CATALYST SELECTION FOR HYDROGENATION OF 1,2-DIHYDROACENAPHTHYLENE

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The activity of ruthenium, palladium, and nickel catalysts for the hydrogenation of 1,2-dihydroacenaphthylene in cyclohexane solution was studied at temperatures up to 180 °C and pressures up to 8 MPa. The GC-MS technique was used to identify most of the perhydroacenaphthylene stereoisomers, whose fractions in the product were found dependent on the nature of the active component of the catalyst. The hydrogenation was fastest on the palladium catalyst (3% Pd/C). The nickel catalyst Ni–NiO/Al$_2$O$_3$, which is sufficiently active also after repeated use, can be recommended for practical application. The activation energy of 1,2-dihydroacenaphthylene hydrogenation using this catalyst is 17 kJ/mol, the reaction order with respect to hydrogen is unity.

Key words: 1,2-Dihydroacenaphthylene; Hydrogenation; Nickel; Ruthenium; Palladium; Catalyst; Acenaphthene; Heterogeneous catalysis.

Hydrogenation of aromatic hydrocarbons to the corresponding cyclic compounds is of practical importance in relation to environmental issues[1] and also it may lead to interesting intermediates for the synthesis of chemical specialties[2]. The hydrogenation follows the Scheme 1.

The complete hydrogenation of the aromatic skeleton has been examined and metal catalysts have been recommended for this reaction[3]. The kinetics of liquid-phase hydrogenation of aromatic hydrocarbons have been studied (*e.g.*, ref.[4]). While benzene derivatives have been investigated most frequently, information regarding the hydrogenation of polynuclear aromatic compounds is rather scarce[5–7].
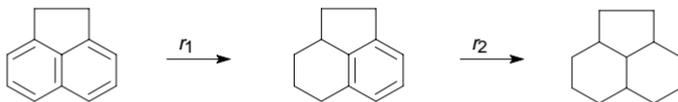
SCHEME 1

The raw material stock for the starting 1,2-dihydroacenaphthylene (or acenaphthene) is based on the processing of bituminous coal tar[8,9]. Acenaphthene is the tenth most abundant compound in bituminous coal tar, and therefore modern distillation units pro-

duce directly the acenaphthene fraction (b.p. 260–285 °C) containing up to 40% 1,2-di-hydroacenaphthylene. This fraction represents roughly a 3% in distilled tar. 1,2-Dihydro-acenaphthylene can also be isolated by crystallization from washing oil[9].

Hydrogenation of 1,2-dihydroacenaphthylene has been studied, for instance, in refs[5–7,10–13], and various mixtures of tricyclododecane stereoisomers have been obtained in dependence on the catalyst nature and reaction conditions used.

The feasibility of isomerization of tricyclic perhydroaromatic compounds to polyal-kyladamantanes has been studied in relation to the hydrogenation of various phe-nalenes[5]. Raney nickel, temperature of 200 °C, and pressure of 13.6 MPa were applied in the hydrogenation of 1,2-dihydroacenaphthylene.

A comparison of reactivities of various aromatic hydrocarbons in catalytic hydroge-nation on nickel–molybdenum sulfide catalysts at 350 °C and 13 MPa shows that the reaction rate decreases in order[6,7]: anthracene > fluoranthrene > (phenanthrene, naph-thalene, pyrene, 1,2-dihydroacenaphthylene).

The proportions of the stereoisomers depend substantially on the reaction conditions[10], *i.e.* temperature, reaction time, and catalyst. After heating the not completely reacted hydrocarbons at 100–500 °C in the presence of hydrogen and of Group VI and group VIII metals of the Periodic Table or their mixtures, their oxides or sulfides as catalysts, the reaction products are isolated by crystallization or destillation. In this way the for-mation of some stereoisomers can be suppressed completely, and conversely, some desired stereoisomers can be obtained in high yields. This enables us to prepare stere-oisomers possessing specific physicochemical properties and different reactivities, which is of importance for their further applicability. For example, hydrogenation of 1,2-dihydroacenaphthylene on Raney nickel at 180–200 °C and 12 MPa gives a mixture of up to 5 stereoisomers in a ratio depending on the reaction temperature but not on the reaction time.

