CATALYTIC PROPERTIES OF RANEY NICKEL AS A FUNCTION OF ITS PREPARATION

By

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The recognition of the prominent factors which influence the catalytic properties of catalysts is both of theoretic interest and practical importance. Through their knowledge preparation techniques may be improved and the production of reproducible catalysts enhanced. Our main target was to develop such a method.

The effect of the various steps of the Raney Ni preparation upon catalytic activity has been repeatedly studied. We dealt with the problem in a previous work [19] and also referred to the relevant literature.

Experimental procedure

Preparation of the catalysts

Dissolution of the aluminium from the alloys was performed in the apparatus shown in *Fig. 1.*

Alkali solution of controlled temperature reaches the alloy placed in space *3* through a glass filter, flowing from the calibrated Deville flask *1* via Mohr's clip *2*. It leaves the system together with the hydrogen evolved through the stump. *5*. Reaction temperature was measured by the thermometer *4*. The "spent" alkali, leaving together with the H_2 gas reaches the separator *6*. Here the gas and liquid phases separate, the former passing through stump *8*, via condenser and buffer vessel into the gasometer *9*, the latter via bypass *7* reaches the receiving flask or the drain.

The sintered glass filter *A* placed in *3* serves as a support for the catalyst, whilst *B* is used to prevent the loss arising from the discharge due to the H_2 evolution.

Using this apparatus, we were able to register the circumstances of the dissolution, as well as to control the reaction of aluminium dissolution. The alkaline dissolution was performed as follows: The alkali solution was placed into *1*, and its temperature adjusted according to the chosen alkali concentration and experimental temperature. (Ice cooling or preheating) 50 g of Ni-Al alloy (composition: 48.1 parts/weight of Ni and 51.9 p/w of Al; particle size: passes through sieve No. 12, but is retained upon No. 30) was placed into the space *3*, followed by filling up the apparatus with water, under careful avoidance of any bubbles. Bypass *7* was then set to enable the alkali solution to flow out — equalizing the overpressure of the small amount of H_2 evolved during dissolution — but to prevent the escape of H_2. Water cooling of the condenser preceding the gas was started and a receiving vessel placed under the bypass.

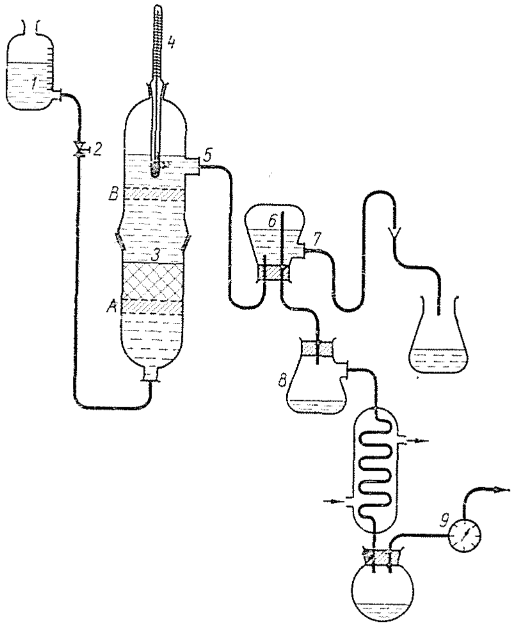

Fig. 1. Diagram of apparatus used for the preparation of the catalyst

Dosage of the alkali through *2* was started at a rate which permitted to keep the apparatus at constant temperature by means of external control (ice-water cooling or warm water bath).

After a unit volume of alkali solution has passed through, the readings of stop watch, thermometer *4* and gasometer *9* were recorded and the receiver of the outflowing alkali changed. Dosage of alkali was stopped, when no further hydrogen evolution could be read on the gasometer (this has been already indicated prior to the last reading by the sudden fall of temperature in the reaction space). The apparatus was then dismantled and the finished catalyst washed with distilled water until neutral reaction was reached. Hereafter water was replaced by absolute alcohol and the product stored in a powder bottle at room temperature.

Data of the catalysts prepared in the manner described appear in *Table 1.*

Table 1

Conditions of catalyst preparation

Sign of catalyst	Temperat. of prep. °C	Concentr. of alkali %	Alkali consumed litres	Time of preparation mins.	Evolved H_2, litres
½/75	75	½	11.2	320	24.500
½/90	90	½	14.0	345	27.500
1/22	22	1	21.0	314	21.250
1/41	41	1	14.0	246	24.740
1/61	61	1	13.0	229	25.120
1/61	61	1	13.0	229	25.120
1/82	82	1	10.0	182	25.780
1/92	92	1	10.0	181	27.100
2/20	23	2	7.0	207	21.500
2/43	43	2	3.5	127	25.300
2/60	62	2	4.0	112	27.500
2/82	82	2	3.5	113	28.200
2/90	92	2	3.5	126	29.300
5/20	20	5	4.8	162	22.300
5/40	40	5	3.3	120	26.540
5/58	58	5	2.5	70	26.780
5/78	78	5	1.7	60	27.660
5/94	94	5	1.3	59	28.200
10/22	22	10	3.9	169	24.800
10/40	40	10	1.8	79	26.200
10/60	60	10	1.3	58	27.600
10/75	75	10	1.3	41	27.460
10/90	90	10	0.7	37	27.100
15/20	22	15	4.0	170	25.700
15/42	42	15	2.0	87	27.940
15/60	60	15	1.5	47	27.500
20/35	35	20	2.0	76	25.700
sz/50	50	25	0.35	80	—

Testing catalyst properties

a) *Hydrogen content of the catalyst*

The determination was performed by quinone method [1].

b) *Measurement of potential*

Approx. 1/2 ml catalyst was placed into part *A* of the apparatus shown in *Fig. 2*, and covered with distilled water. After inserting the two electrodes (platinum and saturated calomel electrodes) — as illustrated — the potential of the catalyst was measured with a pH electrometer. Equal values were found for the potential both in distilled water and in a buffer solution of pH 7.*

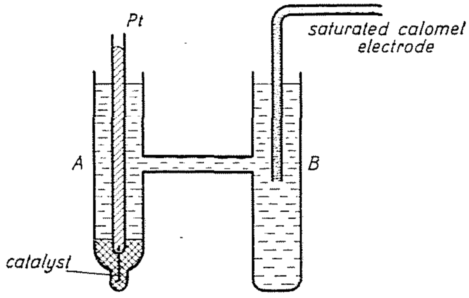

Fig. 2. Potential measurement of catalyst

c) *Measurement of activity*

Activity was measured upon acetone, benzyl-cyanide, eugenol and nitrobenzene models, in abs. alcoholic medium, at room temperature and atmospheric pressure in a shaker of 120/min speed. In each case the amount corresponding to 0.01 mol H_2 absorption (244 ml at room temp. and atm. pressure) was weighed in from the model substance. 1 ml catalyst (weighing approx. 1.5 g) was added and the total volume made up to 14 ml with abs. alcohol.

