THE ACTIVITIES OF SOME HETEROGENEOUS CATALYSTS FOR ISOMERIZATION OF TRICYCLIC NAPHTHENES INTO ADAMANTANES

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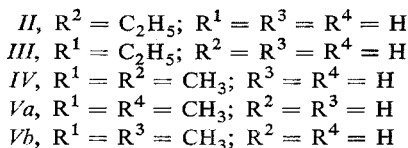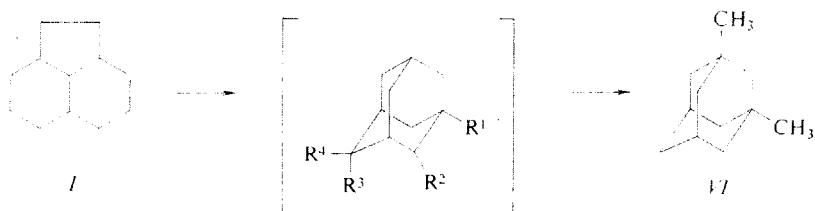*Institute of Chemical Technology, 166 28 Prague 6*

The activities of six catalysts for isomerization of perhydroacenaphthene into alkyladamantanes in gaseous phase have been investigated in a through-flow reactor. Nickel on aluminosilicate and alumina impregnated with aluminium fluoroborate gave very low yields of alkyladamantanes. A higher activity was observed with catalysts prepared from alumina or aluminosilicate by treatment with sulphuric or chlorosulphonic acid. Alumina containing platinum and activated with thionyl chloride had the highest activity and was the only catalyst effecting isomerization of trimethylenenorbornane into adamantane. However, the initial high activity of the chlorinated, platinum-containing alumina rapidly decreased with the continuing feed of the reactor, so that the life of the catalyst was a very short one.

Adamantane, certain alkyladamantanes and other adamantanoid hydrocarbons can be obtained by isomerization of suitable saturated polycyclic hydrocarbons in liquid phase by the action of Lewis acids[1−3]. However, the reaction is generally accompanied by fragmentation and the formation of undesired products and polymeric tarry substances.

To raise the yields of adamantane hydrocarbons in such isomerizations various modifications of the reaction conditions and catalysts have been recommended. Good experience was reported on some combinations of aluminium halides with hydrogen halides, alkyl halides and other co-catalysts and promoters, which improve the contact of the catalyst with the hydrocarbon layer, compared to the use of pulverized aluminium chloride or bromide alone. Efforts to improve the contact of the catalyst with the compound to be isomerized have led, in recent years, to attempts at heterocatalysed isomerization in gaseous phase. The formation of an adamantane by a reaction in gaseous phase on a solid catalyst was first reported by Plate and coworkers[4], who found 6 to 13% of this hydrocarbon among the products of catalytic.cleavage of trimethylenenorbornane on an aluminosilicate catalyst at 450°C. Isomerization of polycyclic hydrocarbons into adamantanes, proceeding in the gaseous phase at relatively low temperature (to reduce cracking) have only recently been described. Among the catalysts recommended for this purpose are alumina treated with sulphuric acid[5,6], alumina with nickel[7] and chlorinated alumina with platinum[8].

To obtain comparable data on the usability of solid catalysts for a continuous production of adamantane hydrocarbons in gaseous phase we have compared the activities of some alumina catalysts and aluminosilicate catalysts for two types of adamantane rearrangement: for isomerization of perhydroacenaphthene (I) to a mix-

ture of C_{12} alkyladamantanes $(II - VI)$, as a high-rate adamantane isomerization, and for isomerization of trimethylenenorbornane into adamantane, which is rather slow.

$$II, \; R^2 = C_2H_5; \; R^1 = R^3 = R^4 = H$$
$$III, \; R^1 = C_2H_5; \; R^2 = R^3 = R^4 = H$$
$$IV, \; R^1 = R^2 = CH_3; \; R^3 = R^4 = H$$
$$Va, \; R^1 = R^4 = CH_3; \; R^2 = R^3 = H$$
$$Vb, \; R^1 = R^3 = CH_3; \; R^2 = R^4 = H$$

