ISOMERIZATION OF α-PINENE TO CAMPHENE USING INDIGENOUS CLAYS AS CATALYST

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Abstract. China and fire clay samples from the Salt Range, Mianwali, have been investigated for isomerization of α-pinene to camphene. The mode of preparation of the catalyst and its quantity have been varied. China clay treated with sulphuric acid, activated at 350° and 2% by weight of α-pinene, gave the best results. Clays treated with HCl and activated at 550° lose catalytic efficiency.

Camphene, discovered by Berthelot[1] in 1858 occurs fairly widely in various essential oils. [2] These natural resources, however, are either insufficient or uneconomical to meet the demand of camphene as a raw material for insecticides like thanite, bornyl acetate and camphor. Various methods were, therefore, developed for its production from abundantly available pinenes which isomerize under the influence of acids,[4] acidic salts[5] and salts containing water of crystallization and capable of retaining it even no heating.[6]

Kuwata[7] introduced the use of Japanese acid clay in 1929 for the isomerization of pinene to camphene. Tischchenoko[8] used some unspecified clay, activated with 10% hydrochloric acid for the same purpose and obtained a 62% yield of camphene. Fullers earth[9] and the clay from Houden region[9] when used as catalysts gave 45–47% camphene and 25% polymers with higher boiling points. Another Russian clay used by Rudakov [10] as a catalyst gave only 50–55% yields of camphene. Rutovskii[11] developed a successful catalyst from the residue of kaoline or nephaline obtained in the production of aluminium sulphate. He termed this catalyst as Si-Stoff and developed similar compositions[12] to investigate the effect of various ions on these isomerizations. The use of Japanese acid clay activated by ammoniation[13] and that of Montomorillonitic clays activated by heating at 360° in an atmosphere of hydrogen[14] have also been described in the literature. The objective of all these studies has been to increase the yield of camphene and to reduce the formation of other byproducts. The mechanism of the isomerization of α-pinene to camphene in the prescence of activated clays has been discussed in detail. [15, 16]

As no such work using Pakistani clays has been reported in the literature, the present studies were made using one sample each of china and fire clay from Mainwali District as catalysts. The effect of temperature, mode of activation and addition of catalyst have been studied.

Experimental

α-Pinene (BHD) was used without further purification.

Preparation of the Catalyst. The clay (150 g, 177μ was placed in a 500-ml round-bottomed flask equipped with a condenser and a mechanical stirrer. The sample was charged with 300 ml 6N acid and refluxed for 4 hr. The flask was cooled and the contents filtered. The residue was washed first with tap water and then with distilled water till acid free. It was dried first at room temperature and then heated at the desired temperature for 2 hr. The activated clay was stored in a desicator for subsequent use.

Isomerization of Pinene. α-Pinene (13) was taken in a two necked 50 ml round-bottomed flask having a magnetic stirrer and a condender. The reaction vessel was lowered in an oil bath maintained at the required temperature and the stirring started. The requisite amount of the catalyst was added through the second neck of the flask either portionwise over a period of 3 hr or as a whole. The reaction mixture was further heated for 1 hr and then cooled to room temperature. The liquid reaction product was separated from the catalyst by filtration and analysed.

Analysis of the Product. The rection product was analysed on Griffin — George gas liquid chromatograph having a thermal conductivity detector. A 1.6m long and 0.63-cm i.d. glass, column packed with Celite 545 (420-177 microns) coated with apiezone grease 10% (w/w) or rape seed oil 2% (w/w) was used for separation. Nitrogen at the rate of 50 ml/min was employed as carrier gas. The sequence of elution of the constituents was: 4 unreacted α-pinene; 2, camphene; 3, limonene; 3,5,6 unidentified; the idenfication was made by comparing the retention times and by the addition of known constituents. The percentage of individual components was calculated by triangular method. The results are given in Tables 2-7.

Discussion

The chemical composition of the clays used as isomerization catalysts is given in Table 1. In addition to the physical differences such as topology, porosity and structure of the clays, the major chemical difference lies in silica and alumina content. The volatile matter is removed by heating the clays at 110° and some physical properties may also be affected. On refluxing the clays with mineral acids Al, Fe, and Ca are partly leached out, resulting in a change in the topoloigy and increase in the porosity and silica

content. The corresponding ions, out of which aluminium ions are of prime importance [11] get deposited on the newly developed silica surface. The chemical analysis of the catalysts (Table 1) shows that sulphuric acid leaches out Al more effectively than does hydrochloric acid. However, a qualitative test on the catalysts for sulphate ions was negative and for chloride ions slightly positive.

