

Catalysis, a younger sister of chemical technology

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The present paper describes current directions of our studies and investigations in the broad sense of heterogeneous catalysis in scientific research. There are given some examples connected with catalysts preparation, their characterisation and test reactions used. At the end, there is a brief summary of our main activities.

1. INTRODUCTION

Catalysis was not invented. Actually, it is a phenomenon, which was observed and exploited long before the word was used to describe its underlying scientific reality. It is defined by the action of substance, which either promotes a particular reaction, or accelerates that reaction. Another definition of a catalyst is more informative: a catalyst is a substance that transform reactants into product, through an uninterrupted and repeated cycle of elementary steps in which the catalyst participates while being regenerated in its original form at the end of each cycle during the life of the catalyst. Furthermore, the amount of catalyst introduced is minute with respect to the quantities of starting materials. There is a very wide range of catalysts, each adapted to a particular reaction.



Figure 1. Major directions in catalytic investigations

Current research in catalysis has a twin objective. On the one hand, fundamental research is aimed at understanding the complex reaction steps or mechanisms involved in these reactions processes. On the other hand, a specific economic, social or environmental request can be proposed. Then applied research is carried out to close liaison with industry to develop a specific catalyst with usually particular requirements. There are different but complementary divisions of catalysis now existing within industrial and academic fields. They are homogeneous, heterogeneous, and enzyme catalysis.

Catalysis as a science has evolved along three major directions: preparation of catalyst, catalyst characterisation and kinetics (test reaction).

2. PREPARATION OF CATALYSTS

"The Scientific Bases for the Preparation of Heterogeneous Catalysts" is the title of a number of periodic meetings organised by B. Delmon, with proceedings published by Elsevier in a series Studies in Surface Science and Catalysis, since 1975. The role of solid state chemistry in the preparation of solid catalysts is paramount.

The two main classes of methods for preparing catalysts are conventional and nonconventional using surface anchoring reactions. The conventional methods include: impregnation, adsorption, coadsorption and precipitation. Nonconventional methods using surface anchoring include grafting, controlled surface reactions, and electrochemical methods.

Double impregnation method. Several methods can be applied to obtain dispersed metals on the support surface. Supported catalysts in common use are typically in the form of small crystallites of a catalytically active component dispersed in a porous support of a high surface area. Impregnation of the support with an aqueous solution of a compound containing the appropriate catalytic component is an important and frequently used method of preparing this type of catalysts. This classical impregnation method (CIM) results in obtaining small metal crystallites but only at very low metal contents in the catalysts. In our laboratory there was elaborated an original technique of obtaining nickel catalysts characterised by small metal crystallites, so called double impregnation method (DIM) [1,2]. The main preparation steps are given in Figure 2. In contrast to the CIM [3], in the DIM preparation procedure the carrier is preliminary "activated" (modified) by ethylenediaminetetraacetic acid (EDTA).

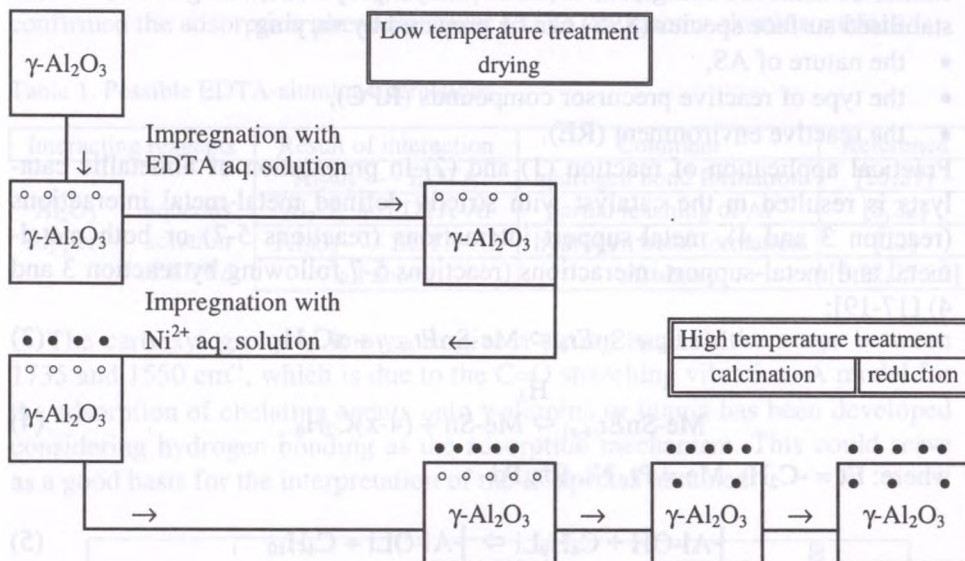
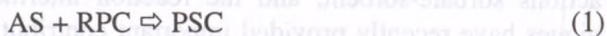