EXPERIMENTAL

Apparatus. The catalysts were compared in a through-flow apparatus with a solid catalytic bed and an automatic temperature control with a precision of $\pm 1 \cdot 5°C$. The all-glass reactor for measuring at an atmospheric pressure was placed in a glass oven, heated electrically. The reaction temperature was measured with a thermocouple reaching into the catalytic bed. The hydrocarbon to be isomerized was brought at a constant rate into a separately heated evaporator, where its vapour mixed with hydrogen or nitrogen. The carrier gas was dried by passage through washing bottles with sulphuric acid, or it was first saturated with hydrogen chloride and then dried. The reaction products were collected in a glass spiral freezer, cooled to $-78°C$.

Catalysts. The supporters used for the preparation of the catalysts were aluminosilicate (83·3% SiO_2, 11·1% Al_2O_3, 0·31% Fe_2O_3, specific surface 351 m^2/g, mesh 0·15—1·0 mm) and alumina (98·6% Al_2O_3, 0·3% SiO_2, specific surface 214 m^2/g, mesh 0·15—1·0 mm). Aluminosilicate with 0·5% of Ni was prepared[7] by impregnation of the supporter in a solution of nickel chloride, dried in a vacuum evaporator and, just before use, reduced in a jet of hydrogen for 2 h at 350°C. Alumina impregnated with sulphuric acid was prepared by placing a layer of 10%-H_2SO_4 over γ-alumina[6]. After 20 h the excess of the acid was poured off and the catalyst was dried at 130°C and calcinated at 300°C. Aluminosilicate impregnated with sulphuric acid was prepared analogously using 50%-H_2SO_4. Aluminosilicate with 25% of aluminium fluoroborate was prepared by impregnation of the supporter in a solution of $Al(BF_4)_3$, prepared from boric acid, hydrogen fluoride and aluminium hydroxide. The catalyst was dried in a vacuum evaporator, then heated 1 h to 330°C. Alumina impregnated with chlorosulphonic acid was prepared by the addition of $ClSO_3H$, pre-heated to 40°C, to γ-alumina in an evacuated flask. After aeration of the flask and 18 hours' standing the bulk of the acid was poured off and its remaining part was removed by heating to 200°C. The catalyst was immediately employed for the isomerization experiments.

Alumina with 0·5% of platinum was prepared by impregnation of the supporter with an aqueous solution of chloroplatinic(IV) acid[8]. After having been dried in a vacuum evaporator the alumina was heated to 130°C, then 12 h to 260°C. In the activation the catalyst was heated in the reactor under a stream of nitrogen to 480°C and calcinated for 2 h. Then pure hydrogen was passed over the catalyst at a rate of 450 l/h kg_{cat}, and after elevation of the temperature to 500°C hydrogen saturated with hydrogen chloride was passed over for 1 more hour. Hydrogen was then replaced by nitrogen (flow rate 110 l/h kg) and at 500°C the catalyst was exposed to the action of thionyl chloride (5·4 mol $SOCl_2$/kg). The catalyst was cooled to the working temperature and used immediately for the isomerization experiments.

Chemicals. Perhydroacenaphthene and trimethylenenorbornane were prepared by hydrogenation of acenaphthene (Lachema) and or dicyclopentadiene (Koch-Light) in a rotatory steel autoclave on Raney nickel at a starting hydrogen pressure of 100 atm and temperatures 180°C and 140°C, respectively. The hydrogenated products were shaken with sulphuric acid, washed in water, dried, distilled and freed from the last traces of polar compounds on a column of silica gel.

