Influence of acidity of montmorillonite and modified montmorillonite clay minerals for the conversion of longifolene to isolongifolene

Baldev Singh [a,*], Jyoti Patial [a], Parveen Sharma [a],
S.G. Agarwal [a], G.N. Qazi [a], Sudip Maity [b]

[a] Catalysis Discipline, Regional Research Laboratory (CSIR), Canal Road, Jammu 180001, India
[b] CFRI, Dhanbad, Jharkhand, India

Abstract

Isolongifolene and various other isolongifolene-based products are commercially important chemicals that find applications in perfumery and fragrance industry. These important commodity chemicals are generally prepared by homogeneous catalyzed reactions of longifolene in liquid phase. In the present study, role of acidity and acid distribution on montmorillonite, pillared interlayered clay and modified pillared clay catalysts have been studied for the first time in vapor phase system for the conversion of longifolene to isolongifolene. The number and strength of acid sites of montmorillonite clay mineral have been modified by steps of synthesis and by cations selection. Reaction of Al- pillared montmorillonite with Ru^{3+} yielded a catalyst with significantly higher distribution of weak acid sites while fortification of montmorillonite with Ce^{3+} and La^{3+} had little effect on total acidity and its distribution. In the present study, an attempt has been made to correlate the activity of the catalysts with total acidity, number and strength of the acid for the conversion of longifolene to isolongifolene. NH_3 TPD determined the concentration and strength of acid sites.
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1. Introduction

Clays have long been used as acidic catalysts and existence of both Lewis and Bronsted acid sites [1–6] is well established. Bronsted acid sites in the solid can be generated when trivalent cations is present in tetrahedral co-ordination with oxygen. Lewis acid sites results from the Bronsted acidity, essentially results from the dissociation of water molecules in the hydration shell of the interlay ring exchangeable cations. These clays catalyze many organic reactions and constituted the first generation of FCC catalysts.

Pillaring of montmorillonite by mono or complex oligomeric cations yields porous solid that possess some properties of zeolites like strong acidity and regular porosity. Thus, a great variety of catalysts have been prepared that are active for cracking, alkylation, dehydrogenation and epoxidation, according to the nature of the pillars.

The objective of this paper is to develop an active, selective and stable catalyst based on PILC and to determine the acidity of the catalysts in order to study the effects of acid strength and number on activity for the conversion of longifolene to isolongifolene.

Isolongifolene, $C_{15}H_{24}$ obtained by acid catalyzed rearrangement of longifolene is a tricyclic sesquiterpene with a trisubstituted double bond and has a different carbon skeleton from that of longifolene.

Isolongifolene and its oxygenated derivatives (ketones and oxide) posses extremely agreeable odors and occupy vintage place in the perfumery industry. Isolongifolene a tricycle sesquiterpene is produced by deep-seated rearrangement of longifolene involving a number of steps catalyzed by acids like sulfuric acid, acetic acid, BF_3, amberlyst-15 or acid treated silica gel [7–10]. In view of the industrial importance of this compound, patents have closely guarded the details of the catalysts and process parameters. Rearrangement of longifolene to isolongifolene with partial racemization of longifolene involves series of 1,2-alkyl/hydride shifts. Isolongifolene is still a high-energy molecule due to the presence

* Corresponding author. Tel.: +91 191 2572002; fax: +91 191 548607.
E-mail address: drbaldevsingh@yahoo.co.in (B. Singh).

of the strained [2,2,1] heptane system and due to this nature it has tendency to undergo further rearrangements to number of side products. However, the reaction can be terminated at the isolongifolene stage by careful reaction conditions and catalyst.

Further, the acidic properties of the catalyst so prepared were determined by ammonia TPD method.

2. Experimental

2.1. Preparation of catalyst

Pillared montmorillonite were prepared [11] by the reaction of montmorillonite (Fluka Ag, Chemishe Fabric CH- (9470 Buchs) with alumina and zirconia oligomeric solution. Modified montmorillonite catalysts were also prepared by incorporating Ce^{3+} and La^{3+} ions. Further, Al-PILC catalysts were fortified with ruthenium salt.