Determination of aluminate content in the alkali solution

Considering the respective quantities of the alkali which passed through the alloy and the hydrogen evolved, — the dissolution of aluminium appeared to be an inhomogeneous process. Hence in a few experiments the flowing-off alkali aluminate has been analysed by the turbidimetric method [3]. The method is based upon the following consideration: When acid is added to the alkali aluminate, the acid will neutralize first the free sodium hydroxide present in the solution. This being neutralized, the subsequent drop of acid will start the precipitation of $Al(OH)_3$. The transition point cannot be observed visually. Illuminating the titrating flask in a dark chamber by means of a strong, parallel beam of light from below, — in presence of a minute amount of fluorescein indicator — even a minimum of precipitate may be observed,

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* It should be noted, that the potential is not defined in the electrochemical sense. It is an index which represents the conditions developed upon the surface of the catalyst and its value will depend upon several factors (e.g. upon the amount of adsorbed NaOH, H_2 and substrate or end-product present on the surface, on the type of solvent used).

when looking sideways at the flask; the clear solution turns slightly white and hazy. The prescribed motoric stirring has to be omitted because of the glaring light scattering and was substitued by manual shaking. The end point, however, could be well observed within the limits of error and was determined by comparative test of a solution of known composition (where the calculated amount of acid required was 22.1 ml of N HCl against the measured requirement of 22.4 ml of N HCl).

The analysis was performed as follows: Depending upon the concentration of the alkali, — 5.0 to 50.0 ml of the formed alkali aluminate were transferred after straining into an Erlenmayer flask, using a pipette. Adding one drop of fluorescein indicator, the titration was carried out in dark with NHCl and the beginning of aluminium hydroxide precipitation observed in the manner described. Subsequently the titration was continued in daylight with phenolphtalein until decolouration. Another sample of similar volume was titrated — after addition of 50 ml saturated sodium fluoride -- in presence of phenolphtalein until loss of colour.

The following data may be obtained from the results of titration:

A = free NaOH (fluorescein indicator, until incipient precipitation)

B = bound NaOH (from start of precipitation to loss of colour of phenolphtalein)

C = aluminium (with NaF, until loss of colour of phenophtalein, $(A + B)$).

From the above data, the number of bound Na atoms corresponding to one aluminium atom is:

$$\frac{B}{C/3} = \frac{3B}{C} .$$

Thermogravimetric tests*

From among the catalysts prepared, the samples signed 2/20, 2/60, 2/90, 10/75 and 15/20 were tested by the derivatographic method [3] as well. These experiments were performed with the Paulik—Paulik—Erdey Derivatograph, Type No. 676 (produced by Orion-Gyem). The instrument measures simultaneously the weight change of the sample under test (TG), the rate of weight change (DTG), the change of its temperature and the change of enthalpy (DTA) due to the thermic (chemical and physical) transformations. The heating rate was 5°C per minute in each case. The experiments were performed in an argon atmosphere, heated to about 500°C and deoxidized over copper shavings. In order to exclude even traces of oxygen, the sample placed in the sample holding crucible of the derivatograph was covered with a layer of Al_2O_3, annealed at 1500°C. The crucible was covered with a lid and a quartz

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* The tests with the Derivatograph were carried out at the Institute of General Chemistry Polytechnical University, Budapest.

bell put over it. The samples were stored under alcohol. When the alcohol had evaporated from the samples soaked in alcohol and weighed-in for the test, — the explosion-like recombination of the hydrogen atoms sorbed upon the catalyst foiled repeatedly the performing of the test. Therefore the samples

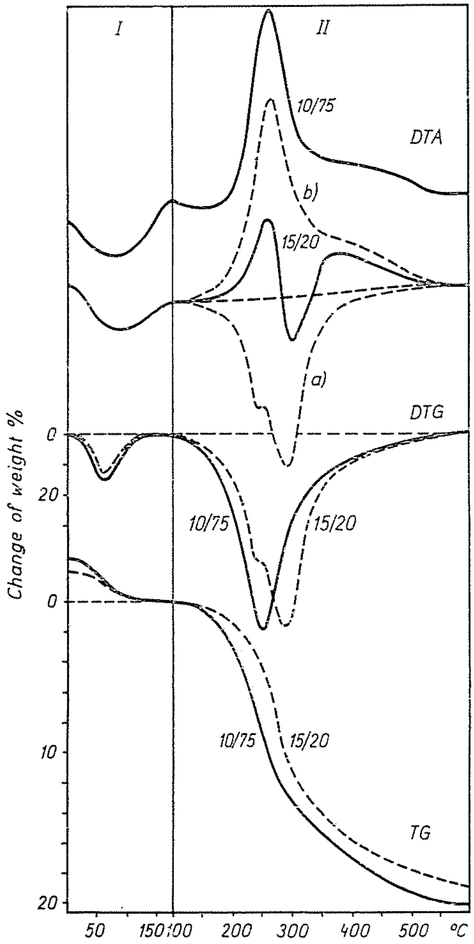

Fig. 3. Curves obtained in thermogravimetric analysis of catalysts prepared with concentrated alkali solution. Curve 10/75 — catalyst prepared with a 10% NaOH solution at 75°C. Curve 15/20 — catalyst prepared with a 15% NaOH solution at 20°C *a)* and *b)* are the graphic components of the resultant heat effect of catalyst 15/20

had to be prepared by a special heat treatment for the test: after distilling the alcohol off, they were covered with silicon oil. The pretreated samples were then heated to 180°C in the derivatograph and the weight- and thermal effects of the transformation measured in the mean time. The experimental data appear in the I. part of *Figs. 3 and 4*, and also in *Table 2*.

Except for the removal of adherent moisture (see in column *h* of Table 2) no characteristic transformation is indicated by the curves TG, DTG and DTA, which means, that under such conditions the removal of the adsorbed hydrogen occured smoothly, without any particular change in weight or heat content.

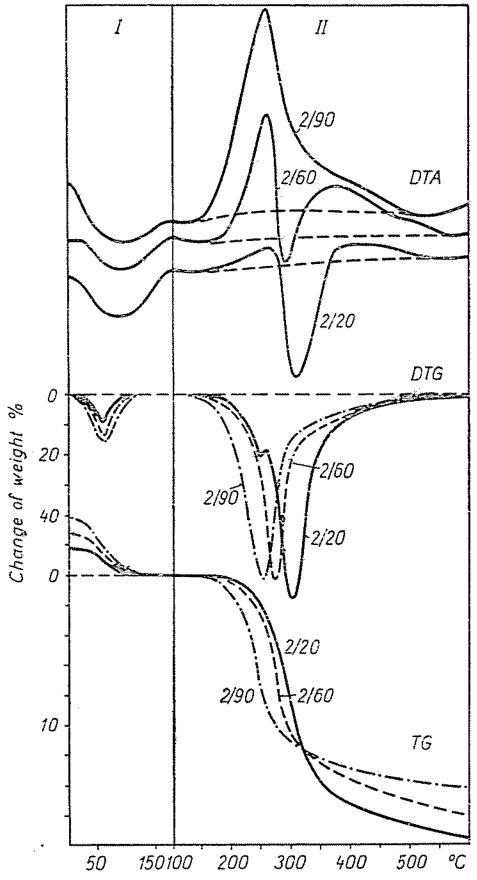

Fig. 4. Curves obtained in thermogravimetric analysis of catalysts prepared with dilute alkali solution. Curve 2/20 — Catalyst prepared with a 2% NaOH solution at 20°C. Curve 2/60 — Catalyst prepared with a 2% NaOH solution at 60°C. Curve 2/90 — Catalyst prepared with a 2% NaOH solution at 90°C

Hereafter the silicon oil was removed from the samples by repeated washing, and centrifuging first with benzol and finally with ether and subsequent drying. These heat-treated samples are no more pyrophoric at room temperature and retain their constant weight. Derivatograms of these pretreated samples are shown in the II part of *Figs 3* and *4*.