Analyses. The composition of the reaction mixtures was followed by gas chromatography in an apparatus Chrom III (Laboratorní přístroje, Nat. Corp., Prague) on 50 m capillary columns of stainless steel, I.D. 0·2 mm. The fixed phase was Squalane, Apiezon L or OV-225 (cyanopropylmethylphenylsilicone, Applied Science Laboratories). The carrier was nitrogen. The individual compounds were identified by mass spectrometry. The data were recorded at 70 eV on a combined apparatus gas chromatograph - mass spectrometer LKB 9000 (LKB Produkter AB, Stockholm), with oscillographic recording of the spectra. The chromatographic columns were again the 50 m stainless capillaries wetted with one of the above-mentioned fixed phases. The carrier was helium.

Procedure. The isomerization powers of the catalysts were first tested on perhydroacenaphthene at temperatures close to 200°C. The reaction proceeded in hydrogen (partial pressure 0·875 atm). From the feeding rate, amount and proportion of the detected reaction products we calculated for each catalyst the amount of C_{12}-alkyladamantanes formed under comparable conditions per a mass unit of the catalyst and a time unit. The effect of the reaction temperature was investigated in the same way at several temperatures in a range of 200 to 350°C. The most active catalysts were also tested for the power to isomerize (at 200–215°C) trimethylenenorbornane to adamantane.

The chlorinated platinum-alumina catalyst ($Pt/Al_2O_3.Cl$) was tested for life in the isomerization of perhydroacenaphtene to C_{12}-alkyladamantanes. With the freshly prepared catalyst the decrease in activity was first investigated in relation to the amount of the compound to be isomerized. After a partial deactivation the catalyst was reactivated by thionyl chloride and the decrease in activity with time was followed again by determining the composition of the reaction mixture. The reactivation was repeated and the catalyst was regenerated and tested as in the three preceding cases. Unlike the procedure published[8], the catalyst was not activated by a stream of dry hydrogen chloride, but by hydrogen saturated with dry hydrogen chloride or by hydrogen chloride generated *in situ*, by decomposition of tert-butyl chloride. The reactivating procedure consisted in 30 minutes' heating of the catalyst to 500°C in a stream of hydrogen, followed by 30 minutes' heating to the same temperature in a stream of hydrogen saturated with dry hydrogen chloride. Further procedure was the same as in the activation. The deactivated catalyst was regenerated in a stream of air at 510°C. The course of the regeneration was followed in an all-glass apparatus by a change in colour of the catalyst. When the carbon-containing compounds were removed the temperature was reduced to 480°C and the catalyst was exposed to hydrogen for 2 h; further procedure was as in the activation. In experiments with tert-butyl chloride the starting perhydroacenaphthene was mixed with tert-butyl chloride in an equimolar ratio. Employing this mixture the fresh catalyst was tested as in the life tests.

RESULTS AND DISCUSSION

Comparison of the isomerization powers of the individual catalysts (Table I) showed that the yields of the adamantane hydrocarbons differed greatly. The least active were the fluoroborate catalyst and nickel on aluminosilicate, which gave 1 to 5 ml of alkyladamantanes per h and kg of the catalyst. Yields higher by an order of magnitude (36 to 42 ml/h . kg) were obtained with catalysts of protonic acidity (sulphuric acid or chlorosulphonic acid on alumina or aluminosilicate). Alumina with a small content of platinum, activated by thionyl chloride, was another order of magnitude more efficient; the yield given in Table I (485 ml/h . kg) was attained in a 100% conversion of the starting perhydroacenaphthene, so that a higher flow-rate can be expected to raise the yield still further. The results of attempted isomerization of trimethylenenorbornane to adamantane are compiled in Table II. The data show that

