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Scientific co-operation with professor Nazimek♣

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In present paper there will be discussed examples of author's scientific co-operation with professor Nazimek. Generally all of them are from the area of heterogeneous catalysis including high dispersed metal phase mostly in the hydrogenolysis reactions of simple alkanes.

1. INTRODUCTION

The impact of catalysis and catalysts is substantial. Today over 90% of all industrial chemicals are produced with the aid of catalysts [1,2]. Catalysts impact a sizable fraction of any nation's gross domestic product [2].

The story of catalysis has been told in the past by practitioners with different perspectives [2]. Lindstrom and Pettersson [3] chose to look at the development of catalysis over periods of time back to the dawn on civilization. This was the base of drawing scheme presented below (Figure 1) [4,5].
Taking into account published data [3-5], in present paper there will be discussed facts which took place in the 7th period of catalysis development.

♣This article is dedicated to Professor Dobiesław Nazimek on the occasion of his 65th birthday

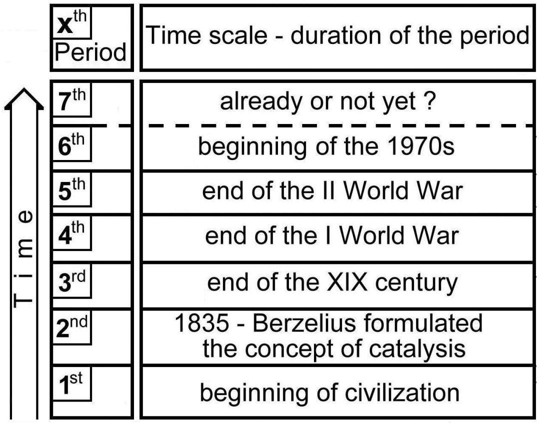

Fig. 1. Historical development of catalysis [4,5].

2. BACKGROUND

The classical definition of chemistry is as follows: chemistry is the study of the composition and properties of matter, the transformations they undergo, and the associated energies. In this respect an applied chemistry is the application of the theories and principles of chemistry to practical purposes. All discussed examples fit well into this category [6-25]. As it is shown in Figure 2, all indicated sub-constituents are named in a classical way and cover broad areas of heterogeneous catalysis. Moreover, there is strong correlation between them.

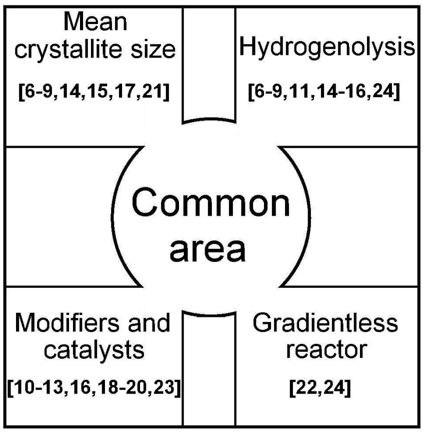

Fig. 2. Areas of author's scientific co-operation with professor Nazimek – simplified scheme.

3. MEAN CRYSTALLITE SIZE

The activity and selectivity of a supported metal catalyst are strongly influenced by the amount of metal, the size of dispersed metal particles, the preparation method and the support composition. To improve the catalyst activity and its durability, it is necessary to obtain a well dispersed active phase in the catalyst.

In our laboratory an original technique of obtaining metal catalysts characterized by small metal crystallites, the so-called double impregnation method (DIM) was elaborated [26,27]. In contrast to the classical impregnation method (CIM), in the DIM preparation procedure the support is preliminary "activated" (modified) by EDTA (Figure 3).

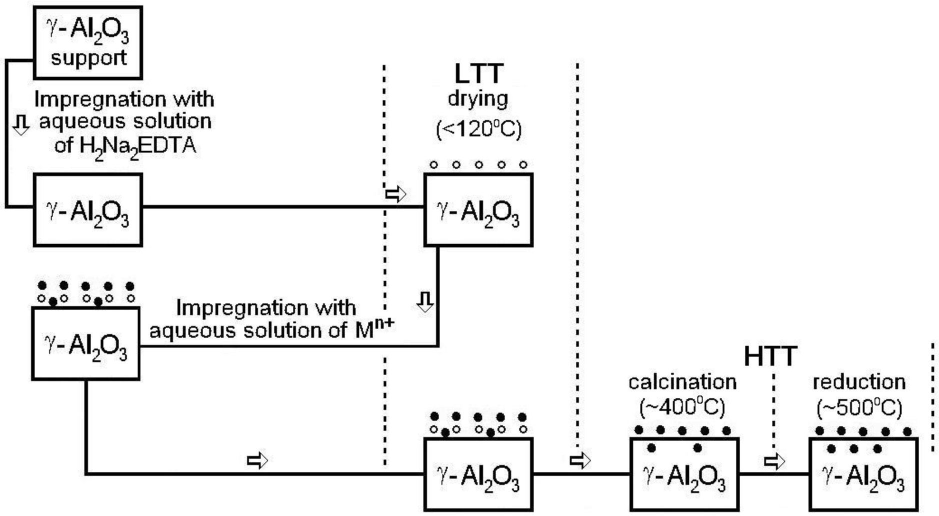

Fig. 3. Scheme of catalyst preparation by DIM (° - H_2Na_2EDTA, • - different M^{n+} and $M^{\delta+}$ species; where M is a metal; LTT – low temperature treatment, HTT – high temperature treatment) resulted in high dispersion of the metal in the final catalyst [5].

