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RESEARCH AND PRODUCTION OF CATALYSTS[1/]

by

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I.- INTRODUCTION

The chemical and petrochemical industry in Romania has developed considerably in the last two decades. There is an important production of fertilyzers for agriculture, especially with nitrogen, plastics, s ynthetic fibres, ethylene oxide, glicols, phthalic anhydride, phenol,etc.

Refinery of petroleum also produces important quantities of petrol with high octan number (90 - 100), of aromatics hydrocarbons - benzene,xylenes, ethylbenzene, row materials for the petrochemical industry.

This great and varijed production, is conditioned as it is known, of the use and of the highest valorification of catalytical proocesses and especially of heterogeneus catalytical processes.

These reasons have imposed in our country the development of complexe researchs in the field of solid catalysts and heterogeneous catalysis, and also the organisatio on of some branches of science and laboratories in the universitary education, for the training of the personnel necessary to these activities.

In 1950 was set in our contry the first economical plan, in the same year I have organisied the first research collectives in the field of heterogenous catalysis, at the University of Bucharest - chair of chemical technology and catalysis and at the Institute of Petroleum researches (IPP) functioning then in Bucharest too.

Today there exist in our contry a whole network of research groupes, which co-operate between them and

discusses the plans of researches.

Thus, within the Ministry of Education are working three strong research groups at the University of Bucharest; at the Centre of Physical Chemistry and at the Institute of Petroleum, Gas and Geology. Less strong groups are working at the University of Cluj and Timişoara.

Within the Ministry of Chemical Industry are functioning research branches specialized in the technology and engeneering at the Institutes PETROCHIM Ploieşti, I.C.P.T.P.T. Ploieşti, CHIMICAZ Mediaş.

To these are joining the specialized collectives from the chemical Combinates, which manufacture catalysts (Chemical Combined Group of enterprises Craiova, the Industrial group Borzeşti, as well as those using catalysts and especially at the petrochemical Industrial Group of Ploieşti and the Industrial Group of Piteşti.

As "catalysis" is an interdisciplinar science, in the last year have developed researches in the Institutes of Physics in Bucharest and Cluj. The researchers in these Institutes co-operate with chemists and technologs.

The research activity in the Ministry of the Chemical Industriy as well as applied research in the ministry of Education is co-ordinated by the Central Institute of research in the Ministry of Chemical Industry and by the National Council of Science and Technology.

The researches collectives have on principle an own structure determined by the researchers's experince and interest, by the material posibilities and especially by the guiding lines of development of the Industry

and by the necessity to ensure a technic-scientific potential for the future.

The researches carried on in Romania in the field of catalysts and catalysis may be grouped in the following direction :

a.- the setting of some relations between the chemical composition, the preparations conditions, the physical and chemical properties, with the activity and selectivity of catalysts in specific reactions or determined ones.

A further aim of this field of activity is also the idea of elaboration of some criteriums to appreciate the performance and to select the catalysts.

b.- The improvement of the existent technologies and the elaboration of new technologies for processes and manufacturing of catalysts.

c.- the mathematic modelling of the catalytic processes and problems of catalytical engineering.

The entire present and future activity of our collectives is contained in this general topic.

In the following we are going to present the methodology of the elaboration of industrial catalysts and then the stade of the manufacturing of catalysts in Romania. This because the problems of the manufacturing and of the use of catalysts in the industrial reactors have generated many times our orientation and our research topics.

We use the opportunity to mention - as exemples- some results of the applied researches elaborated especially in the University laboratories and in the laboratories of the Center of Physical Chemistry.

II.- ELABORATION METHODOLOGY OF INDUSTRIAL CATALYSTS.

The elaboration methodology of industrial catalysts, in the idea of our researches is referring to a complex activity of research and experience on different stages (scheme fig.1):

a) we call the first activity conception research of laboratory, the finalization of which is the technologic process of laboratory