Figure 2. Scheme of catalyst preparation by DIM (° - EDTA, • - different $\text{Ni}^{\delta+}$ species)

Procedures and studies of the catalysts prepared by DIM were published in several papers [1-10] as well as test reactions utilising prepared catalysts [6-16].

Controlled surface reactions. Surface anchoring reactions are widely used to prepare immobilised enzymes, immobilised chemical reagents, functionalised chromatography supports, heterogenised metal complexes and many different supported catalysts. For catalyst preparation, the major advantage of anchoring is that the chemistry of the system controls the formation of the desired surface species, an advantage not often found using conventional preparation methods.

The involvement of adsorbed hydrogen is the characteristic feature of the surface anchoring of organometallic compounds on bulk, supported and skeletal metals. Reaction (1) and (2) describe the general reactions of the surface anchoring process:

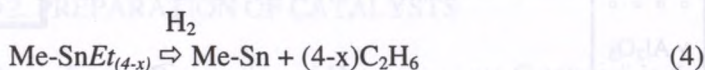
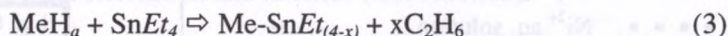


In reaction (1), the anchoring site (AS) can exist on the active phase or on the support. The key to achieving selective modification of the active phase or the support is for the anchoring reaction (1) to thermodynamically or kinetically differentiate between the active phase and support phase sites. This distinction

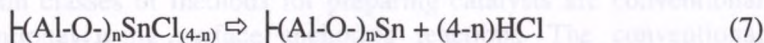
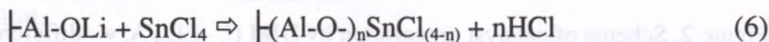
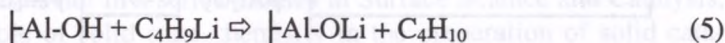
cannot be achieved using conventional catalyst preparation. In general, various stabilised surface species (SSS) can be prepared by varying:

- the nature of AS,
- the type of reactive precursor compounds (RPC),
- the reactive environment (RE).

Practical application of reaction (1) and (2) in preparation of bimetallic catalysts is resulted in the catalyst with strictly defined metal-metal interactions (reaction 3 and 4), metal-support interactions (reactions 5-7) or both metal-metal and metal-support interactions (reactions 5-7 following by reaction 3 and 4) [17-19]:



where: Et = -C₂H₅, Me = Pt, Ni, Rh, Pd



Catalyst prepared according the procedures described above are applied in selective hydrogenation of acrylonitrile to propionitrile on lead poisoned nickel catalysts, selective hydrodechlorination of aromatic compounds on alumina supported ionic palladium catalysts, alkylation of amines with metanol or butanol on copper catalysts, reductive amination of ketones on nickel and palladium catalysts, and many others.

3. CATALYST CHARACTERISATION

The various methods of infrared spectroscopy (IR) are widely used techniques in catalysis laboratories because few physical methods can give so much information so easily on the catalyst structure, its surface properties, the interactions sorbate-sorbent, and the reaction intermediates. Spectroscopic techniques have recently provided important contributions to the understanding of the influence of preparation conditions on the properties of heterogeneous catalysts. Several bonding schemes have been suggested to explain the adsorption of organic's on hydrous solids. There are few literature data dealing with this problem that are based on IR investigations [9,16,20-26]. Preparation of nickel alumina supported catalysts with high metal dispersion involves adsorption of EDTA or its sodium salt on the $\gamma\text{-Al}_2\text{O}_3$ or TiO_2 surface [1,4,6,27].

