	43	70.2	83.7
N ₇	215	0.22	44	65.0	82.7
N ₈	264	0.27	42	59.5	81.8
N ₉	236	0.28	46	59.5	80.8

designated as N₁–N₉ with subscript denoting the normality of H₂SO₄ taken for acid digestion.

Acidity of acid treated clays was measured by taking 0.5 g clay kept in dry air oven at 120 °C for 6 h. Thus dried clay was treated with 15 ml of 0.1N aqueous solution of NaOH with stirring for 15 min. This slurry was titrated with 0.1N H₂SO₄ using phenolphthalein indicator. Clay acidity was determined in terms of meq of NaOH/100 g of clay. All the physicochemical characteristics of acid treated clays are given in Table 2.

2.2.2. Cation-exchanged clays

For the preparation of cation-exchanged clays, the slurry of up-graded clay, N₀, was passed through H-SBA cation-exchange resin to get H⁺ clay. H⁺ clay was used for further cation exchange by taking in ratio of 1:20 clay and 0.1 M solution of chloride or nitrate of the cation to be exchanged, followed by heating at 80 °C under stirring conditions for 2 h and then filtered, washed with distilled water until removal of Cl⁻/NO₃⁻ anions. LiCl, MgCl₂, CaCl₂, FeCl₃, AgNO₃, CeCl₃ were taken as a source of cation. For La³⁺, La₂O₃ was taken and it was dissolved in minimum amount of HCl and then the solution was diluted with water. Extent of cation exchange in clay was determined from the analysis of the solution taken for exchange before and after cation exchange and data for cations studied are given in Table 3.

Table 3
Physical characteristics of cation-exchanged clays

Clay	Percentage cation exchange (meq/g)	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
N ₀	–	112	0.13	45
H ⁺	–	102	0.12	46
Li ⁺	49	111	0.13	47
Mg ²⁺	43	117	0.13	46
Ca ²⁺	54	109	0.13	46
Fe ³⁺	29	127	0.15	48
Ag ⁺	108	110	0.15	44
La ³⁺	61	126	0.14	44
Ce ³⁺	41	124	0.14	47

2.3. Characterization of clays

Structural analysis of natural and modified clays was done by X-ray diffraction using Philips X'PERT MPD diffractometer with Cu Kα1 (λ = 1.5405 Å) as a radiation source in 2θ range from 2 to 70.

Surface area, pore volume and pore size distribution volume were determined from the analysis of N₂ adsorption data measured at 77 K using Micromeritics ASAP 2010 surface area analyzer employing BET and BJH equations [14].

Surface acidity of cation-exchanged clays was measured using a dehydration reaction of cyclohexanol to cyclohexene.

2.4. Catalytic activity for α-pinene isomerisation

Typically, 0.1 g of the catalyst and 2 ml of α-pinene was taken in a 50 ml single neck round bottom flask for the reaction without taking any solvent. Reaction mixtures were heated at 150 °C under reflux condition with stirring for 2 h. Magnetic stirring was done for efficient contact with reactant to the catalyst. Precautions were taken to maintain the temperature and to check the vapor loss of the products. All catalysts were activated at 120 °C for 2 h before using in isomerisation reaction.

For cyclohexanol dehydration, 0.1 g of the catalyst in 2 ml of cyclohexanol with 1 g of molecular sieve 4 A was taken in a 50 ml two neck round bottom flask. Reactions were conducted at 150 °C under stirring for 9 h. All catalysts were activated at 120 °C for 2 h and molecular sieve 4 A was activated at 450 °C for 4 h before using in reaction. Molecular sieve 4 A was used for in situ adsorption of water generated during dehydration of cyclohexanol.

The reaction products were analyzed by gas chromatography (Hewlett-Packard, model 6890) equipped with HP-5 capillary column 30 m long and having 0.25 mm internal diameter. Nitrogen was used as a carrier gas (0.5 ml/min) with injection port temperature of 250 °C and column temperature ranging from 40 to 180 °C. Pure α-pinene, camphene, limonene α-terpinene and tricyclene were used for calibration of gas chromatography response.