The data appearing in the columns *a* and *d* of the rows marked "anal." were obtained by classical gravimetric analysis. The values in column *b* are derived from the measurement of the volume of evolved H_2 during the alkali extraction of the alloy and from the knowledge of the initial Al content of the alloy. The data in columns *c* and *e* are evidently the same (because of the chemically bound Al in $Al_2O_3 . 3H_2O$). The above value corresponds to the difference of the data in columns *d* and *b*.

The data of columns *g* and *h* in the rows marked "deriv." are obtained from the derivatograms. Data in columns *c* and *e* are again equal because of the reasons mentioned. The values of column *b* are to be considered as the difference between the figures in column *d* of the "anal." row and those in column *e* of the "deriv." row.

Table 2

Composition of catalysts prepared under varied conditions with reference to the results obtained by derivatography

		Ni	Al			Chem. bound H_2O	Hydrargillite	Ni + Al Hydrargillite	Moisture	H_2 content
			Metal	bound	Total					
		%	%	%	%	%	%	%	%	ml/ml
		a	b	c	d	e	f	g	h	i
2/20	anal.	*42.5	*13.7	8.1	*21.8	8.1	23.4	79.6		
	deriv.		4.4	17.4		*17.4	50.3	97.1	*1.9	* 68
2/60	anal.	*51.0	*6.5	11.5	*18.0	11.5	33.2	90.7		* 99
	deriv.		2.3	15.7		*15.7	45.4	98.6	*2.4	
2/90	anal.	*56.1	*1.2	13.7	*14.9	13.7	39.6	96.9		*184
	deriv.		0.8	14.1		*14.1	40.7	97.6	*3.9	
10/75	anal.	*48.7	*5.3	12.7	*18.0	12.0	36.7	90.7		*144
	deriv.		−2.3	20.3		*20.3	58.6	107.3	*2.9	
15/20	anal.	*46.6	*8.6	9.4	*18.0	9.4	27.2	82.4		*100
	deriv.		−1.1	19.1		*19.1	55.2	101.7	*2.0	

In the apparatus shown in Fig. 1 aluminium-oxide-hydrate has been prepared separately as well. This was done by conducting the experiment under strictly identical conditions to those in the preparation of catalysts 2/60, 2/90 and 10/75, but replacing the aluminium alloy by pure aluminium. The precipitate was collected, washed, dried and tested in the derivatograph. (See derivatogram in *Fig. 5)*

Own experiments

Composition of catalyst as a function of its preparation

a) *Structure of aluminium hydroxide*

It is well known, that the ready Raney nickel catalyst always contains more or less aluminium, partly in the metallic, partly in the compounded form [4, 5, 6, 22]. The latter adheres strongly to the nickel surface and cannot be removed by washing. Very few data in literature refer to the relative proportion between metallic aluminium and that in compound form in catalysts produced under varied circumstances; or to the composition, or rather crystal structure [6] of the compound which is assumably aluminium hydrate.

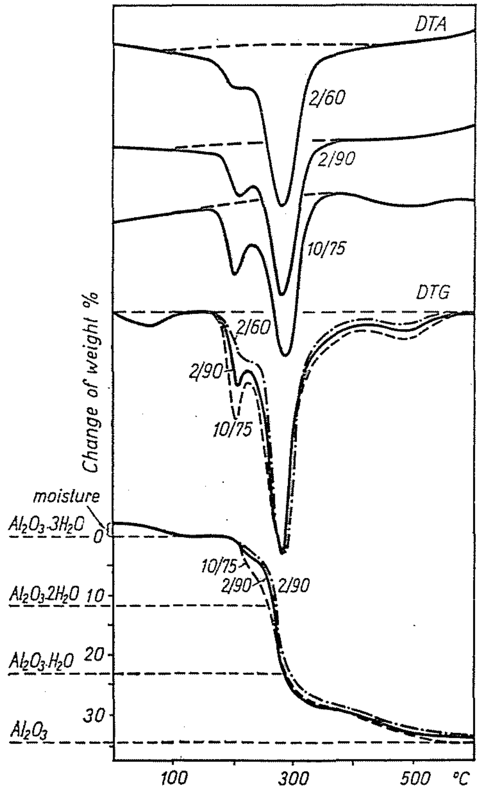

Fig. 5. Thermogravimetric analysis curves of aluminium hydroxide samples prepared from metallic aluminium under similar conditions as catalysts. Curve 2/20 — sample prepared with a 2% NaOH solution at 20°C. Curve 2/60 — sample prepared with a 2% NaOH solution at 60°C. Curve 2/90 — sample prepared with a 2% NaOH solution at 90°C

From the results of derivatographic [3] tests we could establish, that the aluminium compound precipitating during dissolution — consist mainly of hydrargillite in the cases tested. The products prepared by dissolving pure aluminium metal instead of the nickel-aluminium alloy — where of particularly high purity under the conditions of catalyst preparation (using a 2% NaOH solution at 60° and 90°, 10% solution at 75°) (Fig. 5). The bound water content of these products was found to be 32.9, 33.0 and 34.5%, against the 34.6% of water in pure Hydrargillite. The characteristic temperatures of the derivatographic curves obtained for these samples as well as the whole trend of the curves correspond with our previous experiences in thermic tests of hydrargillite [7, 8, 9] and also with data published by others. One may assume, that the lattice of the hydrargillite contained in the ready catalysts is not of a perfect, ideal order, it approaches the gel structure. This seems to be substantiated by the bound water content as well, which is slightly higher than the calculated amount.

The composition of the catalysts was calculated from the derivatographic tests, as shown in Table 2. In this table "negative" values of metallic aluminium content appear in certain cases, such as for catalysts 10/75 and 15/20. The thermal decomposition of these samples was drawn out through a wider temperature interval, which is a special characteristic of gel structure [7, 9]. In general, the composition and the crystalline structure of aluminium oxide-hydrates is influenced by the rate of precipitation and by the pH of the solution to a considerable extent [7]. The differences found in the composition of the samples tested are plausible, if one considers the many possible variations of the hydrogen ion concentration and of the rate of dissolution. This rate varies according to the changing conditions during the alcaline extraction, whilst the pH within the capillary system of the catalyst might vary because of the bad conditions of diffusion.