Transmission FT-IR [21,23,27], ATR technique [22], and ^{27}Al NMR [3] have confirmed the adsorption phenomenon of EDTA on gamma alumina surface.

Table 1. Possible EDTA-alumina interactions

Interacting reagents	Result of interaction	Comment	Reference
Al_2O_3 support aqueous solution of EDTA	Al_2O_3 - - EDTA	hydrogen bond formation	[25,27]
	Al_2O_3 + EDTA-Al	partial leaching of Al^{3+}	[3,22]
	Al_2O_3 - - EDTA-Al	hydrogen bond formation	[22]
	all above	all above	[3,22,25,27]

The carboxyl group is known to give a strong band in the range between 1735 and 1550 cm^{-1} , which is due to the $\text{C}=\text{O}$ stretching vibration. A model for the adsorption of chelating agents onto γ -alumina or titania has been developed considering hydrogen bonding as the adsorption mechanism. This could serve as a good basis for the interpretation of the IR spectra obtained.

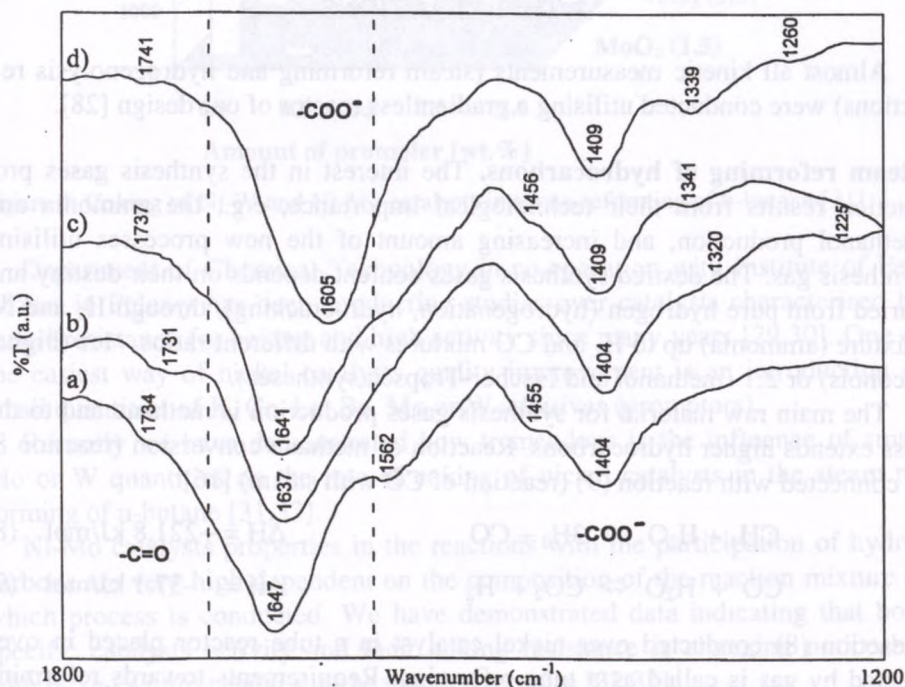


Figure 3. FT-IR spectra of acid and sodium salts of EDTA adsorbed on the surface of TiO_2 : a) acid, b) disodium salt, c) trisodium salt, d) tetrasodium salt

It should be noted that, from the point of view of EDTA-type molecule structure it could be treated as tertiary amine or acetic acid derivative. Treating an EDTA-type compound as acetic acid derivative better fits to the model of adsorption mechanism [27].

An increasing amount of sodium atoms in the EDTA salts causes an intensity shift from the $\nu_{(C=O)}$ to the $\nu_{(COO^-)}$ vibration.

The observed changes in the IR spectra of the supported chelates are mainly due to interactions of the chelate carboxyls with inorganic hydroxyl groups. The isoelectric point of the surface (IEPS) has a strong influence on the band position of the adsorbed species. A change of the support is connected with a change of the IEPS, so in each case the distribution of the existing surface hydroxyl groups is different.