3. Results and discussion

α -Pinene conversion and selectivities for different products obtained during the liquid phase isomerisation of α -pinene using acid treated clays are given in Table 4. It is observed from the data that mainly bicyclic camphene and monocyclics limonene, α -terpinene and terpinolene are formed on isomerisation. It is further observed from the data (Table 4) that the activity of clay towards α -pinene conversion increases by acid treatment. Clays N₃–N₉ show almost similar conversion values. Natural upgraded clay showed only 34% conversion whereas acid treated samples gave conversion ranging from 84 to 100%. Acidity measured by sodium hydroxide titration also show similar trend. It is seen from the data in Table 2, the surface area of clay substantially increases on acid treatment. It is earlier reported [12] by us that clay structure is retained when natural clay is treated with acid having H₂SO₄ normality up to 2N, beyond which the de-alumination of clay starts with acid affecting octahedral aluminium sheet. Both acidity and surface area of the clay increases [12] with increasing normality of H₂SO₄ with which clay is treated. Therefore, the increase in α -pinene conversion for clays N₃–N₉ is attributed to combined effect of increased acidity resulting from treatment with high normality sulphuric acid and increase in surface area of the clay.

However, selectivities for bicyclics in case of N₀, N₁ are similar to other clays. For the clays studied, selectivity towards camphene is in the range of 40–49%. Camphene selectivity does not vary significantly with acidity of clays, though, N₈ and N₉ clay samples displays slightly higher values. Among monocyclics, α -terpinene and limonene are the major compounds observed with all the clays. An interesting observation is made from formed monocyclics selectivity data that, for N₀–N₃ clays with lower acidity limonene is

a favoured product. For clays samples N₅–N₉ having higher acidity, α -terpinene is a favoured product. Therefore, increased clay acidity N₆–N₉ also results into higher selectivities for tricyclene.

Earlier from the kinetics studied by Allahverdiev et al. [6], proposed reaction pathway for α -pinene/camphene re-arrangement is shown in Fig. 1. It is proposed that, the reaction takes place following two routes one to bicyclic and tricyclic compounds and another to monocyclic compounds. The nature of products formed observed in Fig. 1 shows that with acid treated clays both routes are followed. In first route, camphene is the major product, wherein with ring expansion of α -pinene, formation of camphene skeletal structure proceeds through initial shift of the gem dimethyl bridge to give cation rather than a shift of methylene bridge to give a precursor of fenchene skeletal structure. This is keeping in with the greater electron donating effect of previous bridge to the latter. Among monocyclic terpenes, limonene and α -terpinene are the major products, other monocyclics are formed in less amount and form by further rearrangement of limonene and α -terpinene. F. Ebmeyer from theoretical studies on the α -pinene/camphene re-arrangement has recently reported [15] that the first step is the protonation of the double bond with the formation of the pinanyl cations 2 and 3 (Fig. 1). However, cation 2 being 13–20 kcal/mol more stable than 3, is the initial cation. Further opening of the four membered ring, results into the formation of isobornyl cation (Fig. 1). However, the formation of *p*-menthenyl cation (Fig. 1) is also energetically as favorable as isobornyl cation as there is very small difference (1.8 kcal/mol) in Gibbs free enthalpy between the two cations. Therefore, *p*-menthenyl cation further results into the formation of monocyclics namely α -terpinene, terpinolene and limonene in proton catalyzed reaction. The isobornyl cation not only reacts to form camphyl cation

Table 4
Conversion and selectivity of the products formed on isomerisation of α -pinene using acid treated clays^a