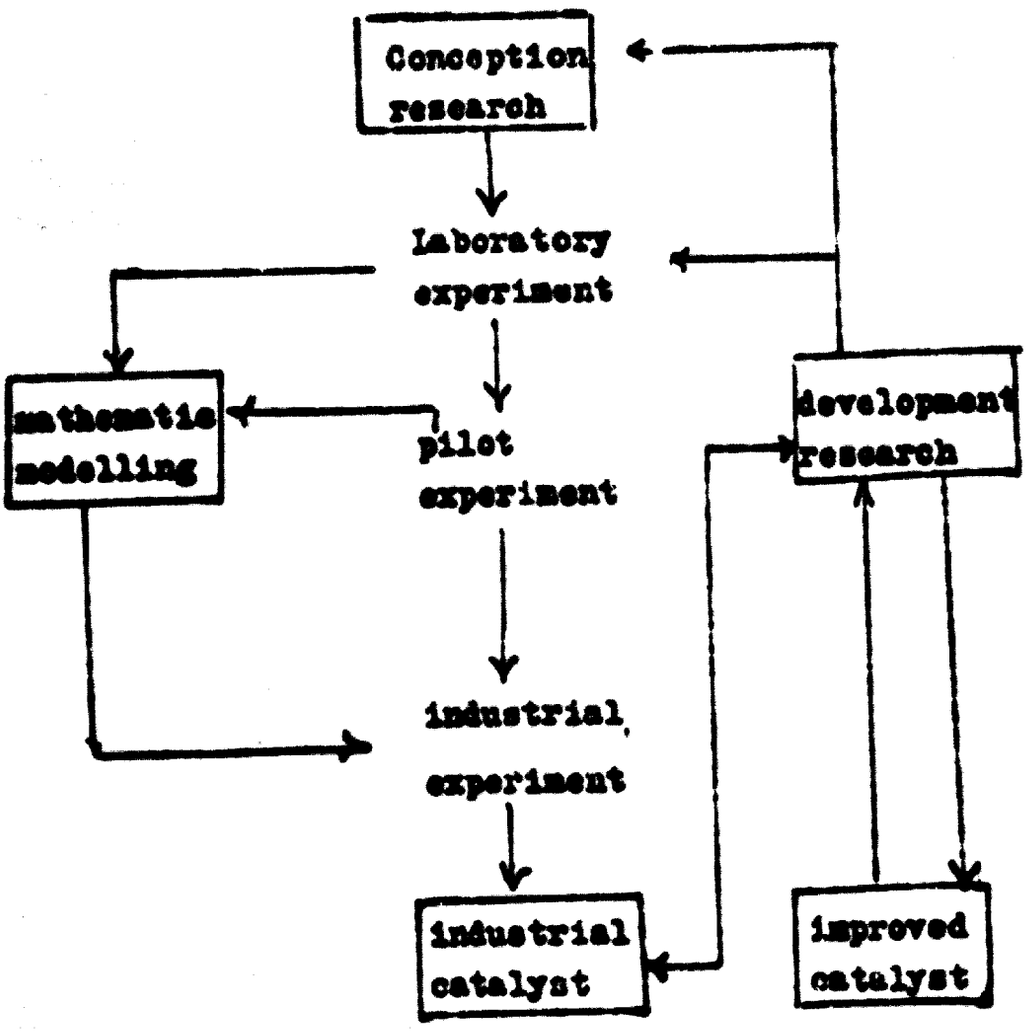


Figure 1

Methodology of elaboration and improvement of industrial catalysts.

This activity is dependent on the knowledge, experience, intelligence and inspiration of the researchers, on the material basis of the laboratory, of the ability to use the electronic computers.

The conception research comprises the choise of active components, the conditions and preparation technic of catalyst, the study of the physical, textural, structural properties of catalyst, the analyses of the thermodinamical paramters of the test reaction, the fixation of the kinetics parameters with a view to determine the activity and the selectivity of the catalysts in test reactions which are specific to its use in practice.

On basis of the results got in laboratoy, there is elaborated a first optimisation of the synthesis technic of the catalysts and of the specific chemical process.

The activity is continued in the pilot instalation on two directions, preparation pilot and process pilot. By this occasion there are cheked and completed the macrokinetics parameters diffusion, mass and heat transfer, there are specified the yields, the balance of materials, the purity of main product, as well as other characteristics necesary to the designers.

In the case of catalysts less pretentious having a functioning life of 1 - 2 years it was eliminated the bulding of some pilot plants, by introducing the pilot reactors in the circuit of industrial plant. This method presents besides economic advantages, the advantage that the catalyst is experienced in the conditions of the industrial process and in contact with

the same raw material.

b) The transposition of the preparation technology of catalysts of pilot plant (100- 150 Kg) in industrial plant sometimes creates difficulties and surprises, which are not very big.

In exchange the transposition of the results from pilot plant to industrial plant concerning the catalysts life, its activity, its poisoning creates more serious difficulties, needs longer time, possible production reductions and consequently important expenses.

These difficulties are due also to the fact that the change of the shape in dimensions of the reactors thoroughly modify the concentration of the raw material on the length of the layer of catalyst, as well as the intensity of the mass and heat transfer. The classic theory of similitude doesn't solve the matter.