2.2. Experimental set-up

The experimental set-up and reactor design is same as that used by Roy et al. [12] with some modifications. Bottom feedings with nitrogen flow was employed in each experiment, instead of top feeding.

2.3. Analytical technique

2.3.1. GC analysis

GC analysis with respect to isolongifolene conversion was carried out on Nucon 5765 gas chromatograph equipped with FID and AIMIL chromatography data processor. The separation was achieved using a FFAP, SE-30 fused-silica capillary column (20 m × 0.25 mm i.d., 0.25 μm film thickness); column temperature, 90 °C (2 min)–220 °C at 4 °C/min; injection temperature, 240 °C; detector temperature, 260 °C; mode, split; carrier gas, helium at column flow rate of 1.05 ml/min (100 kPa). Retention indices (RI) of the sample components and authentic compounds
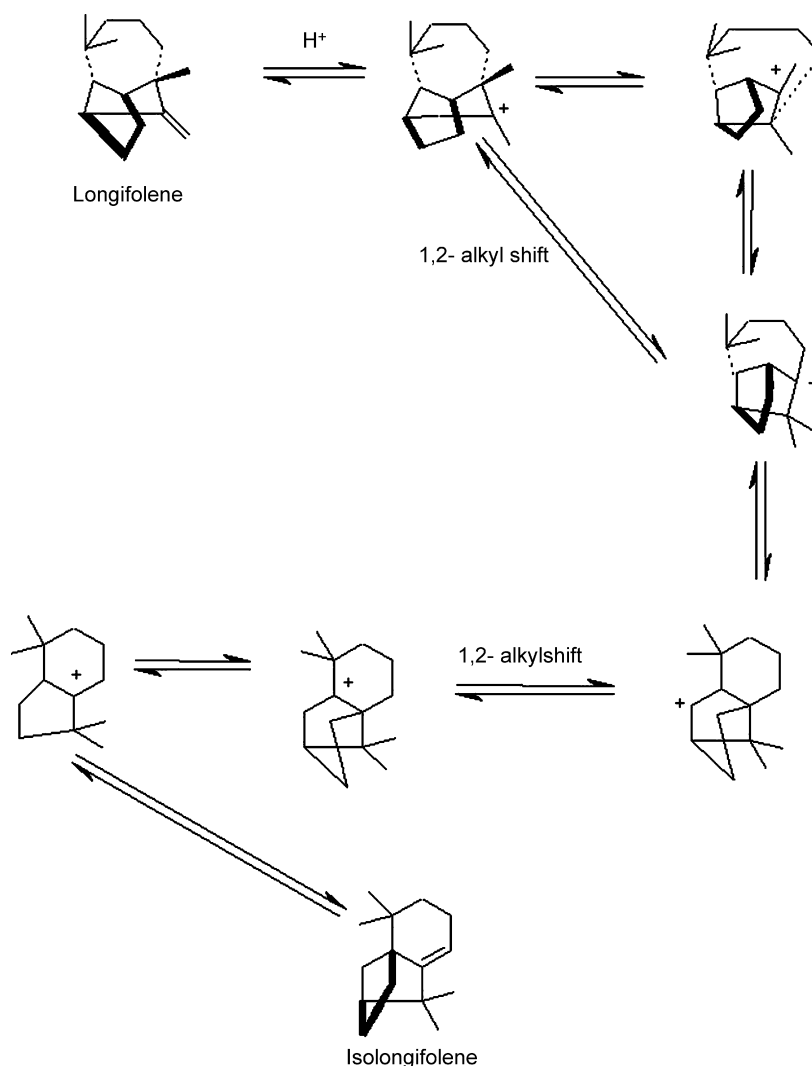
Scheme 1. Isomerization of longifolene to isolongifolene in presence of acids/acidic catalyst.

were determined on the basis of homologous *n*-alkane hydrocarbons (*n*-nonane to *n*-nonadecane) under the same conditions. The quantitative composition was obtained by peak area normalization, and the response factor for each component was considered to equal 1.