The results of the derivatographic tests pointed to the fact, that the greatest part of the structural water of the catalyst samples is bound in the hydrargillite. As we knew the nickel and aluminium content of the original samples from the determination by gravimetric analysis (columns *a* and *d* in Table 2.) and also the residual amount of metallic aluminium in the catalyst (column *b)* from the volumetric measurement of hydrogen during the alkaline dissolution, — we were able to calculate not only the amount of hydrargillite (column *f)*, but the total amount of the metallic nickel and aluminium plus the hydrargillite present in the catalyst (column *g)* as well from the extent of weight decrease of the samples (column *e)*. Those data of the table, which have not been marked with an asterisk [*], were calculated on basis of the measured data.

We made the same calculation based on the data obtained from the analysis of the catalyst and of the measured amount of H_2 evolved during its preparation (see Table 3). From the tables an approximative image may be drawn about the composition of an active, unchanged catalyst which has not yet been submitted to destructive analytical interference.

Table 3

Composition of catalysts prepared under varied conditions on basis of analysis and based upon the amount of hydrogen evolved

Sign of catalyst	1 Ni %	2 Total Al %	3 Metal Al %	4 Al in $Al(OH)_3$ %	5 $Al(OH)_3$ %	6 Hydr. upon Ni %	7 $\frac{Ni}{hydr.}$	8 1+3+5 %	9 Water %	10 H_2 content ml/ml cat.
2/20	42.5	21.8	13.7	8.0	25.5	60.0	1.7	81.7	18.3	68
2/60	51.0	18.0	6.5	11.4	36.3	71.1	1.4	93.8	6.2	99
2/90	56.1	15.0	1.2	13.8	38.7	68.9	1.4	96.0	4.0	184
10/75	48.7	18.0	5.3	12.6	40.1	82.3	1.2	94.1	5.9	144
15/20	46.6	18.0	8.6	9.5	30.5	65.4	1.5	85.7	14.3	100

Note: In arranging of the data, we have disregarded, that — particularly when alkalis of higher concentration are used — part of the aluminium may be present in form of $Na[Al(OH)_4]$.

According to the DTA curves, the catalysts lost the hydrogen adsorbed approx. 20° — 180°C, and the chemisorbed hydrogen between 200° and 500°C.

During the preliminary heat treatment — when the samples were heated to 180°C under silicon oil — the apparatus did not show any change in heat content, the weight change observed being due to loss of part of the moisture (part I in *Figs. 3—4.).* In the mean time the samples lost their pyrophoric nature. In this temperature interval no substantial amount of dissolved atomic hydrogen was lost, as the recombination of atomic hydrogen involves extensive liberation of heat. The recombination could only be observed at a far higher temperature, between 200° and 500°C. (See DTA curves in part II of the *Figs. 3—4.*) During this temperature interval, two simultaneous transformations took place: the hydrargillite decomposed involving an endothermic reaction, and at the same time the dissolved hydrogen was liberated with a substantial release of heat and then recombined. The DTA curves show the resultant of both heat effects. The probable trend of the two heat effects is specially marked by a broken line for the sample 15/20 in Figure 3. In plotting the endothermic maximum (curve *a)*) caused by the decomposition of hydrargillite, we took the maximum of the DTG curve which indicates decrease in weight as a basis, because it could be assumed, that the weight and heat effects of the thermic decomposition are running parallel. In the knowledge of the endothermic maximum and the resultant curve DTA, the exothermic maximum (curve *b)*) was constructed by difference-calculation. There exists a close relation between the magnitude of the maximum and the amount of dissolved hydrogen. The area limited by the curve is proportional to the amount of heat liberated, hereby the indirect determination of the amount of dissolved hydrogen is enabled. However to this purpose the apparatus has first to be calibrated and the measuring techniques are to be changed as well. But semi quantitative conclusions as regards the amount of chemisorbed hydrogen may already be drawn from the trend of the DTA curves. E.g. it may be noted, that in case of samples containing more hydrogen (column *i* in *Table 2*), the section between 200° and 500°C of curve DTA is shifted more towards the exothermic direction. The total hydrogen content of sample 2/20 was small and according to the DTA curve only a negligible portion of it was bound by chemisorption.

The greater the amount of heat liberated in course of the loss of chemisorbed hydrogen, the more the peak temperatures of the DTA curves seemed to shift in the direction of lower temperatures. The thermic decomposition of hydrargillite starts already at 200°C. Here the reaction is still a slow one; it reaches its maximum in the vicinity of 300°C. The thermic decomposition of each of the samples would have taken place at this temperature with a maximum of speed, if the simultaneous exothermic heat effect had not ranged the temperature spontaneously throughout the whole cross section of the samples in uniform manner. The trend of the thermoanalytical curves and with it the development of the peak temperatures is influenced to a great extent by the fall of temperature within the sample (due to rate of heating, to heat-conductivity of the sample, etc.) [10].

The thermograms also show, that the *loss of weight occurs only at about 200°C in the catalysts prepared with 2% NaOH, whilst those prepared with alkali solutions of higher concentration will loose weight already from 100°C upwards, which indicates the greater stability of catalysts prepared with isolate alkalis. (Figs 3,4.)* The greater the extent of aluminium dissolution, the lower the temperature at which the decomposition will reach its highest rate (DTG curves in *(Figs 3, 4)*.

From the thermogravimetric tests it may be concluded, that the aluminium compound present in the ready catalyst is a fairly well defined hydrargillite which is partly sorbed upon the surface of the nickel. This means that a smaller or greater portion of the nickel surface is covered. This is an inavoidable phenomenon which might be decreased but by no means fully stopped. The data in Table 2 point to it as well. They show, that using alkali of similar concentration (2%), the hydrargillite content (which cannot be expelled by washing) will increase with the relative nickel content, i.e. the freshly formed nickel surface will bond immediately and strongly the hydrargillite in quantities depending upon the experimental conditions. Part of the hydrargillite remains in the pores of the catalyst, in the vicinity of the place where it was formed and its relative amount increases with increasing Ni-content. The above as well as the fact, that depending upon the conditions of the experiment (concentration of NaOH, temperature) aluminium hydroxide can also reprecipitate upon the nickel surface from the solution — should draw attention to the importance of the method of preparation.

Those data of the thermogravimetric tests which show that the decomposition of hydrargillite and desorption of substantial amounts of hydrogen occur in general simultaneously in the range of 300°C point to a close interaction between nickel surface and hydrargillite.