TABLE I

Catalyst Activities in the Isomerization of Perhydroacenaphthene

Catalyst	Reaction temperature °C	Feeding rate ml/h . kg	Condensate %	Alkyladamantanes in the condensate, %	Yield of alkyladamantanes ml/h . kg
$Al(BF_4)_3/Al_2O_3 . SiO_2$	198	50	90	2·2	1
$Ni/Al_2O_3 . SiO_2$	204	75	90	7·6	5
$H_2SO_4/Al_2O_3 . SiO_2$	203	82	90	48·2	36
$ClSO_3H/Al_2O_3$	202	100	90	41·0	37
H_2SO_4/Al_2O_3	210	86	85	58·2	42
$Pt/Al_2O_3 . Cl$	185	550	90	98·0	485

TABLE II

Catalyst Activities in the Isomerization of Trimethylenenorbornane

Catalyst	Reaction temperature °C	Feeding rate ml/h . kg	Condensate %	Adamantane in the condensate %	Yield of adamantane ml/h . kg
$Ni/Al_2O_3 . SiO_2$	200	75	90	0	0
$ClSO_3H/Al_2O_3$	215	100	90	traces	0
H_2SO_4/Al_2O_3	210	86	90	traces	0
$Pt/Al_2O_3 . Cl$	210	408	90	33·5	123

the chlorinated platinum alumina catalyst was the only usable one for this rearran-
gement. With any of the other catalysts practically no adamantane was formed[6,7].

The effect of an increase in reaction temperature on the yield (Table III) was fa-
vourable with the nickel and the fluoroborate catalysts, but in a rather narrow tempe-
rature range of 200 to 300°C. In all cases, however, an elevation of temperature
enhanced the side reactions, mainly the skeleton cracking and dehydrogenation. The
cracking increased very markedly with chlorinated platinum alumina catalyst; the
amount of the fragments in the condensate rose from 2·2% at 188°C to 37·3% at 230°C.
Also marked was the decrease in the portion of the condensable reaction products
(with the fluoroborate catalyst it was from 90 to 50% for a temperature elevation by
200°C), which had a considerable effect on the yield.

Measurements of life of chlorinated platinum alumina are represented in Fig. 1,
where the total content of alkyladamantanes in the reaction product is plotted vs
the quantity of perhydroacenaphthene passed through the reactor. From the deacti-
vation course of the fresh catalyst (curve 1) it is seen that at first the activity of the
catalyst decreased moderately, since after a passage of perhydroacenaphthene corres-
ponding to 400 ml/kg_{cat} the overall conversion into alkyladamantanes was still over
90%. Then, however, further decrease in activity was rapid; at a passage of 3000 ml/kg
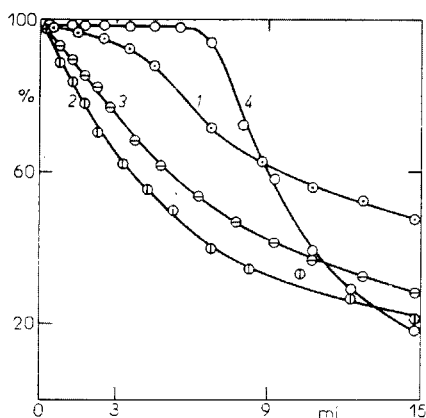the total content of alkyladamantanes in the reaction mixture dropped to below 30%.

Fig. 1

Contents of Alkyladamantanes (%) in the Reaction Product in Relation to the Feeding by
Perhydroacenaphthene (ml)

1 Fresh catalyst, 2 reactivated catalyst, 3 regenerated catalyst, 4 fresh catalyst with tert-
butyl chloride. Temperature 188°C, catalyst weight 10 g ($Pt/Al_2O_3.Cl$), space velocity
530 ml/h kg.