The catalytic efficiency of both china and fire clays activated by simple heating at 110° is given in Table 2. The overall transformation of α-pinene and the yields of camphene are higher with fire clay than with china clay. This observation supports the low alumina silica ratio theory advanced by Rutovskii.[11] However, the yields are too poor to be of any practical use.

The catalytic efficiency of the acid treated clays activated at 110° by heating for 2 hr is given in Table

2. China clay which without acid treatment was least effective proves to be a better catalyst as far as the transformation of α-pinene is concerned. On the other hand fire clay treated either with sulphuric acid or hydrochloric acid caused lower transformation but yields more camphene based on consumed α-pinene. In this case camphene is the major product and the number of byproducts is less than in the case of china clay.

When the acid-treated clays a reactivated at 300–350° the catalytic performance is increased to some extent (Table 3). The transformation of α-pinene is lower in the case of china clay but higher in the case of fire clay. The yield of camphene is better compared to the clays activated at 110°.

Table 4 shows the results obtained with catalyst activated at 500–550°. Both the clays in 1% amount are less effective in the transformation of α-pinene

TABLE 1. CHEMICAL COMPOSITION OF THE CATALYSTS USED.

Type of catalyst				SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Loss on ignition
C	..	..	..	46.55	39.20	0.17	0.600	—	13.90
F	..	..	..	51.10	34.92	0.82	0.75	—	12.05
CH	..	..	..	51.00	36.30	0.14	Traces	—	13.28
FH	..	..	..	57.00	31.00	0.60	0.50	—	11.72
CS	..	..	..	58.00	35.75	0.15	Traces	—	5.79
FS	..	..	..	55.60	30.90	0.62		—	12.50

C china clay, F fire clay, CH and CS china clay activated by HCl and H_2SO_4 respectively, and FH and FS fire clay activated by HCl and H_2SO_4 respectively.

TABLE 2. EFFECT OF AMOUNT OF CATALYST (ACTIVATED AT 110°).

Type of catalyst				Catalyst %	Composition of the product (%)					
					1	2	3	4	5	6
C	..	..	..	5	93.4	1.5	2.0	3.1	—	—
CS	..	..	..	1	40.0	43.8	—	15.4	—	0.7
"	..	..	..	2	6.6	45.3	1.3	29.1	3.3	14.3
"	..	..	..	5	6.6	43.9	4.9	22.9	3.9	18.0
CH	..	..	..	5	94.7	—	2.4	2.7	—	—
F	..	..	..	5	80.0	13.7	0.6	5.4	—	0.8
FS	..	..	..	1	84.4	9.2	2.2	4.2	—	—
"	..	..	..	2	49.8	35.3	—	12.5	—	2.4
"	..	..	..	5	35.0	37.1	2.9	19.3	0.4	5.2
FH	..	..	..	5	94.8	—	—	5.1	—	—

TABLE 3. EFFECT OF AMOUNT OF CATALYST (ACTIVATED AT 350°).

Type of catalyst				Catalyst (%)	Composition of the product (%)					
					1	2	3	4	5	6
CS	..	..	..	1	44.6	38.3	0.9	13.2	0.4	2.6
"	..	..	..	2	10.9	59.8	0.9	19.3	1.8	7.6
"	..	..	..	5	7.8	50.4	4.0	22.7	3.2	11.9
CH	..	..	..	1	87.4	4.3	2.5	0.5	4.1	1.3
"	..	..	..	2	87.7	3.9	0.9	6.1	0.3	1.4
"	..	..	..	5	37.0	21.0	2.0	32.5	1.0	4.5
FS	..	..	..	1	63.9	25.2	1.1	8.5	—	1.3
"	..	..	..	2	36.3	39.2	2.3	16.3	2.1	3.7
"	..	..	..	5	7.8	47.2	3.0	31.5	2.3	8.0
FH	..	..	..	1	64.7	18.5	2.2	12.5	0.5	1.9
"	..	..	..	2	53.7	17.1	3.7	18.3	1.8	5.5
"	..	..	..	5	12.2	46.4	4.1	20.9	1.7	14.5

TABLE 4.   EFFECT OF AMOUNT OF CATALYST (ACTIVATED AT 500 600°).