2.3.2. Ammonia TPD

Ammonia TPD was recorded using Servotrace of sefran (Paris), model no. PF 7547, attached to Intersmat instrument chromatography of GC12M. About 0.1–0.2 g of the samples were placed in glass tube reactor. Helium gas is passed at low rate of 20 cm^3 min^{-1} under 2 bar pressure. The programming of temperature was as follows: The temperature was raised from room temperature to 120 °C in 12 min. It was then kept constant for 1 h and again raised from 120 to 600 °C at the rate of 5 °C per minutes. Temperatures were kept constant for 4 h and are brought down to 50 °C. The system was then evacuated for 15 min and ammonia gas was passed over the catalyst at 2 bar pressure for 15 min. Applying vacuum using a catharometer flushed out the ammonia from the system. This was continued for 30 min and then application of vacuum was stopped. The desorption of ammonia gas was started from 50 to 500 °C at 50 °C interval, while continuing the flow of helium. The desorbed gases at the end were adsorbed in 0.001 N H$_2$SO$_4$, was titrated against 0.001 N NaOH solution using phenolphthalein as indicator.

3. Results and discussion

The present studies deal with mainly PILC and modified montmorillonite clays as catalysts. It is well known that the acido–basic properties of the catalyst play very vital role in the conversion of longifolene to isolongifolene. The mechanism for the conversion may be assumed to take place through the following routes [13].

From the mechanism shown in Scheme 1, it appears that the acidity of the catalyst depends mainly on the surface acid sites. By analogy of the data on the surface chemistry of H$^+$ ions of zeolite, it is possible that silanol groups possessing protonic acidity are present at the surface of the hydroxyl pillars. The acidity of clay is believed to result from partial thermal dehydration and dehydroxylation. The existence of both Lewis and Bronsted acidity on pillared clays has been previously demonstrated [2–6] Keeping in this view PILC have been employed as catalysts for the conversion of longifolene to isolongifolene and an attempt has been made to establish the relation between the catalytic activity and acidity.

Ammonia TPD histograms of pure montmorillonite, Al-PILC, Zr-PILC, Ru-modified Al-PILC catalysts and Ce^{3+} and La^{3+} exchanged montmorillonite are shown in Figs. 1–6.

It is observed from histograms that on pillaring with Al and Zr oligomeric cations and montmorillonite modified with La^{3+} ions the number of medium and strong acid site increases, where as montmorillinite modified with Ce^{3+} ions weak and moderate acid sites slightly decreases and strong acid sites increases to noticeable extend. Ru^{3+} exchanged modified montmorillonite shows sharp increase of weak acid sites.
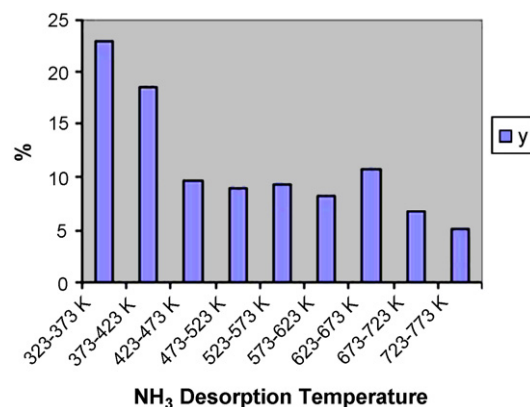
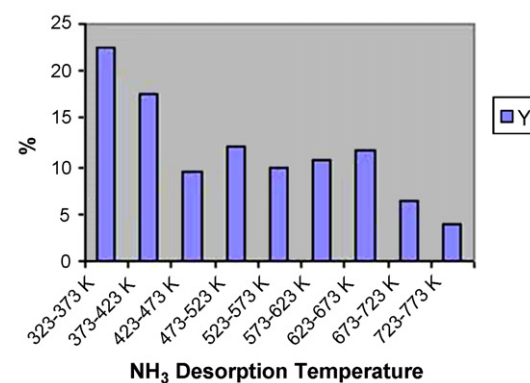

Fig. 1. TPD pattern of montmorillonite.