The progress in the catalytic engineering and the disponibility of the electric computers has made possible the use of the method of mathematic simulation by the transposition of the results from pilot plant or laboratory directly in the industrial reactor.

c) The catalyst having succeded in the experimental industrial conditions may be considered an „industrial catalyst" . From that moment begins the "<u>development research</u>" which aim is to continuously improve the catalyst. The development research can refer anew to the conception research in laboratory or in pilot.

On the whole the creation and development research must dispose of all factors determining and conditioning the catalyst performance according to the scheme of

interdependence shown in figure 2 and which is followed up in our researches.

The chemical composition, the nature of active components and the preparation tehnic determines both the cost of the catalyst and the textural and structural characteristics, the whole surface geometry and also the energetical potential of the surface. Thewh whole of these properties generates during the chemical process - by the contact catalyst - reactant - the active stadies of the catalyst which we conventionally call catalyst properties.

From our works as from those of other researchers, it has come out that the structural,textural properties, the physe composition, the valence degree of active components are very different to those of the catalyst formed during the reaction, in the functioning conditions of the chemical process.

A significant example of the mentioned points of view is presented by the studies of the catalyst used in the synthesis of ammonia.

In figure no.3 we have shown the difference between the pores size distribution of an industrial catalyst before reduction and reaction (curve 1) and of the catalyst after reduction and reaction(curve 2). The surface area increases five times in the case of the reduced catalyst.

Figure 4 describes the electric conductibity isotherms of an industrial catalyst for the ammonia synthesis, made in medium of synthesis gases (N_2+3H_2) and of nitrogen pure, at a temperature of 500°C.

When the initial catalyst, nonreduced, is in contact with the reactant, the electric conductivity increases considerably, prevailing the donor and dissociative chemisorption of hydrogen.

After twelve hours' time ammonia is produced. That time was necesary for the forming of the actives centers during and in the reaction conditions. The electric conductivity remains still practicaly constant.

At point two there is introduced pure nitrogen. The electrical conductivity decreases (point three) and remains constant (point four).

In this case the accepting chemisorption of nitrogen is revealed.

Again the gas wynthesis is introduced (point four), the electric conductivity increases and ammonia is directly produced.

This method first initiated in our laboratory shows the differenciate interactions of the reactions components with the catalyst, the necesary time for the forming of the active centers on the surface and also gives information concerning the reaction mechanism.

The scientific and economic efficiency of the research activity of the groups in the Universitary units may be materialized as follows :

- the chemisorption researches concerning the dispersion and the size of surface area of the active components Pt, Pd have pointed out the preparation conditions of the catalysts, the relations with the activities in the aromatization process of petrol and for selective hydrogenation.

- studies concerning the Mössbauer effect, X Ray determination, thermodifferential analysis, I.R. and R.E.S. spectral determination, have lead to establish some rules for the preparation of catalysts, to define the phases and the active centers on the surface.

The results yelded by this researches have been especially useful for the appreciation of the correspondance relations between composition, preparation and catalytic activity, in the case of the used catalysts for the oxidation and synthesis of methanol, hydrodesalkilation of toluene, dehydrogenation of butane-butenes.

Some catalysts studies by our research groups, are produced by industry, as the desulfurasition catalyst and the catalyst for the methanization of carbon monoxide present in pyrolysis gases.

These works have been elaborated in co-operation and with the help of the Ministry of Chemistry, Industrial Group Brazi, Institutes PETROCHIM, CHIMICAZ and Chemical Combined Group of enterprises Craiova.

III. CATALYSTS MADE IN ROMANIA

The catalysts manufactured in Romania are comprised in chemical Combined Groups of speciality.

So, at the Chemical Combined Groups fo enterprises in Craiova, it has been set up a plant for the manufacture of catalysts destined the fertilizers industry and the annex manufactures.

Another plant has been set up at Petrochemical Group Borzesti, where are being manufactured catalysts used to the synthesis of monomers, necesary to the synthetic rubber and styrene plants.

The catalysts now manufactured are mentioned in table no.1.

Table no.1

No	Production	Crt. no	Process
I	Ammonia industry	1	first and second reforming
		2	desulfurization
		3	CO conversion high temperature
II	Synthetic rubber and styrene	4	butane dehydrogenation
		5	butene dehydrogenation
		6	alpha-methylstyrene-synthesis
		7	ethylbenzene dehydrogenation
III	Monomers, petrochemical synthesis	8	vinyl chloride
		9	vinyl acetic ester
		10	butyl alcohol
		11	CO methanization of the pyrolysis gases
		12	fatty acides hydrogenation
		13	alkylation of cumene
		14	diethylbenzene dehydrogenation
		15	2 - ethylhexanol synthesis

The research laboratories of the plants, in co-operation with the Institutes of the Ministry of Chemistry are carrying on researches for the improving of the manufacturing and exploitation technologies from point of view of performances and of the price of cost.