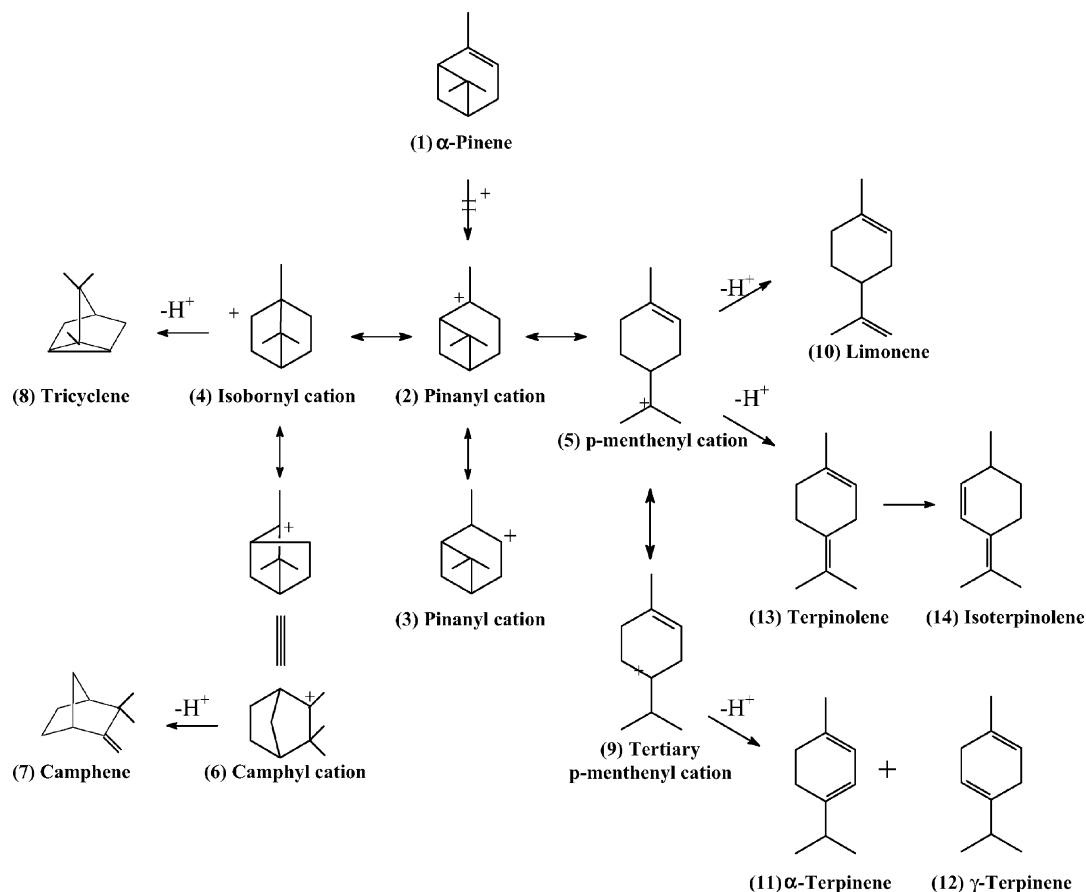
Catalyst	Conversion (%)	Selectivity (%)				
		Camphene	Tricyclene	α -Terpinene	Limonene	Others
N ₀	34	40	3	10	15	32
N ₁	85	49	5	6	17	23
N ₂	98	43	10	12	16	19
N ₃	99	46	10	6	20	18
N ₃ /120 ^b	73	39	4	19	19	19
N ₄	98	46	8	6	17	23
N ₄ /80 ^c	44	30	1	7	30	32
N ₅	96	46	5	19	11	19
N ₆	99	41	10	27	2	20
N ₇	100	45	11	24	3	17
N ₈	99	49	12	21	3	15
N ₉	100	47	13	22	3	15
K-10	97	46	12	27	1	14

Others: terpinolene, isoterpinolene, γ -terpinene, etc.

^a Catalyst: 0.1 g, α -pinene: 2 ml, reaction temperature: 150 °C, reaction time: 2 h.

^b Reaction temperature: 120 °C.

^c Reaction temperature: 80 °C.

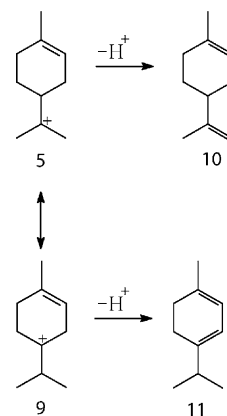
Fig. 1. Reaction pathway of α -pinene isomerisation.

via 1,2-sigmatropic rearrangement but also could give bornylene and α -fenchene as the by-products. But, bornylene being strained molecule due to the endocyclic double bond is shown [15] to be less stable (by 5.2 kcal/mol) than camphene. α -Fenchene possesses the Gibbs free energy (-390.470194 kcal/mol), which is very close to that of camphene (-390.47123 kcal/mol). However, it is formed only in trace quantity mainly due to high activation energy related to the 1,2-shift of the exomethyl group required during its formation from isobornyl cation. Therefore, camphene and monocyclics α -terpinene, terpinolene and limonene are the main products observed during acid catalyzed isomerization of α -pinene. However, if the catalyst is tailor made to possess the environment where an opening of the four membered ring with full stretching of the molecules is not possible, formation of camphene may be maximized.