Mild reaction conditions for the hydrogenation of 1,2-dihydroacenaphthylene allow platinum–metal-based catalysts to be used[11] (*e.g.*, rhodium catalyst, 10 wt.% Rh/C, ac-tive at a temperature of 100 °C and hydrogen pressure of 2–2.5 MPa, WHSV = 8 kg/h, in hexane, yield 93%); such catalysts are easy to recover.

For ruthenium catalysts, the effect of the support nature, dispersity, and specific sur-face area of ruthenium on the hydrogenation rate has been examined for aromatic hy-drocarbons[12] (including 1,2-dihydroacenaphthylene at 160 °C and 8 MPa). The authors demonstrated that the most active catalyst can be prepared by using activated carbon as the support; the perhydroacenaphthylene formed can be isomerized to 1,3-dimethylada-mantane with a 91% yield.

trans-Perhydroacenaphthylene can be prepared selectively on a nickel catalyst[13] (50% Ni/kieselguhr) at 200 °C/20 MPa. At a 100% conversion the *trans*-isomer yield was 96%. On the other hand, if Raney nickel is used, the *cis*-isomers are predominantly

formed (73% yield) under otherwise identical conditions; this is also the case of the palladium catalyst (10% Pd/C) at 160 °C (yield 54%).

The present study is aimed at finding a suitable catalyst and favourable reaction conditions for the hydrogenation of 1,2-dihydroacenaphthylene to tricyclo[7.2.1.0^{5,12}]dodecane (perhydroacenaphthylene), which is an important intermediate in the synthesis of 1,3-dimethyladamantane[2], a compound finding wide application in the preparation of antiviral and antimicrobial agents – or radioprotectives. The selection of catalysts was concentrated primarily on commercially available nickel catalysts; their activity was also compared to that of the available palladium and ruthenium catalysts.

EXPERIMENTAL

Chemicals

1,2-Dihydroacenaphthylene of a minimum purity of 99% (by GC) was a product of DEZA a.s., Valasske Mezirici, purified by recrystallization. Cyclohexane of reagent grade purity (Lachema, a.s., Brno) served as a solvent. Hydrogen 3.0 (Linde Technoplyn a.s., Prague) was used for the hydrogenation.

Catalysts

Comercial catalysts of the manufacturers Leuna, Circik, Engelhard, Doduco, and Chemopetrol Litvinov (Table I) were used. The pelletized catalysts were available in the reduced and passivated form (except for the nickel–chromium catalyst 51-U-12) and were crushed prior to use. A fraction smaller than 0.18 mm (obtained by sieving) was employed for the hydrogenation.

Hydrogenation Apparatus and Procedure

Hydrogenation was conducted in a 200 ml stirred batch autoclave made of stainless steel and fitted with a blade stirrer (1 600 r.p.m.), enabling experiments to be carried out at pressures up to 15 MPa and temperatures up to 250 °C.

Procedure. Finely ground and sieved catalyst (1 g) was placed in the autoclave, and a solution of 5 g of 1,2-dihydroacenaphthylene in 100 ml of cyclohexane was added. The maximum temperature

TABLE I
Catalysts used

Composition	Type and manufacturer	Form, mm
Ni–NiO/Al$_2$O$_3$	6524 Leuna (Germany)	pellets 5 × 5
Ni–NiO–Cr$_2$O$_3$/Al$_2$O$_3$	6542 Leuna (Germany)	pellets 5 × 5
NiO–Cr$_2$O$_3$	51-U-12 Circik (Uzbekistan)	pellets 5 × 5
1% Ru/Al$_2$O$_3$	99830 Engelhard (U.S.A.)	balls 3.5
3% Pd/C	CHEROX 4100 Chemopetrol (Czech Republic)	powder
Raney Ni	Actimet "C" Doduco (Germany)	powder

and pressure during hydrogenation were 180 °C and 8 MPa. The catalyst activation proceeded during the heating of the autoclave to the reaction temperature. The course of the hydrogenation was monitored based by hydrogen pressure decrease in the autoclave; hydrogen was replenished continuously. When the hydrogenation process was over, the autoclave was allowed to cool down and the catalyst was filtered off. Evidence was gained that the experiments proceeded in the kinetic region with respect to both external and internal diffusion: the mean reaction rate was directly proportional to the amount of catalyst.