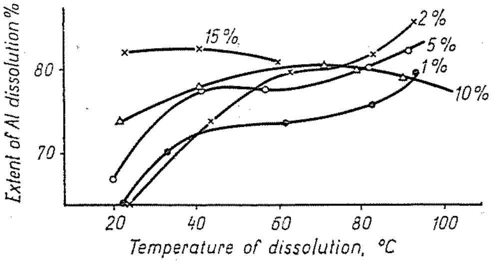

Fig. 6. The extent of aluminium dissolution as a function of reaction temperature in case of using 1—15% solutions of NaOH

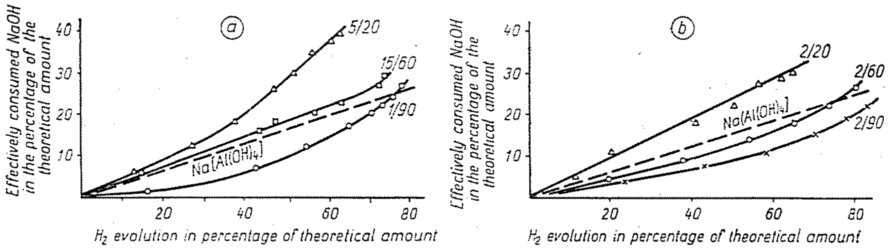

Fig. 7. The amount of NaOH solution consumed for the dissolution of aluminium in case of catalysts prepared as follows:

1/92 — with a 1% NaOH solution at 92°C
5/20 — with a 5% NaOH solution at 20°C
2/20 — with a 2% NaOH solution at 20°C
2/60 — with a 2% NaOH solution at 60°C
2/90 — with a 2% NaOH solution at 90°C
15/60 — with a 15% NaOH solution at 60°C

It seems likely that the phenomenon is due in part to the reaction between the sorbed water and the metallic aluminium, as also assumed by Mars and his coworkers [6].

b) *Dissolution of aluminium*

Using NaOH of varied concentrations, we studied the extent of aluminium dissolution as a function of temperature (dissolution has been regarded as completed, when the evolution of H_2 has practically ceased). The results appear in *Fig.* 6. The dissolution in weak alkali depends substantially upon temperature, but hardly at all, if more concentrated NaOH is used.

We also tried to establish according to what kind of reaction equation the process of aluminium dissolution takes place? According to references [11] $NaAl(OH)_4$ is formed from the metal if dissolved in NaOH, and this might convert by taking up 2 mols of alkali into the hardly stable compound of the formula $Na_3Al(OH)_6$. The equations are as follows:

$$\mathrm{Al + NaOH + 3\ H_2O = Na[Al(OH)_4] + 3\ H} \qquad (1)$$

$$\mathrm{Na[Al(OH)_4]}\begin{array}{l}\nearrow \mathrm{Al(OH)_3 + NaOH} \qquad (2)\\ \searrow \mathrm{Na_3/Al(OH)_6/}\ \text{(instable!)} \qquad (3)\end{array}$$

In order to clear the situation, the effective amount of NaOH consumed during the reaction was measured and equally the amount of H_2 evolved *(Fig. 7)*.

The results seem to show, that the process of dissolution can be mainly formulated by equation (1). However deviations can be observed which fall into two groups. One is characterized by those curves which run above the straight line $Na[Al(BH)_4]$ and which point to some occurrence of the reaction (3), involving high alkali consumption ($Na : Al = 3 : 1$), that is to say they indicate the growing amount of $Na[Al(OH)_4]$ adsorbed upon the catalyst. The curves below the line substantiate reaction (2) when less than the calculated amount of alkali is consumed, i.e. 1 mol of NaOH is capable to dissolve more than one atom of aluminium (hydrargillite is formed and precipitated). The results also prove — what can be read partly from the equations — that low temperature and great excess of alkali (more concentrated solution) will favour the reaction (3), whilst high temperature and a small amuont of alkali (weaker alkali) acts in favour of the reaction shown in equation (2).

As a control, the unchanged NaOH content of the alkali solution which has passed through the alloy was also determined *(Figs 8 and 9)*. The results sustain the above findings with the extension of showing clearly, that from the point of view of economical usage of alkali it is more favourable to work with a more dilute solution at higher temperature. Working at boiling point with a solution of 1 or 2%, 60—80% of the amount of NaOH calculated according to equation (1) will be sufficient *(Fig. 8)*; whilst from a more concentrated solution even the amount of over 200% will be insufficient to attain a similar extent of aluminium dissolution. (See also *Fig. 6)* (The amount sorbed is greater and more of the alkali remains uncreated.)

The rate of hydrogen evolution during the dissolution of aluminium (directional tangent of the linear section of the curves showing the hydrogen evolved during the reaction period) is illustrated in *Fig. 10*. The increase of reaction rate with increasing alkali concentration, as well as the uniformity of the reaction in case of dilute alkali are quite apparent.

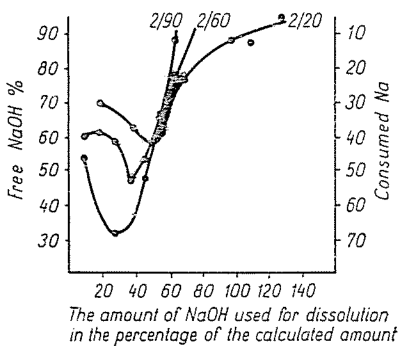

Fig. 8. Analytical diagrams of the outflowing — "used" — NaOH solution in case of catalysts prepared as follows:

2/20 — with a 2% NaOH solution at 20°C
2/60 — with a 2% NaOH solution at 60°C
2/90 — with a 2% NaOH solution at 90°C

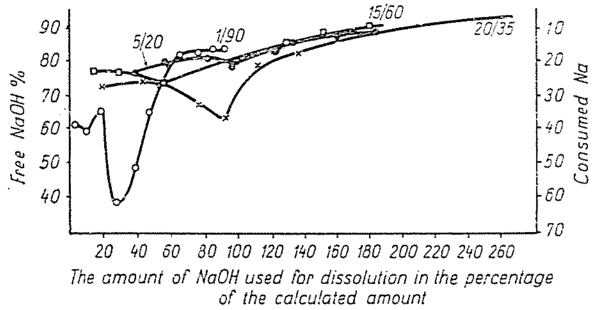

Fig. 9. Analytical diagrams of the outflowing — "used" — NaOH solution in case of catalysts prepared as follows:

5/20 — with a 5% NaOH solution at 20°C
15/60 — with a 15% NaOH solution at 60°C
20/35 — with a 20% NaOH solution at 35°C

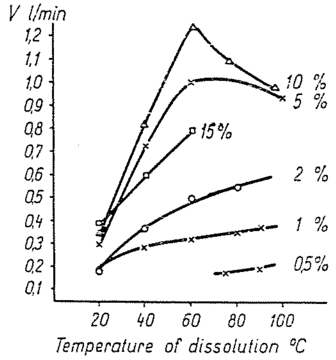

Fig. 10. The rate of hydrogen evolution as a function of temperature in the reaction of aluminium dissolution in case of using alkali solutions of 0.5—15% concentration

c) *Hydrogen content of catalysts*

The hydrogen content of catalysts in relation to the temperature of aluminium dissolution is shown in *Fig. 11.* Using dilute alkali solution, the raising of temperature corresponds to enhanced dissolution of aluminium, i.e. to the increase of the nickel surface. *(Fig. 12.)* The hydrogen content of these catalysts is proportional to the nickel surface. The required degree of aluminium dissolution can already be reached at room temperature or around 40°C by using concentrated alkali. Hence the hydrogen content as a function of temperature cannot be explained in a simple way; H_2 content as a function of Al dissolution may be described by curves passing through a maximum. At temperatures above 80°C the hydrogen content decreases, presumably because of the change in structure (i.e. because of increasing alkali adsorption).