IV.- PERSPECTIVE RESEARCHES

In the last years our collectives are granting a especial atention to the researches concerning the mixdd oxidic catalysts used in oxodehadrogenation reactions of hydrocarbons and the active aluminas.

Diens production and particularly, butadiene production, increased very much in the last decade, by construction of new plants for catalytic dehydrogenation of butane-butenes, as well as by separation and purification of butadiene which results from pyrolisis process.

However, the transformation ratio butene/butadiene is still unsatisfactory, owing to reduced selectivity of the catalysts used.

The development of the oxydative dehydrogenation process of butenes, solves to a great extent the problem of the process selectivity: one obtains increased transformation ratios butene/butadiene, as well as butadiene yields per pass, much more greater.

Along the same line, in Romania, are realised preparation technologies of some catalysts, on Bi-Mo-Fe basis, with reduced percents of Bi_2O_3 and which ensured a good reproductibility of charges.

The procedure for the catalyst synthesis is based on the principle of mechanotopochemical reactions, with increased performances: selectivity with regard to butenes 92-94 % ; butadiene yield, per pass 60 - 62 % for a reaction temperature ranged between 420 - 440°C.

With the purpose of obtaining some alumina-carriers for catalysts, with determined textural, structural and surface properties, our collective start some researches in two directions :

- the introduction of tensioactive admixtures in the formation medium of colloidal aluminium hydroxides :

- the obtention of aluminium hydroxides, from mechanotopochemical reactions, between reagents in solid phase, procedure realised by prof.I.V.Nicolescu.

In the first procedure, using the same raw material, for example aluminium nitrate solution we have shown the influence on the species of aluminium hydroxyde, of tensioactive admixtures introduced in the formation medium of the above. These species of hydroxides through thermical transformations lead to aluminas with different textural and izomerization properties.

Among the tensioactive modifiers used, we mention: polyacrylamide, carboxymethylecellulose, polyvinylalcohol, etc.

In the second procedure, based on mechanotopochemical reactions, for obtaining aluminas with determined properties and isomerizing activity, we used different raw materials : Al nitrate, Al chloride, Al sulphate, or we applied different thermal treatments.

The surface area of obtained aluminas varied between 120 - 320 m^2/g, the greatest part of these having presented bimodale pores distributions, depending also on the aging conditions or on the thermic treatment.

These last aluminas were used for preparing some industrial catalysts, with satisfactory performances.

It is possible that the [illegible]

earches should bring new scientifical elements and of interesting practical applications.