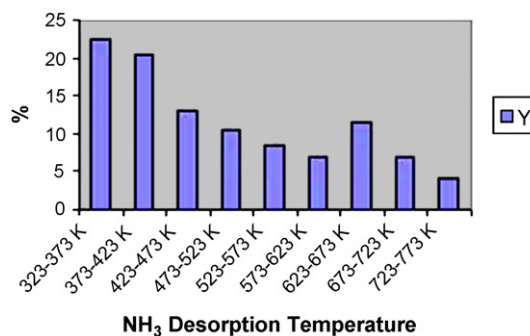Fig. 2. TPD pattern of montmorillonite after pillaring with hydroxy-Al oligomeric solution.

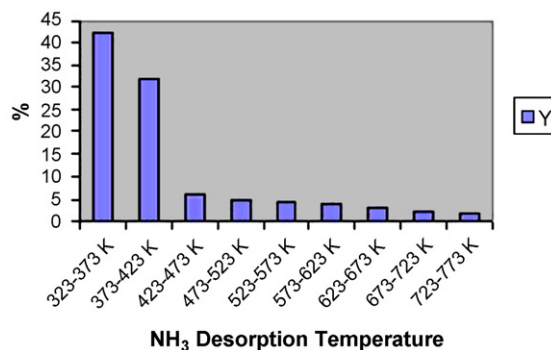Fig. 3. TPD pattern of montmorillonite after pillaring with hydroxy-Zr oligomeric solution.

Fig. 4. TPD pattern of montmorillonite after treatment with hydroxy-Ru salt.
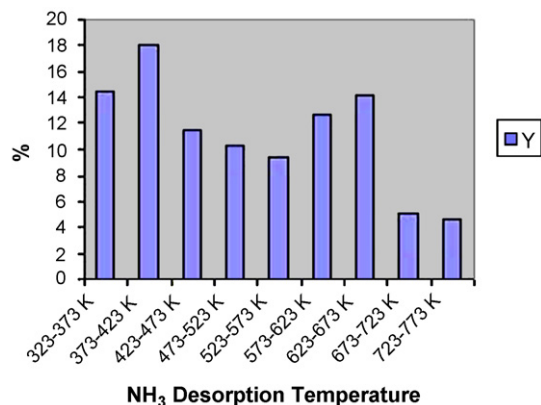
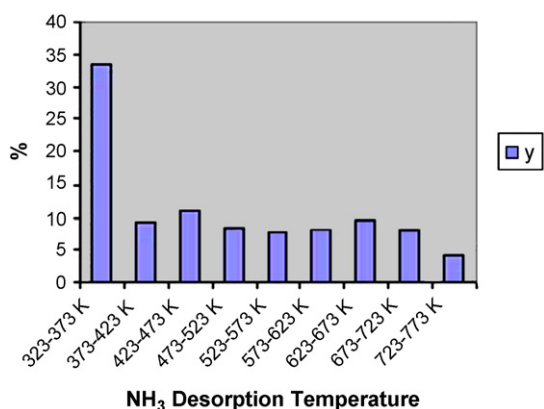Fig. 5. TPD pattern of montmorillonite after treatment with La-salt.

Fig. 6. TPD pattern of montmorillonite after treatment with Ce-salt.

From Table 1, it is observed that in the case of Zr-pillared clay the concentration of strong and medium acid sites were more than that of Al-PILC. More interesting results were observed when montmorillonite exchanged with Ce^{3+} and La^{3+}

cations. Concentration of weak acid sites increases in both cases, but medium acid sites decreases as compared to Al- and Zr-PILC.

Besides the total acidity measurement, the histogram indicates the distribution of strong, medium and weak acid sites. Table 1 indicates montmorillonite clay have total acidity of 0.163 meq. $H^+ g^{-1}$ with a large number of weak acid sites up to 55.82%, medium acid sites up to 34.98% and the rest 9.20% corresponding to strong acid sites (Table 2). It is observed that pillaring of said montmorillonite clay with Al-oligomer solution increases the total acidity to 0.199 meq. $H^+ g^{-1}$ with considerable changes in the distribution of strong (10.06%), medium (39.69%) and weak acid sites 50.25% (Tables 1 and 2).

The total acidity of Zr-pillared clay remains practically the same as that of Al-pillared clay as observed from Table 1. It is evident from Table 2 that there is decrease in weak acidic sites (26.84%) with a consequent increase of moderately (46.84%) and strong acidic sites for Zr-PILC (26.32%). Thus, it may be inferred that the pillaring of montmorillonite clay either with aluminum or zirconium either increases the total acidity or change the distribution of acidic sites.