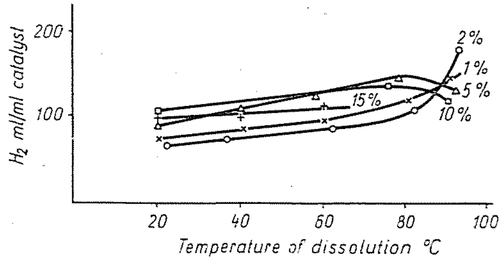

Fig. 11. Hydrogen content of catalyst as a function of the temperature of preparation with NaOH solutions of 1—15% concentration

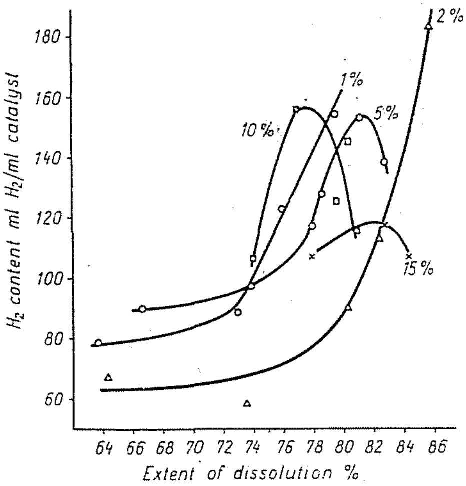

Fig. 12. Hydrogen content of catalyst as a function of the extent of aluminium dissolution with NaOH solutions of 1—15% concentration

Potential of catalyst

Among catalysts of similar hydrogen content, those prepared with more concentrated alkali will have a higher potential *(Fig. 13)*. Accordingly the potential of a catalyst will depend not only on its hydrogen content: the sorbed amount of alkali which can be washed out only with great difficulty or often not all plays also an important role (the amount of sorbed alkali increases with rising concentration).

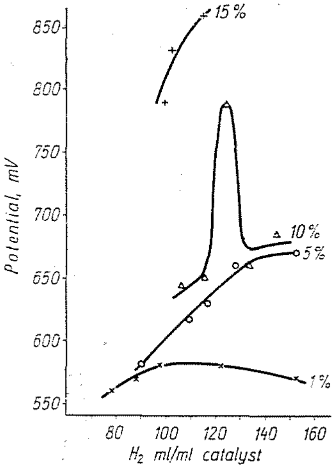

Fig. 13. Variation of catalyst potential with its hydrogen content, with NaOH solutions of 1, 5, 10 and 15%

The observation that in case of dilute alkali the potential is almost independent from the total hydrogen content of the catalyst appears to be of great importance. The sensitivity of the potential towards variation in the hydrogen content is in direct relation to the concentration of the alkali solution used in preparing the catalyst.

At a given alkali concentration, the potential will also depend upon the temperature of preparation. The potential increasing effect of the temperature may be well observed in case of more concentrated alkali solutions (E.g. 10%) — where the increase of temperature is not proportionate to the increasing surface of the nickel *(Fig. 14)* — and may be due to the stronger adsorbtion of the alkali.

Fig. 15 illustrates the potential as a function of the extent of aluminium dissolution. The greater complexity of the functions obtained with more concentrated alkalis is again apparent.

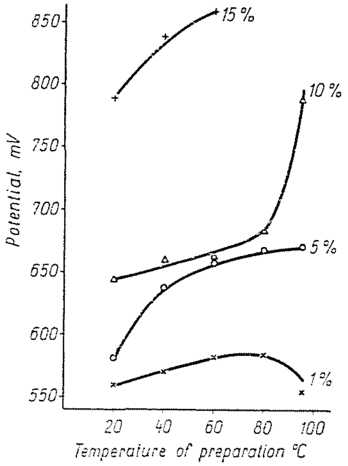

Fig. 14. Catalyst potential as a function of temperature of preparation with NaOH solutions of 1, 5, 10 and 15%

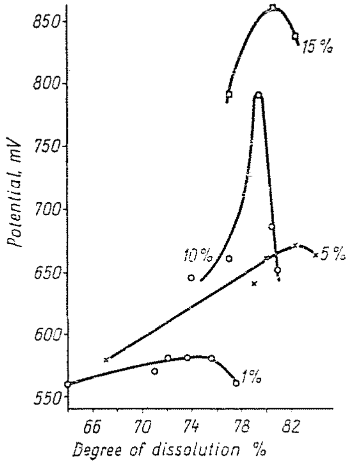

Fig. 15. Variation of catalyst potential with the degree of aluminium dissolution with NaOH solutions of 1, 5, 10 and 15%

Activities

We also studied the development of catalyst activity as a function of the extent of aluminium dissolution. Two major results emerged: a) With alkali solutions of a concentration below 2%, the activity increase is almost a linear function of the extent of dissolution (i.e. of the growth of the nickel surface) [see *Fig. 16. a) — d)*]. b) No such simple relation may be observed with alkalis of higher concentration [see *Fig. 17 a—d)*]; the trend of the activity curves are very similar to those of the corresponding potential curves (compare with Fig. 12), indicating the enhanced role of the potential.

The relation between the activity and hydrogen content of catalysts prepared with dilute alkalis is equally simple *(Fig. 18. a—d)*. The trend of the activity curve of the catalyst prepared with the 10% alkali solution also resembles the corresponding potential curve *(Fig. 19 a—d*, compare with Fig. 13). The relation becomes simple if the activities are represented as function of the potential, Which again indicates the substantial influence of the potential upon the activity of catalysts prepared with alkali solutions of higher concentration. The fact appears to be due to the sorbed alkali.

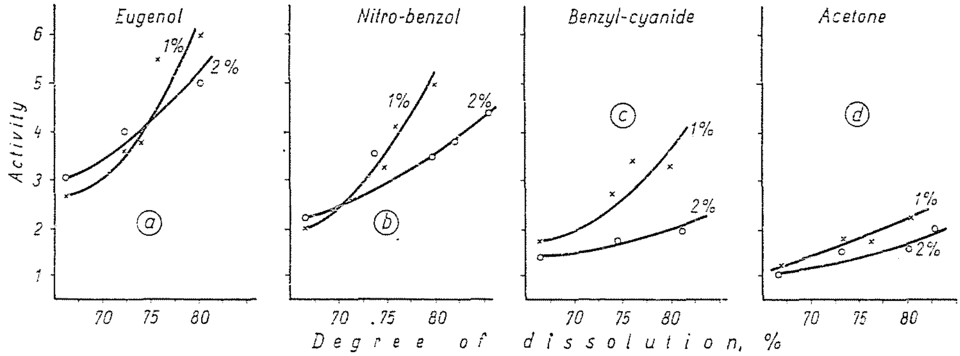

Fig. 16. Catalyst activity as a function of aluminium dissolution, when dissolving with NaOH solutions of 1 and 2%, demonstrated upon *a)* eugenol, *b)* nitrobenzol, *c)* benzyl cyanide, *d)* acetone models