Furthermore, as seen from Table 4, the formation of limonene is higher for clays having lower surface acidity (up to N_4) whereas formation of α -terpinene is observed to be high with clays having higher surface acidity (N_5 – N_9). Both limonene and α -terpinene result from deprotonation of *p*-menthenyl cation (Fig. 2) in the presence of acid catalyst. As the deprotonation occurring is exocyclic for limonene and endocyclic for α -terpinene, the latter requiring higher

acid strength sites is observed to be more for clays having higher surface acidity (N_4 – N_9).

Temperature influences the conversion significantly as seen for N_3 (120, 150 °C) and N_4 (80, 150 °C) clay samples. Temperature also affects selectivity for bicyclics. At lower temperature, the monocyclic products were dominant and camphene was only 30%. Even in monocyclic, limonene is the major compound at 80 °C in N_4 .

Fig. 2. Reaction pathway of *p*-menthenyl cation.

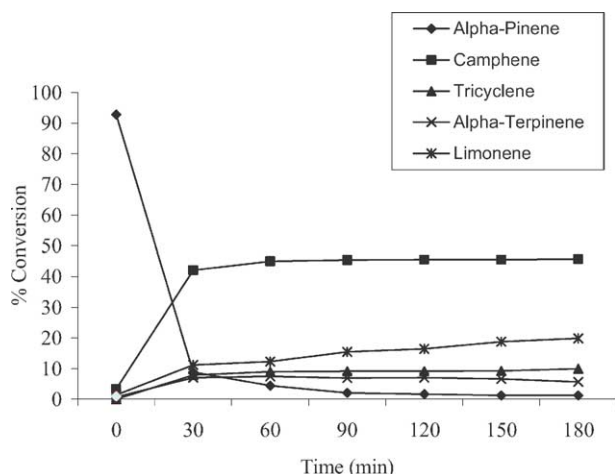
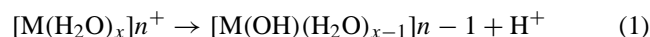


Fig. 3. Variation of percent conversion of products of α -pinene and isomerised products conversion with time for N_3 clay.

Variation of α -pinene conversion with time was studied for N_3 clay and the percentage conversion observed for various products is shown in Fig. 3. It is observed that the α -pinene conversion increases with time, however, after 30 min formation of camphene is nearly constant and formation of tricyclene increases. It seems that initially reaction favours camphene and as the amount of camphene increases, formation of tricyclene increases. Among monocyclics, the amount of limonene increases with time. α -Pinene conversion is complete within an hour. The reaction kinetics with N_1 , N_7 clay catalysts was also observed to be very rapid with α -pinene conversion, respectively, reaching up to 86, and 89% within 15 min and 95, and 97% in 30 min.

The surface acidity of clay is explained in terms of its structure. The structure of montmorillonite clay comprises [16] two tetrahedral silicon layers surrounded by a central octahedral aluminium layer. Substitution of Mg^{2+} for Al^{3+} in octahedral layer and Al^{3+} for Si^{4+} in the tetrahedral layer result in the development of a negative charge in the silicates layer, which is normally neutralised by the hydrated cations present between the sheets. Consequently, clay will have

two types of cations, viz., exchangeable extra lattice cations like Na^+ , Ca^{2+} , etc. and octahedral Al^{3+} , Mg^{2+} and Fe^{3+} cation. The majority of the exchangeable cations Na^+ , K^+ , Ca^{2+} get leached out when treated with acid or exchanged by other cations. Lewis acidity generally arises from exposed Al^{3+} , Fe^{3+} ions at the crystallite edge. Bronsted acidity in clays arises from H^+ ions occupying exchanged sites on the surface or by dissociation of water hydrating the exchangeable metal cations (M) as:



When clay samples are treated with acid, Bronsted sites are generated by the exchange of interlayer cations with protons. The observed enhancement in α -pinene conversion in acid treatment of clay is attributed to increase in surface area and acidity generated as explained above. However, surface acidity in montmorillonite type clays can also be introduced by simple cation exchange into the clay interlayer space without disturbing its structure. Therefore, it was decided to prepare mono-, bi and trivalent cations exchanged clay samples and study their catalytic activity for α -pinene conversion. Surface area, pore volume and average pore diameter of the different cation-exchanged clays are given in Table 3. The X-ray diffraction patterns are shown in Fig. 4 for cation-exchanged clays confirm the retention of the clay structure. The basal d-spacing values observed for different cation-exchanged clays vary in the range of 1–15 Å also confirm the retention of the structure.