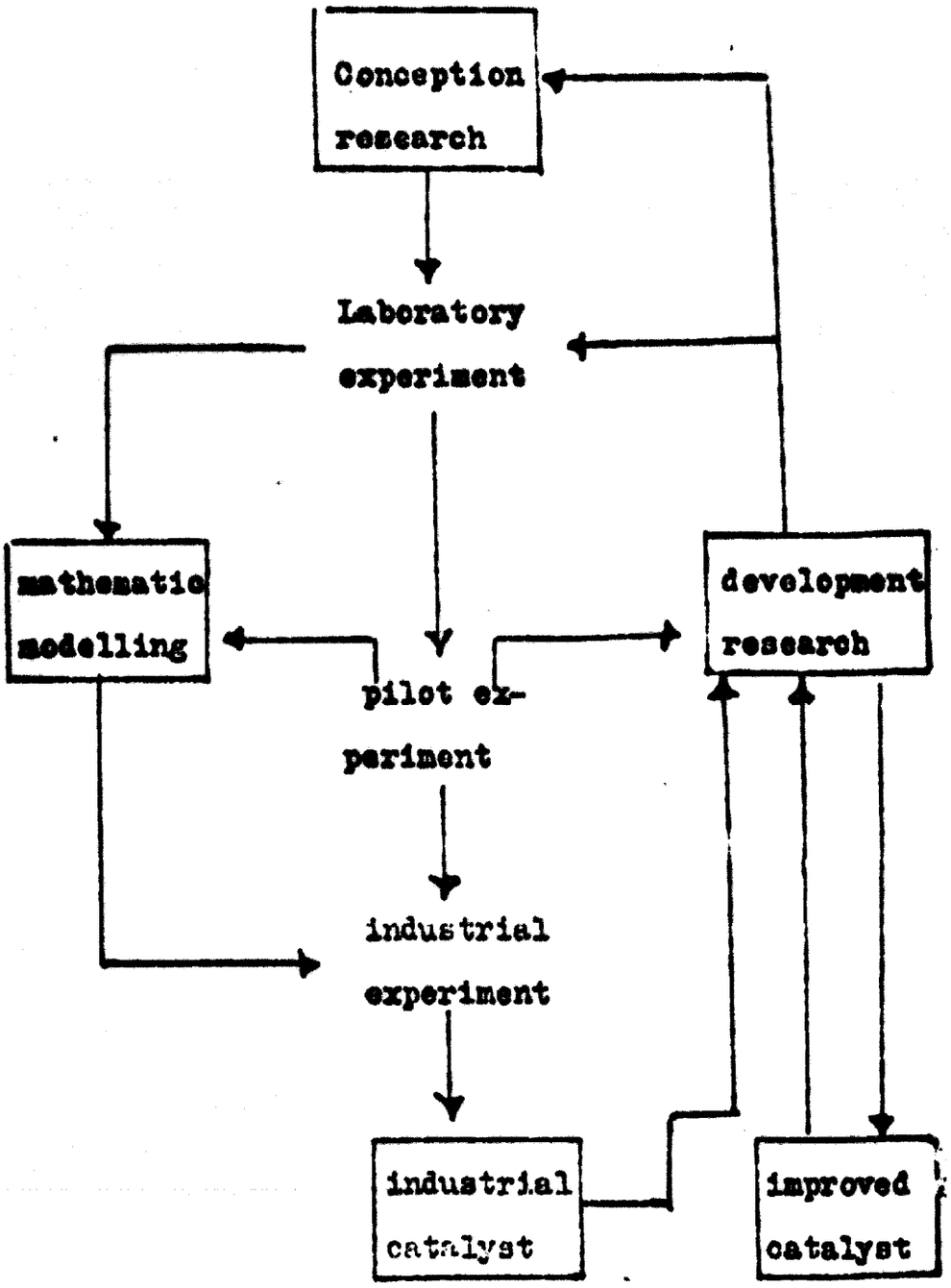


Figure 1

Methodology of elaboration and improvement of industrial catalysts.