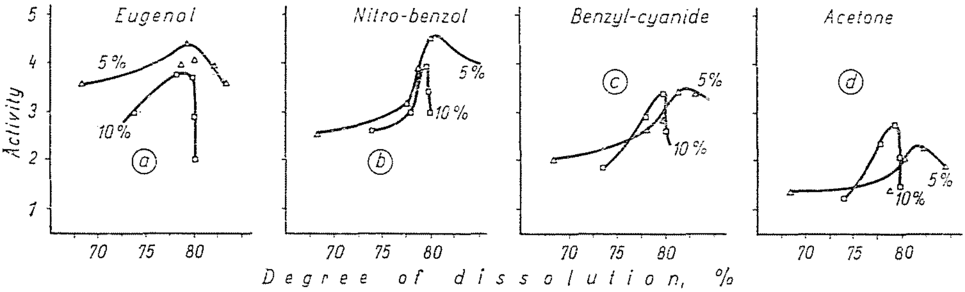

Fig. 17. Catalyst activity as a function of aluminium dissolution, when dissolving the Al with NaOH solutions of 5 and 10%, demonstrated upon *a)* eugenol, *b)* nitrobenzol, *c)* benzyl cyanide, *d)* acetone models

All these data seemed to indicate, that catalysts prepared with dilute alkali in the manner described should be more reproducible than those prepared by traditional methods.

In order to illustrate this supposition, the catalyst with 1% alkali solution was prepared five times in succession and that with alkali of 2% concentration four times. The characteristics of the catalysts, respectively of the catalytic reaction were tested and listed in *Table 4.* The values shown in the first column of the table were measured about 2 months earlier than those appearing in the other columns.

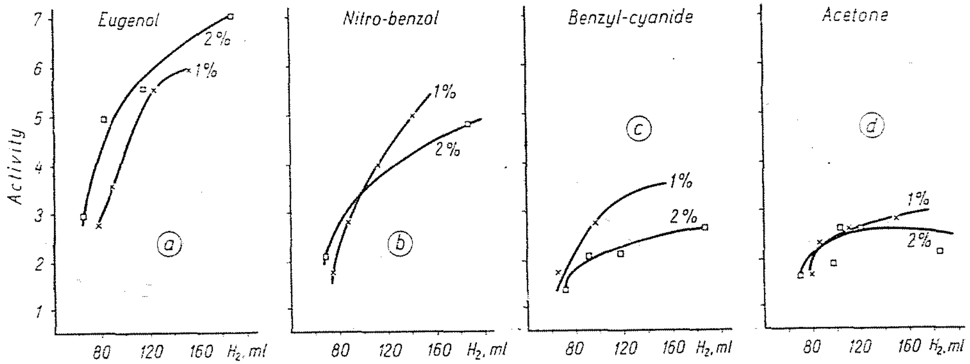

Fig. 18. Catalyst activity as a function of its hydrogen content (dissolving the aluminium with NaOH solutions of 1 and 2%); demonstrated upon *a)* eugenol, *b)* nitrobenzol, *c)* benzyl cyanide, *d)* acetone models

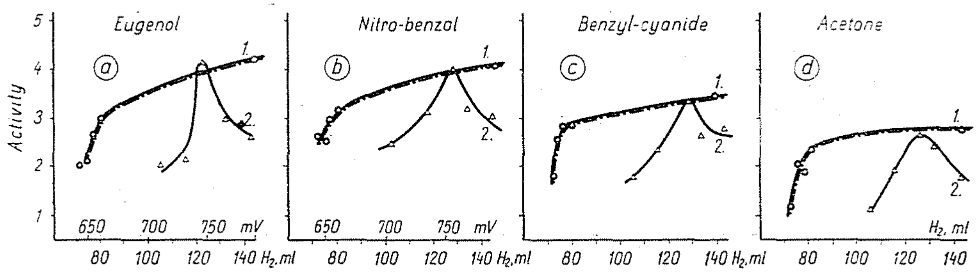

Fig. 19. Catalyst activity as a function of hydrogen content (curve 1) and of potential (curve 2) when prepared with a 10% solution of NaOH. Demonstrated upon *a)* eugenol, *b)* nitrobenzol, *c)* benzyl cyanide, *d)* acetone models

The deviations in activity are relatively small and exceed only slightly those originating of experimental errors. In case of the catalysts prepared by the previous method, out of an average of 20 catalysts, the activities obtained upon the individual models vary — with the exclusion of the most extreme cases — between the following values: 5—15 upon eugenol, 3—6 upon benzyl cyanide, 3—5.5 upon aceton, 2—6 upon nitrobenzol. In case of catalysts prepared by the traditional method (with 20% NaOH, and with additional 50 minutes' aluminium dissolution at 50°C, after the dosage of the alloy into the alkali solution even) two — threefold variations could be observed as regards activity values.

Table 4

Reproducibility of catalytic activity in case of catalysts prepared four and five times in succession using alkali solutions of 1 and 2% conc. at 80°C

Substrate	Method of catalyst preparation*	Activity: Absorbed H_2; ml/min					H_2 content of 1 ml catalyst, ml				
		1	2	3	4	5	1	2	3	4	5
Eugenol	2/80	5.6	5.0	6.0	6.6	—	113	102	108	140	—
Nitrobenzol	2/80	3.7	4.4	5.1	5.1	—					
Benzyl-cyanide	2/80	2.3	2.9	3.0	3.1	—					
Acetone	2/80	2.1	2.0	2.4	2.7	—					
Nitrobenzol	1/80	4.2	4.2	4.3	4.2	4.4	122	90	89	89	96
Benzyl-cyanide	1/80	3.5	2.8	3.2	2.9	3.2					

* The numerator of the fraction shows the concentration of the alkali solution, the nominator gives the temperature of preparation.

Table 5

Data of catalysts having a similar hydrogen content

Sign of catalyst	Conc. of NaOH, %	Temp. °C	H_2 cont. ml/ml cat.	Potential mV	ΔH_2 mlH_2/ml catalyst			
					Eugenol	Nitro-benzol	Benzyl cyanide	Acetone
1/80	1	80	122	580	29	12	19	14
5/40	5	40	114	640	20	8	36	6
10/60	10	60	115	650	2	5	1	—33
15/60	20	60	114	860	39	7	13	3
1/90	1	90	152	550	34	50	42	49
5/78	5	78	152	670	5	—1	1	—21
10/75	10	75	144	685	45	31	49	34

Strength of hydrogen sorption

According to the literature [13—15] as well as to our own earlier tests [12,16] the hydrogen content of the catalyst varies or might vary even during catalytic reaction due to the chemical structure of the unsaturated compound or because of the experimental conditions. This is to say, that the reduction may occur to a greater or smaller degree also with the hydrogen sorbed upon the catalyst. The difference between the hydrogen content of the fresh (initial) catalyst and that of the catalyst after the reaction ("used") is marked by ΔH_2. This difference is positive, if the initial hydrogen content increases and negative on its decrease. The ΔH_2 values were measured upon catalysts of almost equal initial hydrogen content but which had been prepared by means of alkali solutions of varied concentration. The test was performed subsequent to the reduction of the model compounds mentioned and under the same experimental conditions. Hence the values of ΔH_2 can be assumed as being proportional to the strength of hydrogen sorption. From the data listed in *Table 5* it appears that in case of a rising potential (larger amount of sorbed alkali) the strength of hydrogen sorption increases initially (the value of ΔH_2 increases towards the positive values) in agreement with earlier observations published by SOKOLSKIJ [14]. On further rising of the potential, however, the strength of sorption will decrease, confirming our earlier observations in case of increasing alkali adsorption [17].