Type of catalyst				Catalyst (%)	Composition of the product(%)					
					1	2	3	4	5	6
CS	..	..	..	1	49.6	32.7	0.3	17.5	—	—
,,	..	..	.·.	2	5.3	32.5	0.9	45.4	2.4	3.9
,,	..	..	..	5	5.0	43.7	5.0	26.9	3.4	16.3
CH		..	..	1	86.9	90.	1.8	2.3	—	—
,,	..	..	..	2	74.4	18.0	0.3	7.3	—	—
,,	..	..	..	5	70.4	24.8	2.0	2.5	—	—
FS	..	..	..	1	85.5	11.1	0.2	3.3	—	—
,,	..	..	..	2	65.9	22.3	0.7	10.4	—	1.3
,,	..	..	..	5	5.9	48.6	3.5	28.3	2.5	11.3
FH	..	..	..	1	81.9	12.9	1.3	3.8	—	—
	..	..	..	2	42.5	38.2	2.0	17.4	—	—
	..	..	..	2	40.9	38.3	1.4	19.2	—	—

TABLE 5.   EFFECT OF MODE OF ADDITION OF THE CATALYST (5% FH, ACTIVATED AT 350°).

Addition					Composition of the product (%)					
portionwise	..	..	..	..	12.2	46.4	4.1	20.9	1.7	14.6
As a whole	..	..	..	..	7.9	45.3	11.5	15.6	9.4	10.3

TABLE 6.   EFFECT OF REACTION TIME (5% FH, ACTIVATED AT 350°).

Time hr.	..	..	..	..	Composition f the product (%)					
					1	2	3	4	5	6
1	..	..	..	..	6.0	51.6	6.7	11.7	7.7	17.2
2	..	..	..	..	6.2	47.9	10.3	12.1	10.3	13.3
3	..	..	..	..	6.6	47.3	10.6	15.2	9.6	11.0
4	..	..	..	..	7.1	45.3	11.5	15.6	9.4	10.3

TABLE 7.   EEEECT OF RACTION TEMPERATURE (5% FH, ACTIVATED AT 350° ADDED AS A WHOLE, REACTION TIME 2 HR.

Temp.		Composition of the product (%)					
		1	2	3	4	5	6
105-110	..	.69.4	14.7	1.3	10.2	0.7	3.7
135-140	..	6 2	47 9	10 3	12 1	10.3	13.3

and the yield of camphene is also poor. In 2 and 5% amounts the sulphuric acid treated clays become more or less equal in effect to the ones activated at 110 or 350°. There is, however, a marked drop in the efficiency of the clays treated with hydrochloric acid and activated at 550°. This could be explained if the efficiency of hydrochloric acid-treated clays was assuumed partly due to aluminium chloride deposited during the preparation of the catalysts. These deposits volatilise at such temperature resulting in a drop in the efficiency of the catalyst.

It is observed invaiably (Tables 2-4) that with the increase in the amount of catalyst the transformation of α-pinene also increases. China clay (2%) treated with sulphuric acid and activated either at 110 or 350 or 550° causes about 90% transformation of α-pinene, the only difference being in the yield of camphene. Any further increase in the quantity of this catalyst has very small effect. It is noticeable that 2% of this catalyst is better than even 5% of china clay treated with hydrochloric acid or fire clay treated with either hydrochloric acid or sulphuric acid. The best yield of camphene is obtained with 2% china clay treated with sulphuric acid and activated at 350° (Table 3).

When the catalyst is added as a whole a vigorous

reaction occurs which subsides after a few minutes. In this case after 1 hr (Table 5) α-pinene left unreacted is lesser, the yield of camphene is higher and that of limonene lower than when the same catalyst is added portionwise (Table 3). The transformation of α-pinene into other products does not seem to be time dependent (Table 6) the percentage of unreacted pinene remains more or less constant. With the passage of time camphene seems to get converted into other terpenes.

The effect of reaction temperature is shown in Table 7. Fire clay which was capable of transforming 93.8% α-pinene at 135-140° could do so up to 30.7% at 105-110°. A 5% catalyst at 105-110° proved less effective than 1% of the same catalyst at 135-140°. The yield of camphene in the former case was a bit lower and that of limonene a bit higher.

It may be concluded that four components viz. α-pinene, camphene, limonene and another terpene (peak 6) are pesent in all the reaction mixtures. The other two unidentified products corresponding to peaks 3 and 5 are time-dependent and most probably are derived from further isomerization of camphene and the unidentified terpene corresponding to peak 6.

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