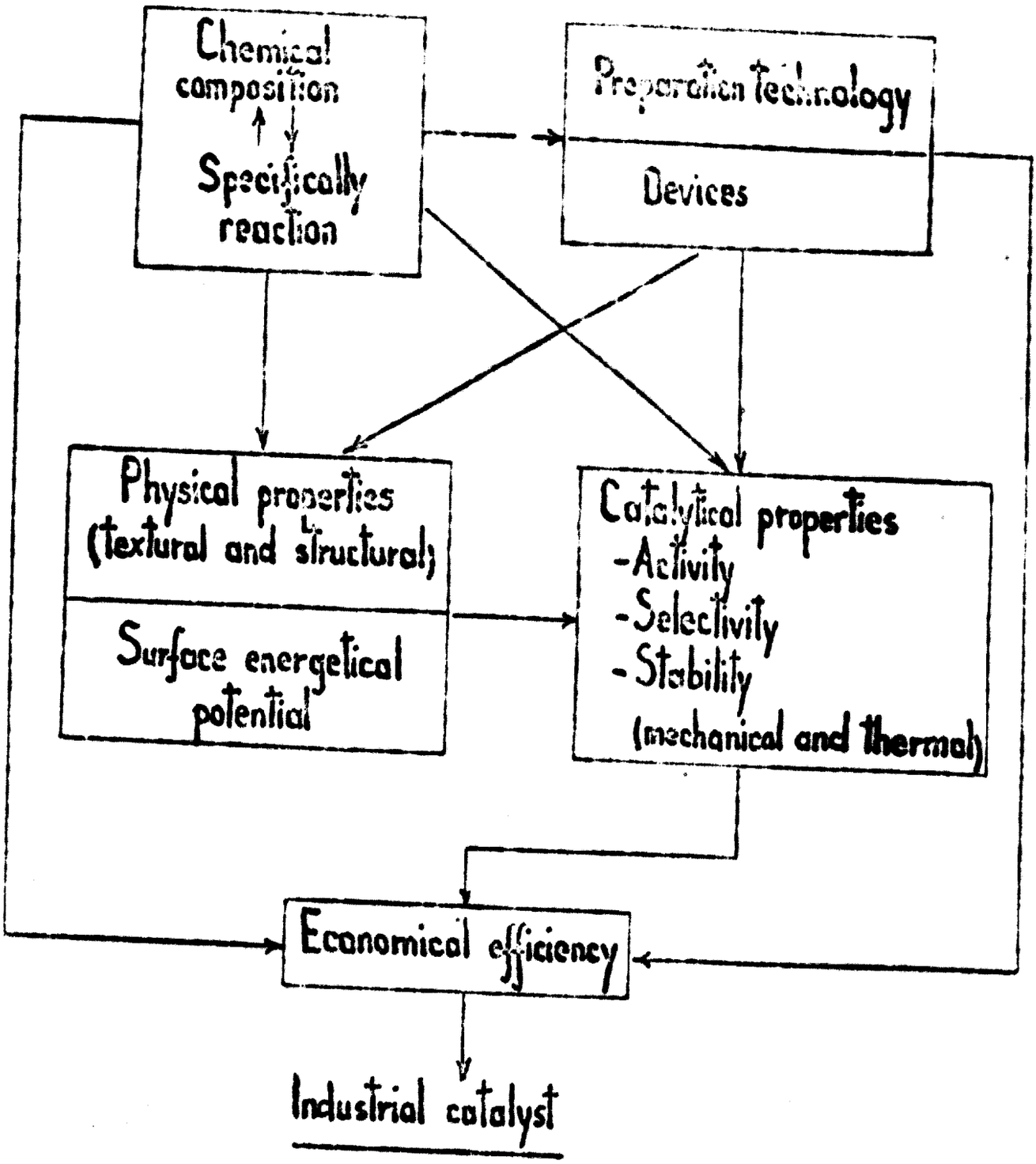


Fig.2-The factors determining the quality of the industrial catalyst.