This preparation procedure allows to obtain high dispersed (according to the calculations of the mean crystallite size) and stable (after high temperature treatment) metal supported catalysts [6-9,14,15,17,21]. Mentioned above catalyst preparation technique (DIM) was utilized in the preparation of some metal supported (Figure 4) catalysts following applied in the catalytic reactions [6-9, 11,14-16, 20, 24].

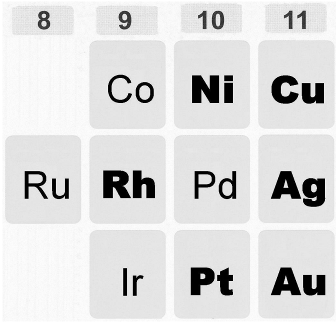

Fig. 4. Investigated metals (bolded) as a high dispersed active phase in the studied catalysts.

4. HYDROGENOLYSIS

Apart from investigating the problems of the kinetics and mechanisms of hydrocarbon hydrogenolysis, catalytic studies often concern general questions of catalysis such as the effect of metal content and the correlation between the catalytic properties and the electronic and structural changes in metals. With supported catalysts, attention has usually been focused on examining the effect of the degree of dispersion, that is, crystallite size, on the electronic properties and reactivity of various systems [6-9,11,14-16,24].

In many papers it has been found that an increased dispersion of crystallites of Group 8-10 metals causes changes in the number and quality of the complex of active centers on its surface. Some scientists suggested that B5 centers may play a special role in alkane hydrogenolysis (Figure 5).

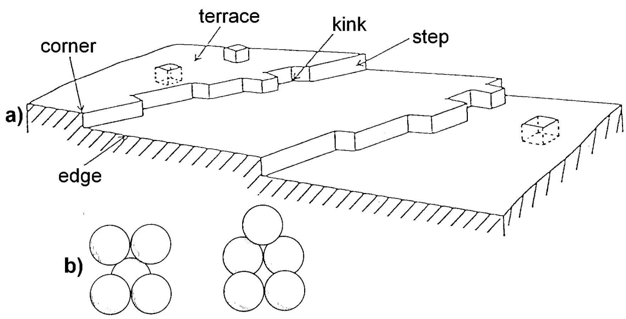

Fig. 5. Microscopic view of a metal surface (a) and alternative B5 site geometries (b) formed at terrace edges on (111) and (100) planes [28,29].

In the research conducted [6-9,11,14-16,24] we studied the effects of metal (nickel, platinum, rhodium) dispersion and changes in the number of B5 centers on the course of simple hydrocarbons (ethane, propane and n-butane) hydrogenolysis.

5. MODIFIERS AND CATALYSTS

Simple and the cheapest way of the catalysts quality improvement is an introduction of promoters. It turns out, that the small amount of additives introduced into the catalysts' formula have a great influence on their textural properties, activity, selectivity and lifetime.

Promoters can be classed as substances which, when added to a catalyst as a minor component, improve one or more of the properties of the material with respect to product formation. However, in the literature dealing with the catalytic problems there is no quantative determination of "small amount" or "minor component". It seems, that the amount will vary with the catalyst (or reaction), and the precise determination of the standard value for the whole systems and processes is impossible [30]. Promoters belongs to the class of positive (+) modifiers (Figure 6).

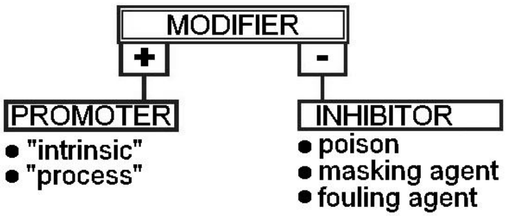

Fig. 6. Division of modifiers based on modifier action type [30,31].

A condensed summary of the scientific activity in the area of modifiers application is given in Table 1.

Tab. 1. Examples of applied modifiers in our research [10-13,16,18-20,23].