Evaluation of results

From our experimental results two factors appear to be predominant among those determining the catalytic properties of the Raney nickel: the potential of the catalyst and the available nickel surface. The potential reflects the nature of the solid-liquid interface, — the importance of which in catalytic hydrogenation in the liquid phase is more and more stressed by several experts [20, 21]. The importance of the available nickel surface lies in the proportionality which exists between the surface of the catalyst and its activity. In case of Raney nickel this availability is primarily determined by the amount of hydrargillite retained upon the surface during its preparation (in course of the aluminium dissolution), but depends also upon the microcrystalline (porous) structure of the nickel.

Hence it is to be considered how the conditions of the preparation of the catalyst — the concentration of the alkali and the temperature applied — will influence the above factors, i.e. which conditions will ensure the best reproducibility?

The roles of alkali concentration and temperature cannot be completely separated, for the sake of clearer understanding, however, they have to be evaluated individually.

The concentration of the alkali is perhaps the more important, as this has a substantial influence upon both the potencial and the nickel surface. If dilute alkali (1—2%) is used, the amount of Na^+ ions sorbed upon the surface of the catalyst is small, the value of the potential is equally small and will hardly depend upon the temperature of preparation; only a small of hydrargillite will adhere to the ready catalyst, which means also the available nickel surface, to which in this case the hydrogen content of the catalyst is proportional. According to literature [18], the microcrystalline structure is equally more favourable than in case of usage of concentrated alkali. The activity of catalysts prepared in this manner has been found proportional to the available nickel surface (to the amount of dissolved aluminium) — when measured upon a few different functional groups.

The simple relation between the above parameters, i.e. the hardly noticeable dependence of the potential upon the temperature, — may be regarded as favourable indications for the reproducibility of the catalyst.

Using alkali of higher concentrations, the potential shows a steep increase, and its value becomes indefinite — particularly above 60° — and cannot be reproduced easily. This phenomenon is related to the increased alkali adsorption caused by the high alkali concentration, which may vary widely within a relatively temperature interval. In our opinion, the most important obstacle of reproducibility is this fast reaction being apparently not at eqilibrium and changing sensitively even on minute variations of the experimental circumstances. Alkali is continuously desorbed from catalysts during storage, hence the potential will also change during storage. Besides the amount of hydrargillite retained upon the catalyst is also higher, if a more concentrated alkali solution has been used.

The potential of the Raney Ni is determined chiefly by its alkali content (and only in second place by its hydrogen content). This alkali amount plays a substantial role in the nature of the interface layer and influences the strength of the Ni-H bondage.

If dilute alkali is used, the temperature plays its part mainly in ensuring the required degree of aluminium dissolution. The effect of more concentrated alkalis is much more complex and may exercise a sensitive influence upon the potential of the catalyst as well. The activity curves of catalysts prepared with more concentrated alkalis have a similar trend to the corresponding potential curves.

All this facts show that Raney nickel catalysts should be prepared with dilute alkali solution (1—2%) around the boiling point of the alkali solution, and not—according to the hitherto generally accepted method — by means of concentrated alkalis (approx. 20%). The usage of concentrations below 1% is (because of the great volumes required) of disadvantage.

Among others, this is also avoided during the continuous process of dissolution which we have developed. It has three important advantages: a) the volume of the apparatus required for catalyst preparation can be reduced; b) the concentration of the sodium aluminate and aluminium hydroxide formed during the dissolution of the aluminium remains always low and therefore the precipitation of considerable amounts upon the surface of the catalyst is unlikely; c) during the traditional process of preparation the alloy is added gradually to the alkali. Considerable time passes between the dosage of the first and last portion, whilst the end point of catalyst preparation is the same for each dose. Consequently the period of contact with the alkali, the extent of aluminium dissolution, the potential, etc. will be different for each portion, resulting in an inhomogeneous catalyst, which cannot be easily reproduced. During continuous dissolution the whole of the alloy remains in contact for the same period with the alkali and always with fresh alkali solution, accordingly the catalyst obtained will be homogeneous and relatively well reproducible.

Adventages of applying dilute alkali solutions: a) much better reproducibility (the relations between activity and potential, extent of aluminium dissolution, etc. characteristics are relatively simple); b) less alkali is required to achieve a similar extent of aluminium dissolution; c) the reaction of aluminium dissolution is less vehement, it is uniform and can be controlled with greater ease.

The investigation of the mechanism of catalyst preparation, together with that of the chemical reactions involved has received much less interest hitherto than it deserves. Knowledge of such information enables to distinguish between the factors which have a beneficial or adverse effect upon activity and catalytic properties. Hereby reaction techniques can be established which ensure a better chance to produce catalysts of optimum effect and more constant quality. It would also be important in creating a possibility for a wider generalization and practical application of results achieved by various investigators, if they could start with well defined catalysts in their research work. This is rarely the case at present; research workers usually prepare their catalysts on basis of a formula described in literature and perform their catalytical experiments herewith. If the method of catalyst preparation is not sufficiently exact, a factor of great uncertainty may be introduced already initially into the results. This — in an extreme case — can prevent the extension of the results obtained with the catalyst in question to a reproduced catalyst sample and finally deviate the evaluation of the whole catalytic reaction into the wrong direction.

Summary

1. We have investigated the chemical and physical reactions involved in the preparation of the Raney nickel catalyst. We have established the role played by the alkali and the nature of the products formed with the alkali. According to thermogravimetric tests, the aluminium hydroxide formed will be sorbed upon the freshly developed nickel surface as hydrargillite, most likely in the shape of aggregates.

2. We have attempted to find relations between the conditions of catalyst preparation and the catalytic properties. Based upon the knowledge of the mechanism of the reactions occurring during the preparation, we have established relations between the nickel content set free from the alloy, the hydrargillite content and the potential of the ready catalyst. According to our investigations the activity of the catalyst is primarily related to its potential.

3. We have found —as distinct of hitherto applied techniques — that the dissolution of the aluminium from the alloy can be achieved with optimum result by a continuous process with dilute (1—2%) alkali solution around the boiling point. Activities of the catalysts prepared in this manner are not inferior to those of catalysts prepared by the traditional method and their reproducibility is better.

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