Evaluation of the experiments. The conversion of 1,2-dihydroacenaphthylene hydrogenation was calculated based on the consumption of hydrogen with respect to the reaction stoichiometry, using the equation of state for the ideal gas and the known gas phase volume in the autoclave, partial pressure of hydrogen, and temperature. The instantaneous hydrogenation rate was determined based on the hydrogen-uptake rate in the autoclave and mean reaction rate was calculated for the total time of the experiment. The time record of pressure and the calculated 1,2-dihydroacenaphthylene hydrogenation conversions are given in Fig. 1.

Analytical Method

The reaction mixture was analyzed by GC on a packed column containing 15% Carbowax 6000 on Chromaton N-AW-DMCS (2.5 m), interfaced to a CHROM-4 instrument fitted with a flame ionization detector. The isothermal mode was used at 153 °C. The perhydroacenaphthylene stereoisomers were identified by GC-MS (Joel DX 303) with a DB-5-MS capillary column (30 m long, 0.25 mm i.d., 0.2 μm film thickness). In Table II, the obtained data are compared with those taken from ref.[15] and from kinetic data[12]. The relative retention times of the reaction components were as follows: cyclohexane 1.0, perhydroacenaphthylene stereoisomers A (*trans,trans,trans*) 3.8, B (*cis,cis,trans*) 4.4, C (*cis,cis,cis*) 5.1, D 5.3, E (*cis,trans,trans*) 6.1, 1,2-dihydroacenaphthylene 16.2.

RESULTS AND DISCUSSION

The compounds formed in the hydrogenation of 1,2-dihydroacenaphthylene on the Ni–NiO/Al$_2$O$_3$ catalyst at a mean temperature of 167.5 °C and pressure of 8.0 MPa were identified. The mass spectra indicate (Table II) that all the compounds possess the same molecular
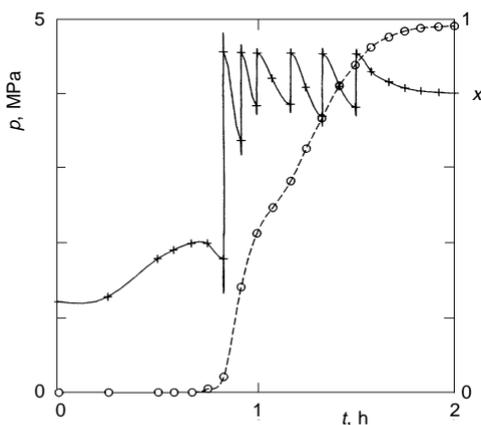
FIG. 1

Example of time development of pressure (+) and degree of conversion (○) in the hydrogenation of 1,2-dihydroacenaphthylene

TABLE II
Mass spectroscopy data of perhydroacenaphthylene stereoisomers

Isomer	m/z	This study	Ref.[15]
A (*trans,trans,trans*)	164	76	75
	136	82	71
	121	100	100
	107	21	20
	94	30	26
	79	40	38
	67	41	37
B (*cis*,cis,*trans*)	164	37	32
	136	90	30
	121	100	100
	107	17	15
	93	26	33
	79	41	50
	67	40	–
C (*cis,cis,cis*)	164	49	50
	136	40	40
	135	19	31
	121	100	100
	107	10	15
	94	21	–
	79	31	–
	67	26	–
D (*cis,trans,cis*) or (*trans,cis,trans*)	164	23	–
	136	100	–
	121	20	–
	107	10	–
	94	20	–
	79	23	–
	67	20	–
E (*cis,trans,trans*)	164	50	–
	136	50	–
	121	100	–
	107	20	–
	94	38	–
	79	41	–
	67	35	–

weight of 164 and are stereoisomers of tricyclo[7.2.1.0[5,12]]dodecane (perhydroacenaph-thylene). The configuration of the stereoisomers labelled A, B, C was elucidated based on a comparison of the mass spectra with the data in ref.[15]. The stereoisomer E, which is formed in the highest concentration under the reaction conditions applied, apparently possesses the *cis,trans,trans*-configuration. Its identity was also confirmed by an experiment where 1,2-dihydroacenaphthylene was hydrogenated on a ruthenium catalyst, where this isomer has been reported[11,12] to be predominantly formed. The component D is either *cis,trans,cis*- or *trans,cis,trans*-perhydroacenaphthylene or their mixture.