It is observed from the data in Table 5, Mg^{2+} and Ca^{2+} exchanged clays do not show encouraging conversions whereas other cation-exchanged clays show more than 93% conversion, except Li^+ clay which shows 47% conversion. Surprisingly, very low activity was also observed for H^+ exchanged, which may be due to incomplete exchange of Na^+/Ca^{2+} present in the interlayer space of the clay with protons as exchange was done only in a single step. Conversion values for clay samples exchanged with triply charged (La^{3+} , Ce^{3+} , Fe^{3+}) cations is higher (93–99%). As shown in Eq. (1), water molecules in the hydration sphere of exchangeable cations act as proton donors due to polarizing

Table 5

Conversion and selectivity of various products formed on isomerisation of α -pinene using cation-exchanged montmorillonite clays^a

Catalyst	Conversion (%)	Selectivity (%)				
		Camphene	Tricyclene	α -Terpinene	Limonene	Others
N_0	34	40	3	10	15	32
H^+	8	39	4	9	12	36
Li^+	47	31	2	8	32	27
Mg^{2+}	4	39	3	9	12	37
Ca^{2+}	12	39	3	11	10	37
Fe^{3+}	93	48	6	10	11	25
Ag^+	98	47	11	11	9	22
La^{3+}	99	47	10	9	13	21
Ce^{3+}	99	49	12	8	12	19

Others: terpinolene, isoterpinolene, γ -terpinene, etc.

^a Catalyst: 0.1 g, α -pinene: 2 ml, reaction temperature: 150°C, reaction time: 2 h.

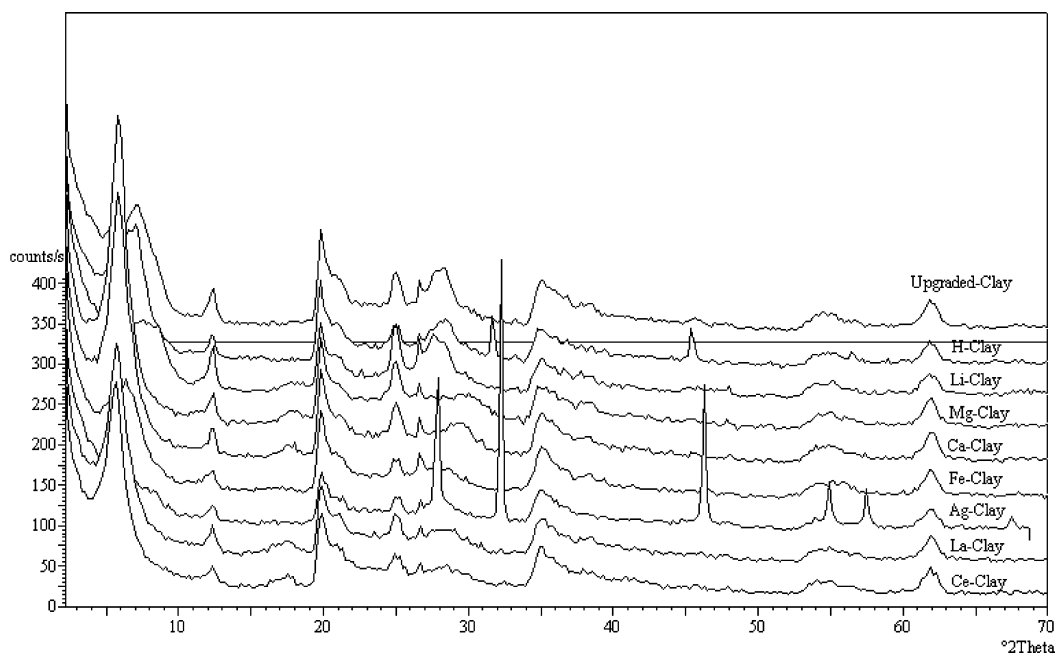


Fig. 4. XRD pattern of cation-exchanged clays.