Catalyst/support	Modifier/adsorbat*	Comment**	Reference
Ni/γ-Al_2O_3	organic compounds	physico-chemical studies	[10]
Ni/γ-Al_2O_3	organic compounds	hydrogenolysis of n-butane	[11]
Ni/γ-Al_2O_3	H_4EDTA, H_2Na_2EDTA	IR studies	[12]
Ni/γ-Al_2O_3	organic compounds	hydrogenolysis of n-butane	[13]
Ni/γ-Al_2O_3	H_2Na_2EDTA, Sn	FT-IR/PAS studies, hydrogenolysis of simple alkanes	[16]
γ-Al_2O_3	H_2Na_2EDTA, $H_2(NH_4)_2$EDTA	FT-IR studies	[18]
γ-Al_2O_3	Na_2IDA, Na_3NTA	FT-IR studies	[19]
Pt/γ-Al_2O_3	Cu, Ag, Au	hydrogenolysis of n-butane	[20]
various	H_2Na_2EDTA, W, Mo	short review	[23]

* – EDTA – ethylenediaminetetraacetic acid, IDA – iminodiacetic acid, NTA – nitrilotriacetic acid;
** – IR – infrared, FT-IR – fourier transform infrared, PAS – photoacoustic spectroscopy.

6. GRADIENTLESS REACTOR

To undertake reaction studies on both pellets or very fine catalyst particles, an internal reactor was constructed of stainless steel (Figure 7) [22,24].

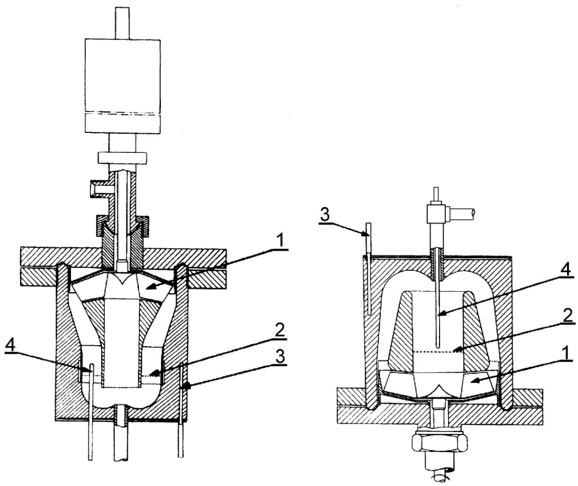

Fig. 7. Schematic diagrams of various versions of gradientless reactor: 1 – impeller, 2 – catalyst bed, 3,4 – thermocouple shields [22].

Construction details are given elsewhere [22,24,32].

7. SUMMARY

Instead of a typical summary let me present a pictorial conclusion (Figure 7) based on the picture presented by A. Baiker (major directions of research and their interdependence) [33].

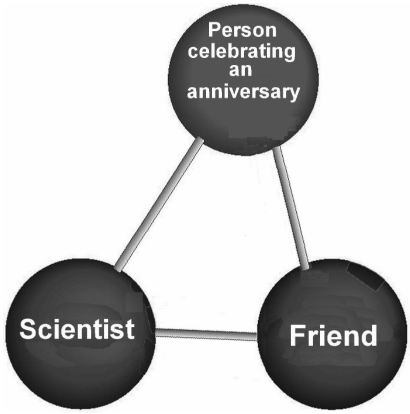

Fig. 7. Major directions of professor Nazimek scientific life activities and their interdependence.

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OTHERS

[1] On the proposal of the Faculty Board of the Faculty of Chemistry of Maria Curie-Sklodowska University, a referee of the M.Sc. Bożena Czech Ph.D. Thesis: *Photocatalytic reduction of the organic pollutants in water*, supervised by prof. D. Nazimek (public defense of the thesis – 21.09.2006).
[2] On the proposal of the Faculty Board of the Faculty of Chemistry of Maria Curie-Sklodowska University, a referee of the M.Sc. Ireneusz Grabowski Ph.D. Thesis: *Selected analytical methods for the analysis of sulfur and benzene contents in liquid fuels*, supervised by prof. D. Nazimek (public defense of the thesis - 19.12.2008).

CURRICULUM VITAE

Janusz Ryczkowski. Born in Poland in 1959. Graduated from Nicolas Copernicus University in Toruń (1983). Received his Ph.D. and D.Sc. degree (1992 and 2004, respectively) in physical chemistry from the University of Maria Curie-Skłodowska in Lublin. Since 2007 university professor. Member of Polish Chemical Society (since 1984), Polish Catalysis Club (since 1993). Besides frequent short visits, he also made long-term stay to Central Research Institute of Chemistry of the Hungarian Academy of Sciences (Hungary) and Ecole National Superieure de Chimie de Lille (France). Within the Socrates Programme (Teaching Staff Mobility) he has visited partner European universities with a series of lectures. Moreover, he is a Faculty representative in the European Chemistry Thematic Network Association. As for today he has been a reviewer of many papers submitted to leading scientific journals. On the request of the Authorities of Quaid-i-Azam and Punjab University (Pakistan) since 1994 eighteen times he was a reviewer of doctoral theses. Moreover, three times he was a referee for a professor position. Seven times he was a reviewer of the Polish Ph.D. thesis. His main field of interest is preparation of supported catalysts, catalyst's modification, their characterization, and application of infrared spectroscopy (including photoacoustic) in catalytic research. He published over 130 papers.