The hydrogenation of 1,2-dihydroacenaphthylene to perhydroacenaphthylene was examined mainly on supported nickel catalysts and, for a comparison, on palladium- and ruthenium-based catalysts. The comparison of these catalysts is summarized in Table III based on the reaction rates and final product composition.

Table III demonstrates that all of the catalysts except $NiO–Cr_2O_3$ were sufficiently active and 1,2-dihydroacenaphthylene was completely hydrogenated to perhydroace-naphthylene. The nickel–chromium catalyst was the only one to be used in the non-re-duced state; its sufficient reduction apparently failed to proceed during heating of the reaction mixture. The remaining catalysts were used in the reduced and passivated state. It is noteworthy that if the Raney nickel catalyst is employed, the reaction product contains a markedly higher amount of the *cis,trans,trans* isomer. This catalyst is also sufficiently active at lower temperatures. The experiment with the ruthenium catalyst confirmed the published data and also gave the largest quantities of the isomer E. The supported palladium catalyst was very active as well and worked at a low reaction temperature, the product, however, contained a very small fraction of *cis,trans,trans*-perhydroacenaphthylene (isomer E).

TABLE III
Mean reaction rate r at temperature T and product composition during the hydrogenation of 1,2-dihydroace-naphthylene (ACN) on various catalysts at 8 MPa

Catalyst	T, °C	r, kmol/h kg_{cat}	Product composition, wt.%				
			A	B	C + D	E	ACN
Ni–NiO/Al$_2$O$_3$	169	0.078	10	8	23	59	0
Ni–NiO–Cr$_2$O$_3$/Al$_2$O$_3$	170	0.042	8	6	21	65	0
NiO–Cr$_2$O$_3$	180	>0.02	5	2	28	33	32
Raney Ni	141	0.06	4	3	8	85	0
Ru/Al$_2$O$_3$	152	0.036	0	0	4	96	0
Pd/C	108	0.12	35	16	30	19	0

Using the Ni–NiO/Al$_2$O$_3$ catalyst, the effect of temperature on the hydrogenation rate and on the stereoisomer proportions in the reaction product were examined, the dependence of the reaction rate on the hydrogenation conversion degree was investigated, and the lifetime of the catalyst was assessed. All experiments were conducted at 3.5–4.5 MPa (Table IV). Experiments Nos 1–3 were performed using the fresh catalyst whereas experiments 4 through 8 were carried out employing the same catalyst repeatedly in order to test its lifetime at different reaction temperatures. The kinetic measurement was found to be well reproducible. The fact that the catalyst could be used repeatedly without apparent decrease in activity (experiments 4 through 6) indicates that the starting 1,2-dihydroacenaphthylene contained no catalyst poison.

TABLE IV
Mean rate of 1,2-dihydroacenaphthylene hydrogenation on an Ni–NiO/Al$_2$O$_3$ catalyst and product composition under various conditions, pressure 4 MPa

Experiment No.	T, °C	t, h	r kmol/h kg$_{cat}$	Product composition, wt.%			
				A	B	C + D	E
1	149	3.5	0.014	9.5	8.8	12.7	68.9
2	170	1	0.047	11.7	6.7	27.3	54.4
3	168	1.7	0.029	10.7	7.2	22.2	59.9
4	175	1.2	0.040	10.3	6.3	24.3	59.0
5	168	1.3	0.035	8.6	5.3	22.1	64.2
6	166	1.2	0.040	7.5	4.7	20.3	68.5
7	141	1.8	0.025	5.2	4.5	20.4	69.9
8	129	1.8	0.025	3.4	3.1	24.2	69.3
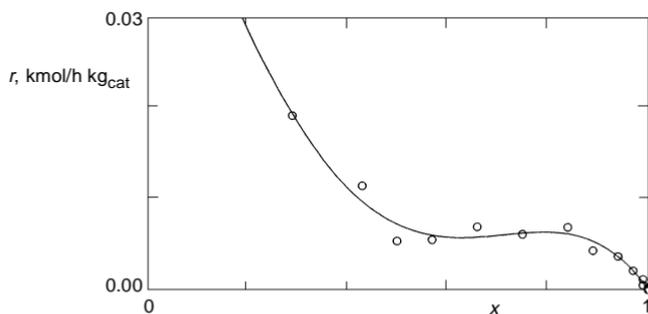
FIG. 2
Dependence of the hydrogenation reaction rate (r) on the conversion of 1,2-dihydroacenaphthylene (x)