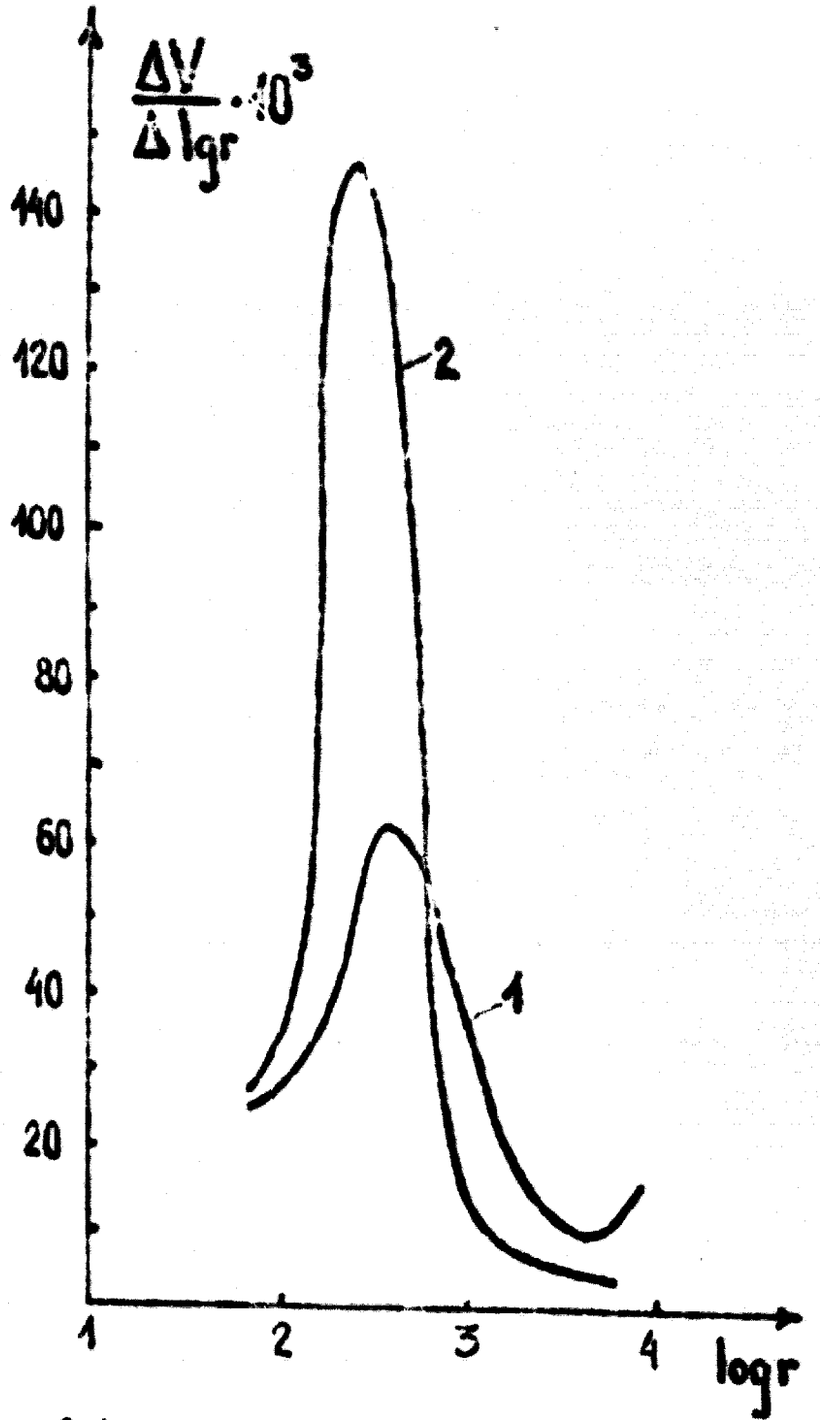


Fig. 3 - Catalyst for NH_3 synthesis. The pores distribution by radium.
1 - initial catalyst; 2 - catalyst after reduction and reaction.