TABLE III

Effect of Reaction Temperature on Composition of the Product in the Isomerization of Perhydro-acenaphthene

Catalyst	Reaction temperature °C	Feeding rate ml/h . kg	Condensate %	Alkylada-mantanes in the con-densate, %	Yield of alkylada-mantanes ml/h . kg
Ni/SiO$_2$. Al$_2$O$_3$	204	75	90	7·6	5
	230	75	90	13·6	9
	260	75	90	35·4	24
	290	75	85	45·7	29
	320	75	75	44·6	25
	350	75	60	37·2	17
Al(BF$_4$)$_3$/Al$_2$O$_3$	195	250	90	1·1	2·5
	298	250	80	2·4	5
	395	250	50	9·6	12
ClSO$_3$H/Al$_2$O$_3$	202	100	90	41·0	37
	300	100	80	38·3	30
H$_2$SO$_4$/Al$_2$O$_3$	210	85	85	58·2	42
	300	85	60	42·5	22
Pt/Al$_2$O$_3$. Cl	170	530	90	99·9	476
	188	530	90	97·8	466
	230	530	90	62·7	300

TABLE IV

Proportion of Alkyladamantanes in the Product in the Isomerization of Perhydroacenaphthene on the Chlorinated Platinum-Alumina Catalyst in the Presence of tert-Butyl Chloride at 188°C, and a Space Velocity of 530 ml/h . kg

Perhydro-acenaphthene passed through ml/kg	Contents of alkyladamantanes in the product, %					
	total	VI	V	IV	III	II
125	98·3	88·9	6·7	1·8	0·9	0
450	98·0	64·0	14·6	5·0	13·4	1·0
925	57·9	10·0	23·7	6·3	6·3	11·6
1225	28·6	3·0	12·5	2·1	2·6	8·4

At this stage the catalyst was reactivated with thionyl chloride. Although its activity was restored to the original level (curve 2) the decrease in activity was then faster than with the fresh catalyst. The treshold of 30% was reached already at a passage of 1 500 ml/kg. Repeated reactivation followed the same course. The decrease of activity of the regenerated catalyst is seen from curve 3. The regeneration restored the activity to the original value, but its decrease was much faster than with the fresh catalyst. However, this decrease was not so fast as with the catalyst that had been reactivated only.

The results of an attempt at a continuous restoration of the active sites of the catalyst by tert-butyl chloride in the course of the reaction are expressed by curve 4 in Fig. 1. In the presence of tert-butyl chloride the catalyst retained a high activity longer than in any of the preceding tests; a 90% conversion was reached after as much as 750 ml of perhydroacenaphthene per kg of the catalyst had passed through the reactor. With the fresh catalyst the conversion dropped to 90% at 400 ml/kg, with the regenerated catalyst at 140 ml/kg and with the reactivated one at a mere 70 ml/kg. However, the initial stage of high activity is followed by a drop much faster than in the previous tests. Consequently, the addition of tert-butyl chloride does not extend the life of the catalyst, but its isomerization power is better utilized since its most active period is extended. Nevertheless, chlorinated platinum-alumina as a catalyst of adamantane isomerization can be used on a laboratory scale only.

In the initial period of high activity of chlorinated platinum-alumina, when the total of alkyladamantanes in the product keeps above 95%, the gradual deactivation of the catalyst manifests itself by a changing proportion of the individual alkyladamantanes $(II - VI)$ in the product. As can be seen from Table IV, the markedly prevailing adamantane in the product obtained by the initial stage with chlorinated platinum alumina was 1,3-dimethyladamantane (VI), which is the thermodynamically most stable C_{12}-alkyladamantane. After a passage of 450 ml of perhydroacenaphthene per $kg_{cat.}$ the reaction product contained a third of the thermodynamically less stable isomers III, IV and V, formed as transitive intermediates. In the region of the ending activity of the catalyst trans-1,4-dimethyladamantane (Va), cis-1,4-dimethyladamantane (Vb) and 2-ethyladamantane (II) were the dominating alkyladamantanes in the product. Alkyladamantanes II to V, formed on chlorinated ·platinum-alumina as intermediates, proved identical with the intermediates detected in isomerizations on aluminium bromide[9] and on alumina activated by sulphuric acid[10]. This fact suggests that with these catalysts the isomerization of perhydroacenaphthene (I) to 1,3-dimethyladamantane (VI) proceeds by the same mechanism.

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