The results were used to calculate the mean hydrogenation rate (Table IV). The dependence of the instantaneous reaction rate on the reaction conversion (Fig. 2) was set up using data of experiment No. 4, in which the hydrogenation reaction was triggered by increasing the hydrogen pressure in the autoclave only after heating up to the reaction temperature (170 °C). It is clear that the reaction rate changes during the process in two steps, in agreement with the reaction pathway. This decrease slows down after attaining roughly 50% conversion, which is clearly a state where 1,2-dihydroacenaphthylene is no more present in the reaction mixture and the intermediate product – tetrahydroacenaphthene – is hydrogenated further on. Clearly the reactivity of this intermediate is lower. A similar effect can be observed in the hydrogenation of naphthalene and tetrahydronaphthalene.

The mean reaction rate, corresponding to the mean temperature and pressure, is seen to be proportional to the partial pressure of hydrogen (Fig. 3). Hence, the reaction order with respect to this component is unity.
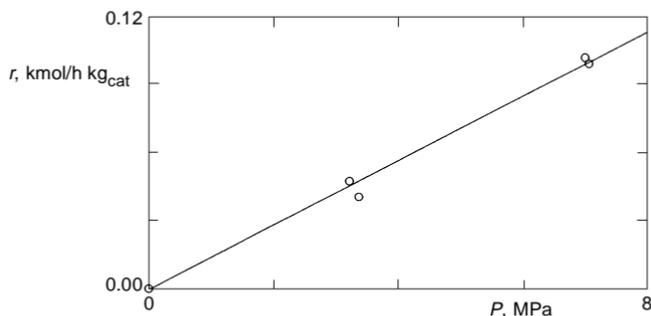
FIG. 3
Determination of the reaction order with respect to hydrogen in 1,2-dihydroacenaphthylene hydrogenation
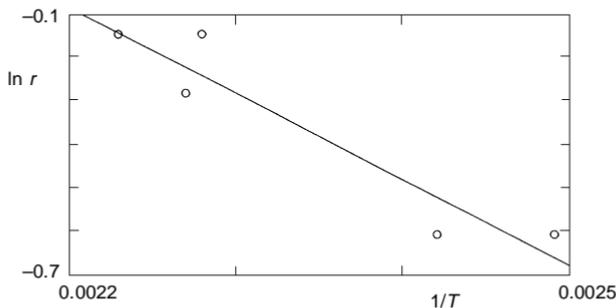
FIG. 4
Dependence of the 1,2-dihydroacenaphthylene hydrogenation rate (r in kmol/h kg_{cat}) on temperature (T); Ni–NiO/Al$_2$O$_3$ catalyst, pressure 4 MPa

Experiments 4–8, aimed at examining the catalyst lifetime, were carried out at different temperatures, so that the effect of the reaction temperature on the hydrogenation rate could also be assessed. The reaction rates are plotted in the Arrhenius coordinates in Fig. 4. The slope of the regression straight line provided an apparent activation energy value of 17 kJ/mol, which is consistent with that of other liquid-phase hydrogenations of unsaturated compounds[14].

The experimental results give an evidence that the hydrogenation of 1,2-dihydroace-naphthylene can be conducted on conventional nickel catalysts. It follows from a comparison of activities of the catalysts used that the $Ni/NiO/Al_2O_3$ catalyst is well suited to practical application: this catalyst is sufficiently active and can be used repeatedly, having a sufficiently long lifetime.

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