effect of cations. It is reported [17] that polarizing effect of cations is much more significant in clay interlayer water due to its decreased dielectric constant when present in the interlayers. It is estimated [17] that degree of dissociation of water is 10^7 times higher in the interlayer space than in liquid water. Higher acidity for La^{3+} , Ce^{3+} , Fe^{3+} exchanged clays is explained in terms of higher Bronsted acidity generated by these cations due to their high charge density (9.7×10^{-20} , 1.1×10^{-19} and 4.4×10^{-19} , respectively) which results into water polarization as shown in Eq. (1). Na^+ , Ca^{2+} and Mg^{2+} exchanged clay samples show lower catalytic α -pinene conversion because of the lack of Bronsted acidity in these samples as also reported [17] from adsorbed pyridine IR spectra. Jankovič and Komadel [17] from their study on acylation of benzaldehyde,

3,4,5-methoxy benzaldehyde and 4-nitrobenzaldehyde have also reported [17] significantly higher catalytic activity for La^{3+} , Ce^{3+} , Fe^{3+} exchanged montmorillonite compared to Li^+ , Mg^{2+} and Ca^{2+} exchanged samples.

However, the observation that Ag^+ having low charge density (1.9×10^{-20}) also show high conversion is also interesting. From XRD data given in Fig. 4, Ag^+ exchanged clay showed two additional peaks at 32.2 and 46.2 (2θ). These peaks are attributed to formation of Ag^0 species in Ag cluster, which might be formed in the interlayer space. Similar species were reported in silver exchanged zeolite-Y [18]. Ag clusters formed in the zeolite cavities are reported to have charge higher than one [19]. The higher activity of silver in clay may be resulting from the formation of

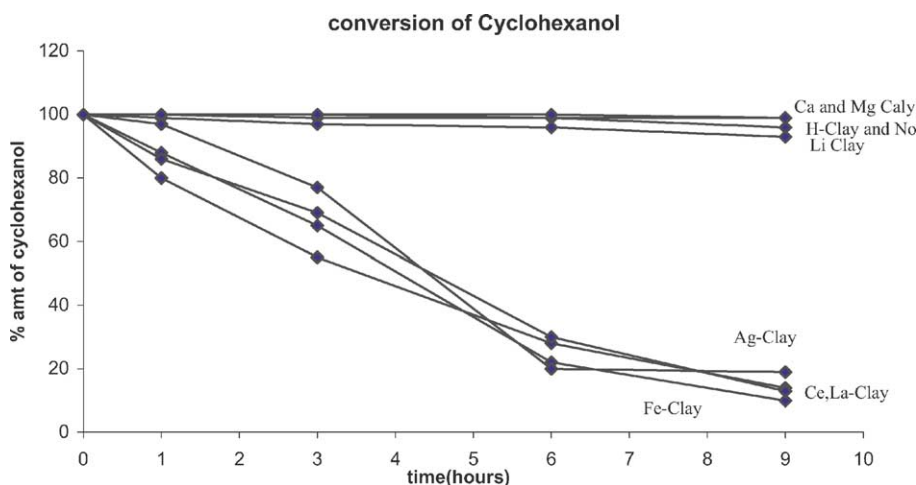


Fig. 5. Dehydration of cyclohexanol at 150°C.

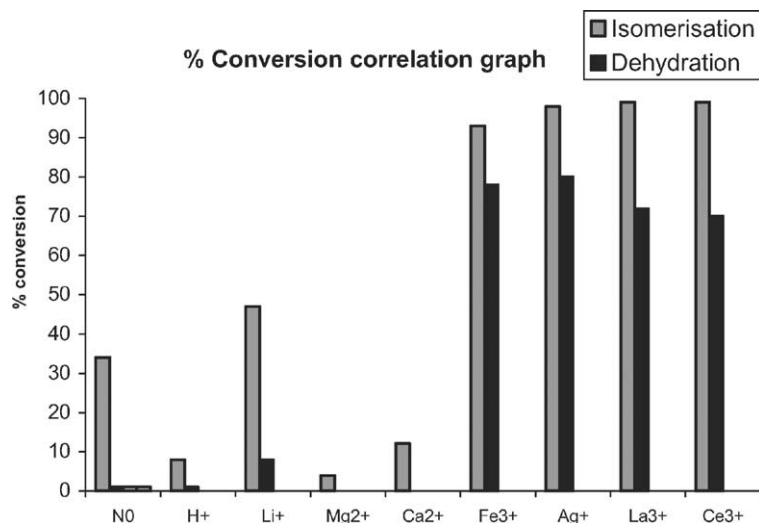


Fig. 6. Correlation of percent conversion of α -pinene with cyclohexanol dehydration.

similar species, which due to their higher charge may generate acidity higher than the monovalent Ag^+ ions.