Exchange of montmorillonite with Ce^{3+} ions further increased the total acidity as evident from Table 1 It is of interest to note that there is considerable increase in weak (0.116 meq. $H^+ g^{-1}$), moderate (0.072 meq. $H^+ g^{-1}$) and strong (0.026 meq. $H^+ g^{-1}$) acidity. Exchange of montmorillonite with La^{3+} resulted in sharp decline in total acidity (0.142 meq. $H^+ g^{-1}$), weak acidity (0.072 meq. $H^+ g^{-1}$) and moderate acidity (0.052 meq. $H^+ g^{-1}$) with slight increase in strong acidity (Table 1).

In addition to montmorillonite, Al-PILC was also exchanged with Ru^{3+} ions. It is of interest to note that exchange of Al-PILC with ruthenium salts resulted in the complete reorientation of distribution of acid sites with sharp increase towards weak acid sites from 50.25% to 80.0% (Table 2).

Table 1
Distribution of total acidity

S. no.	Catalyst	Weak acid sites meq. H^+/g	Medium acid sites meq. H^+/g	Strong acid sites meq. H^+/g	Total acidity meq. H^+/g
1.	Montmorillonite	0.092	0.057	0.015	0.163
2.	Al-PILC (Montnorillonite)	0.100	0.079	0.020	0.199
3.	Zr-PILC Motmorillonite	0.060	0.080	0.050	0.190
4.	Al-PILC (Modified with Ru salt)	0.114	0.022	0.005	0.141
5.	Montmorillonite (modified with La-salt)	0.072	0.052	0.018	0.142
6.	Al-PILC (modified with Ce-salt)	0.116	0.072	0.026	0.214

Table 2
Distribution of acid concentration

S. no.	Catalyst	Weak acid sites	Medium acid sites	Strong acid sites
1.	Montmorillonite	55.82	34.98	9.20
2.	Al-PILC (Montnorillonite)	50.25	39.69	10.06
3.	Zr-PILC Motmorillonite	26.84	46.84	26.32
4.	Al-PILC (Modified with Ru salt)	80.85	15.60	3.55
5.	Al-PILC (modified with La-salt)	54.20	33.65	12.15
6.	Al-PILC (modified with Ce-salt)	50.70	36.62	12.68

Table 3
Production of Isolongifolene

Sample no.	Catalyst	Temperature (°C)	Longifolene	Iso-longifolene
(1)	Original montmorillonite	160	2.1	29.5
		180	5.1	41.8
		200	1.2	45.6
(2)	Al-PILC (montmorillonite clay mineral)	160	17.8	66.2
		180	12.2	77.5
		200	2.8	65.7
(3)	Zr-PILC (montmorillonite clay mineral)	160	72.2	14.7
		180	1.6	70.0
		200	84.0	21.8
(4)	Al-PILC treated with Ru-salt	160	0.5	20.4
		180	3.4	32.5
		200	3.1	10.0
(5)	Al-PILC treated with La -salt	160	65.8	2.85
		180	30.3	7.1
		200	3.2	12.9
(6)	Al-PILC treated with Ce-salt	160	6.7	1.3
		180	2.6	31.0

From the above discussion, it can be safely concluded that exchange of montmorillonite with Al-oligomer and Ce^{3+} salts resulted in increase of total acidity as well as weak, moderate and strong acid sites.

Whereas exchange with Zr-oligomer resulted in increase of total acidity with simultaneous decrease in weak acid sites.

All above-mentioned catalysts were evaluated for isomerization of longifolene to isolongifolene and results are given in Table 3. The detailed analysis of results confirmed that total acid strength along with acid sites distribution plays a vital role in selective isomerization of longifolene to isolongifolene.

Catalyst having very low and very high total acidity with large number of weak acid sites were not suitable for such an isomerization as side reactions predominated the reaction pathway.

Catalysts having moderate acid strength of 0.19–0.199 meq. H$^+$ g^{-1} along with medium acid site concentration in the range of 40–45% and weak acid sites in the range of 41–50% were found to be very selective for the conversion of longifolene to isolongifolene (70–80%) at 180 °C.