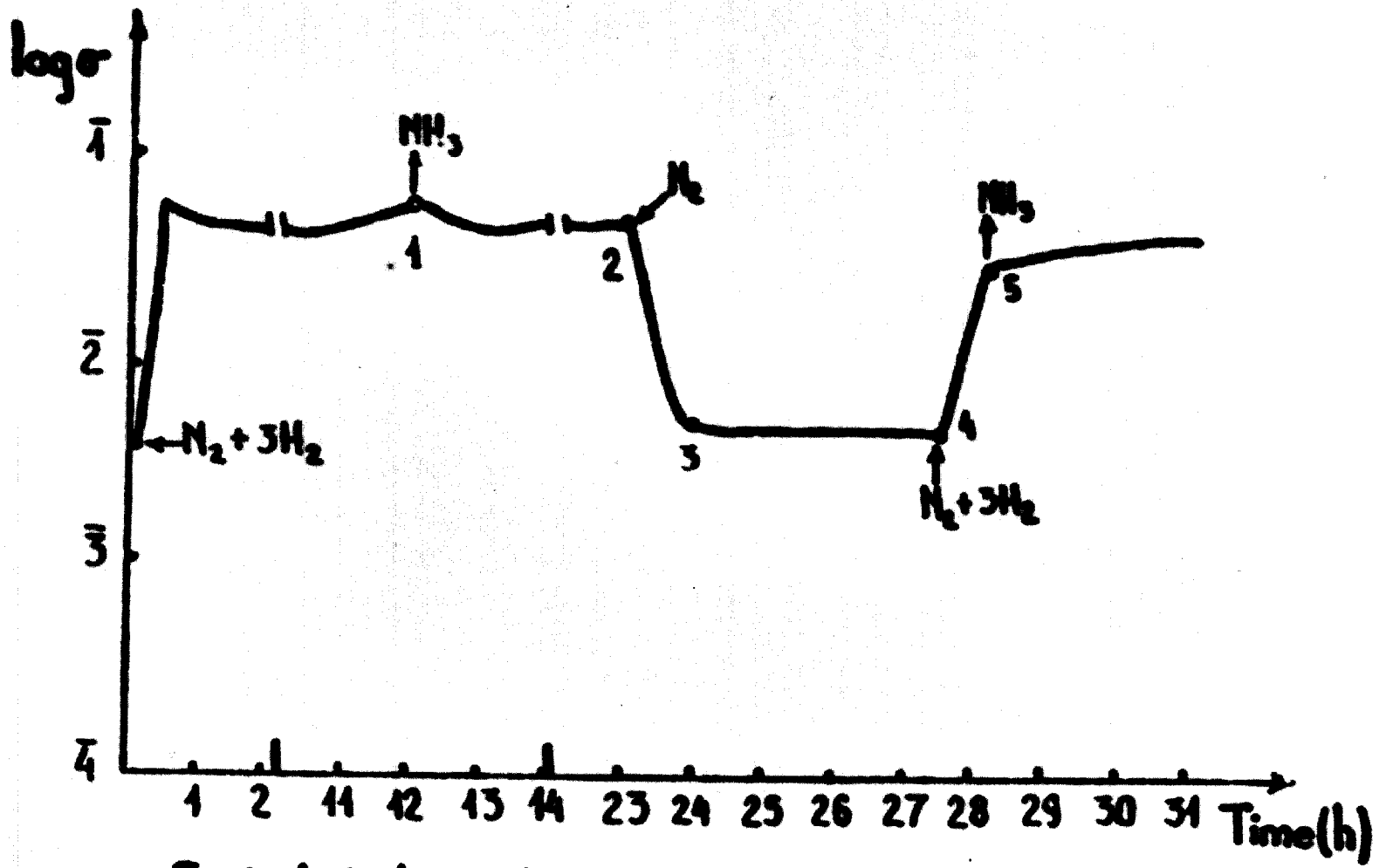
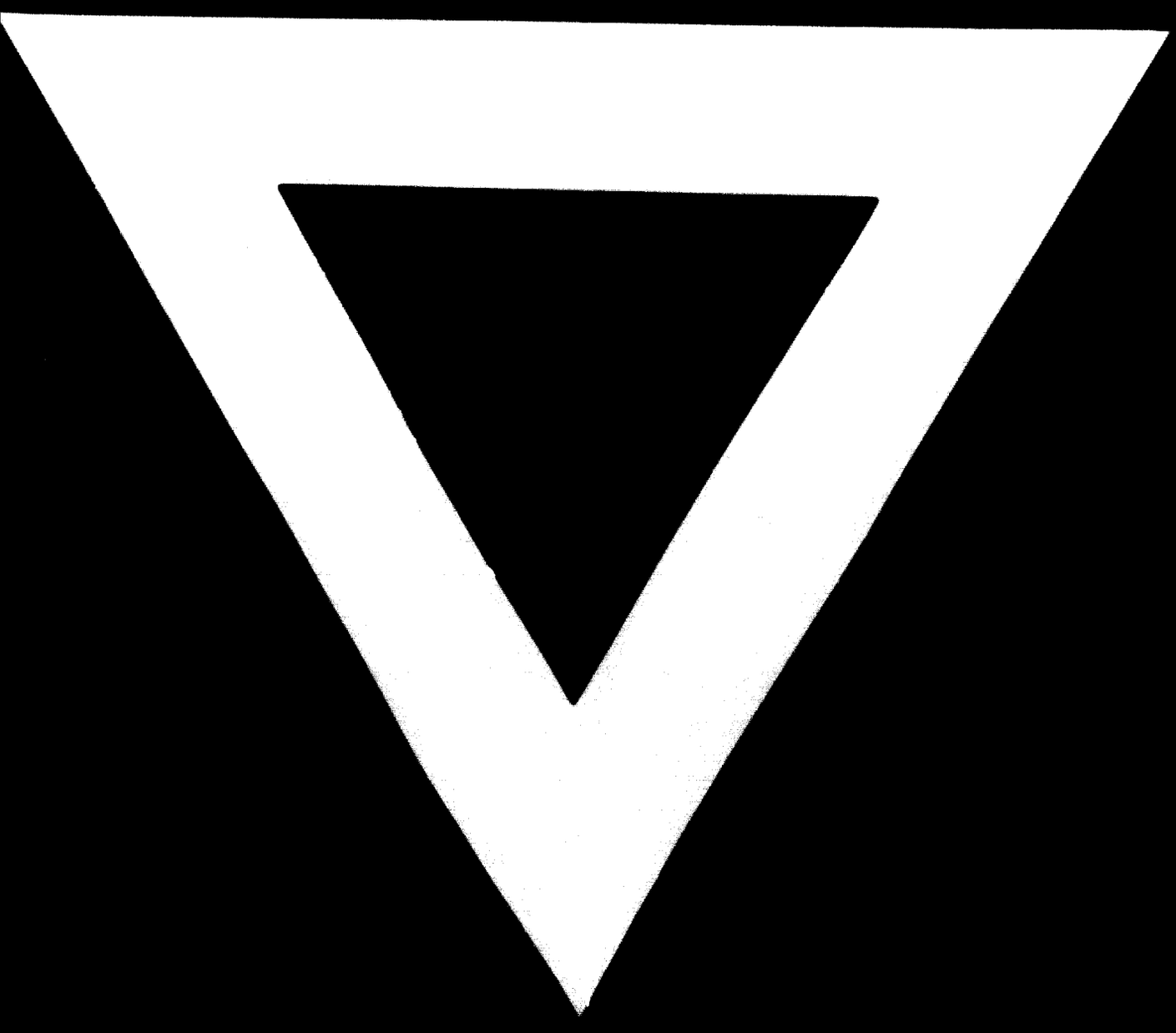


Fig.4 - Industrial catalyst for NH_3 synthesis. The isotherm of electric conductivity in medium of $N_2 + 3H_2$ and N_2 at the temperature of 500°C.



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