To establish that α -pinene conversion is Bronsted acid catalyzed reaction, dehydration of cyclohexanol was studied in all the clay samples. These data given in Fig. 5 show that conversion values for the dehydration of cyclohexanol for natural up-graded clay, H^+ , Li^+ , Ca^{2+} , Mg^{2+} exchanged clays show poor activity (Fig. 5), which is in agreement with α -pinene conversions for these catalysts (0–7%) as given in Table 5. On the other hand, conversion of cyclohexanol to cyclohexene is very high for Ag^+ , Fe^{3+} , La^{3+} , Ce^{3+} exchanged clay conversions (Fig. 5) indicating higher surface acidity for these clay samples. The observed correlation (Fig. 6) between α -pinene conversions and cyclohexanol dehydration clearly show that α -pinene conversions is Bronsted acid catalyzed reaction.

The order of selectivity for cation-exchanged clays towards camphene is observed to as follows:



In these clays conversion to monocyclic terpenes are formed less as also observed for acid treated clays. Ce^{3+} exchanged clay show maximum selectivity 49% towards

camphene. Among monocyclics, limonene is predominant product in most of the reactions.

The above data show that Ag^+ , Fe^{3+} , La^{3+} , Ce^{3+} exchanged clays are effective catalysts for α -pinene conversion. However, products distribution depends upon the intrinsic property of cations or more specifically the carbocation intermediate(s) favored by individual cation-exchanged clays. It is also observed that compared to acid treated cation-exchanged clays in general, show less selectivity towards monocyclic.

α -Pinene conversion data for other clays (Table 6) show that Hectorite and Saponite are not very active catalysts for this reaction. However, poorly crystalline Kaolin showed high conversion (86%). On the other hand, well crystalline Kaolin was less effective for the reaction and the conversion is only 16%. Acid treatment of poorly crystalline Kaolin with 4N normality acid solution enhances the activity for pinene conversion. Poorly crystalline Kaolin is selective towards camphene and limonene but the well crystalline Kaolin is less selective towards camphene and limonene, it is more selective for α -terpinene. Attapulgite, which is essentially $\text{Mg} \cdot \text{SiO}_3$, shows very low conversion values, perhaps due to basic Mg.

Table 6
 α -Pinene conversion study carried out using other clays^a

Catalyst	Conversion (%)	Selectivity (%)				
		Camphene	Tricyclene	α -Terpinene	Limonene	Others
Hectorite	8	40	2	2	26	30
Kaolin poorly crystalline	86	53	5	3	24	15
Kaolin well crystalline	16	34	3	21	8	34
Attapulgite	21	46	2	6	30	16
Saponite	3	49	4	12	17	18
Ca-montmorillonite	38	48	2	4	32	14

Others: terpinolene, isoterpinolene, γ -terpinene, etc.

^a Catalyst: 0.1 g, α -pinene: 2 ml, reaction temperature: 150°C, reaction time: 2 h.

4. Conclusion

Liquid phase catalytic isomerisation of α -pinene with natural Indian Montmorillonite modified by sulphuric acid (1–9N) treatment shows α -pinene conversion of 96% with selectivity for camphene ranging from 43 to 49%. For acid treated clays prepared by treating with low normality acid (1–4N), limonene is the main product whereas clay samples prepared with high normality acid (5–9N), α -terpinene is a main product among monocyclic terpenes. The study on the effect of temperature (80–150 °C) on conversion showed that 150 °C gives higher conversion and selectivity for camphene. Montmorillonite clay exchanged with Ce^{3+} , Fe^{3+} , La^{3+} , and Ag^{+} showed higher than 93% conversion for α -pinene with 43–49% selectivity for camphene. However, alkaline earth cations, Ca^{2+} , Mg^{2+} exchanged clay showed poor conversion (4–12%) and Li^{+} showed 47% conversion for α -pinene. Correlation of α -pinene conversion with cyclohexanol dehydration establishes that α -pinene is Bronsted acid catalyzed reaction.

The study show the potential of both acid treated and cation-exchanged clays for α -pinene selective isomerisation for camphene.

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