3.1. Kinetic analysis

Varying the parameters like catalyst, W/F (g cat/g mole of feed/h) and effect of temperature on reaction velocity constant carried out the kinetic experiments. The studies were carried out at 160, 180 and 200 °C and at 1 atmospheric pressure with W/F values varying from 1.15 to 3.01 at 160 °C, 1.90 to 4.22 at 180 °C and 2.11 to 2.7 (g cat/g rate feed/h) at 200 °C. Values of X (moles converted /gm mole of the feed) was varying from 0.36 to 0.71, 0.36 to 0.65 and 0.49 to 0.93 at the temperature of 160, 180 and at 200 °C, respectively. The kinetic results could be fitted well to first order reaction, when the concentration are expressed in terms of conversion, in integrated form:

$$\frac{KP_T}{RT}\frac{W}{F} = -X - 2\ln(-1X) \tag{1}$$

Data used for confirming Eq. (1) are presented in Fig. 7, as plot of $-X - 2\ln(1-X)$ versus W/F, where a straight line passing through the origin is obtained.

The effect of temperature on reaction velocity constant is related to the reaction temperature by Arrhenius equation, the constants at which are obtained by a plot of $\ln k$ against $1/T$ shown in Fig. 8.

Activation energies for the isomerization of longifolene under experimental conditions were found to be (10.07–12.44 kJ/mol) with Al-PILC catalyst and (11.68–12.60 kJ/mol) with Zr-PILC.

From above kinetic studies, it was observed that Al-PILC showed the higher conversion and reasonable selectivity for the isomerization of longifolene. In the present investigation it has been assumed that the kinetic data are not influenced by internal and external diffusion. Therefore, the diffusion limitation has
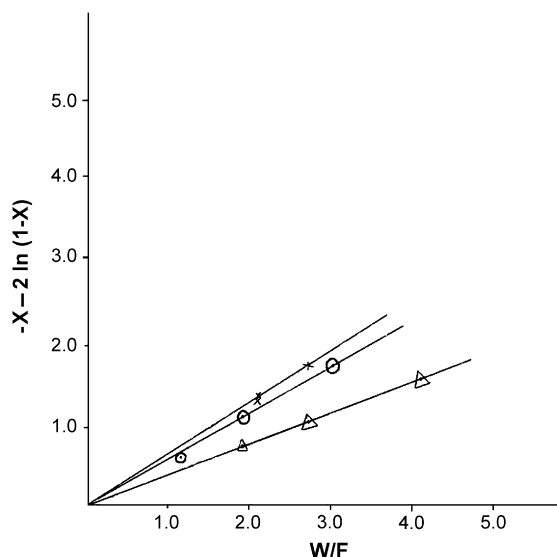

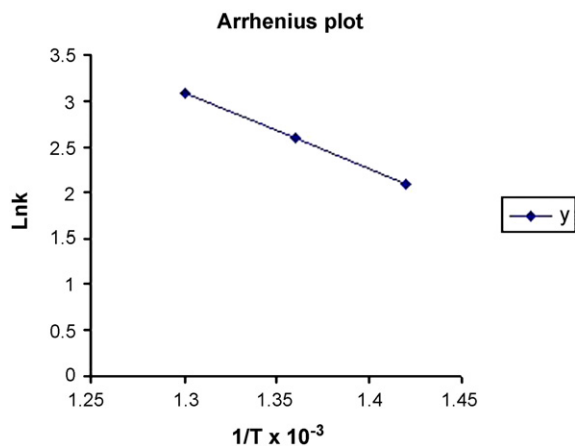Fig. 7. Plot of W/F vs. $-X - 2\ln(1-X)$.

Fig. 8. Arrhenius plot.

no impact on reaction temperature between 160 and 200 °C. Therefore, there is no contradiction to consider that the role of acidity tends to significant impact for the above reaction.

Thus, to design an active, selective and stable PILC based catalyst, the control of total acid strength along with various acid site distributions is very much essential and to achieve the desired selectivity or conversion of longifolene to isolongifolene.

Acknowledgements

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