The results of these fundamental studies are of great importance and have a practical application in the preparation of supported catalysts with a high metal dispersion.

4. TEST REACTIONS

Almost all kinetic measurements (steam reforming and hydrogenolysis reactions) were conducted utilising a gradientless reactor of our design [28].

Steam reforming of hydrocarbons. The interest in the synthesis gases production results from their technological importance, e.g., the ammonia and methanol production, and increasing amount of the new processes utilising synthesis gas. The desired synthesis gases content depends on their destiny and varied from pure hydrogen (hydrogenation, hydrocracking), through H_2 and N_2 mixture (ammonia) up to H_2 and CO mixtures with different ratios - 1:1 (higher alcohols) or 2:1 (methanol and Fischer-Tropsch syntheses).

The main raw material for synthesis gases production is methane and to the less extends higher hydrocarbons. Reaction of methane conversion (reaction 8) is connected with reaction (9) (reaction of CO with steam) [16]:



Reaction (8) conducted over nickel catalyst in a tube reactor placed in oven heated by gas is called as a tube reforming. Requirements towards reforming catalysts are very high. At present, in the tube reformers there are applied almost entirely nickel catalysts supported on low surface area carriers, characterised by high mechanical strength and thermal stability. Hydrocarbon steam reforming is accompanied by processes which result in the formation of carbon deposit on nickel catalysts. For that reason the resistance to coking is regarded

as one of the most important properties of good nickel catalysts for steam reforming.

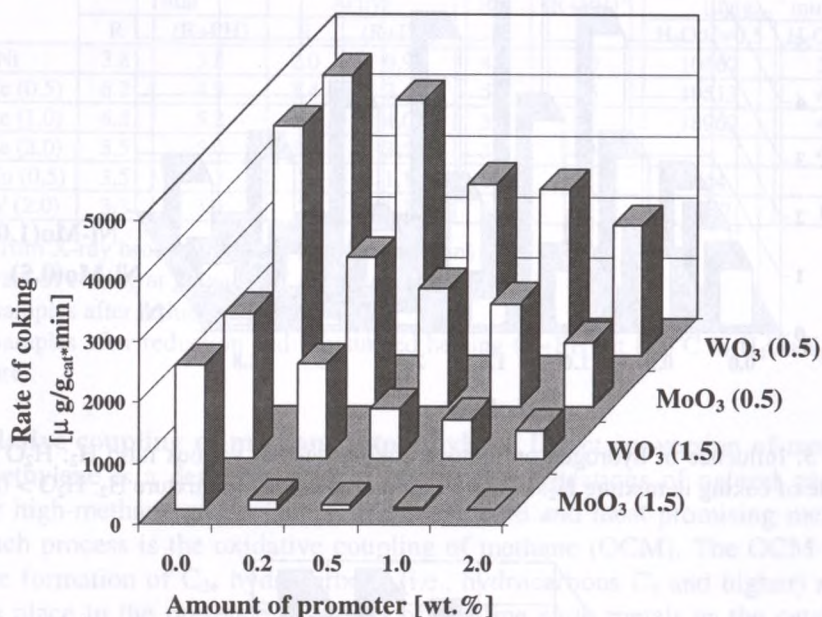


Figure 4. Coking of Ni-W and Ni-Mo catalysts in steam reforming of n-butane [31]

Department of Chemical Technology in co-operation with Institute of Fertilizers in Pulawy has been conducting studies over catalysts characterised by raised resistance for coking and high activity since many years [29,30]. One of the easiest way of nickel catalysts quality improvement is an introduction of small quantities of K, Ce, La, Ba, Mo or W additives (promoters).

Recently we have demonstrated how tremendous is the influence of small Mo or W quantities on the rate of coking of nickel catalysts in the steam reforming of n-butane [31,32].

Ni-Mo catalysts properties in the reactions with the participation of hydrocarbons are very high dependent on the composition of the reaction mixture in which process is conducted. We have demonstrated data indicating that both specific catalysts activity and their coking resistance is changing noticeably with p_{H_2}/p_{H_2O} ratio changes in the reaction mixture [32,33].

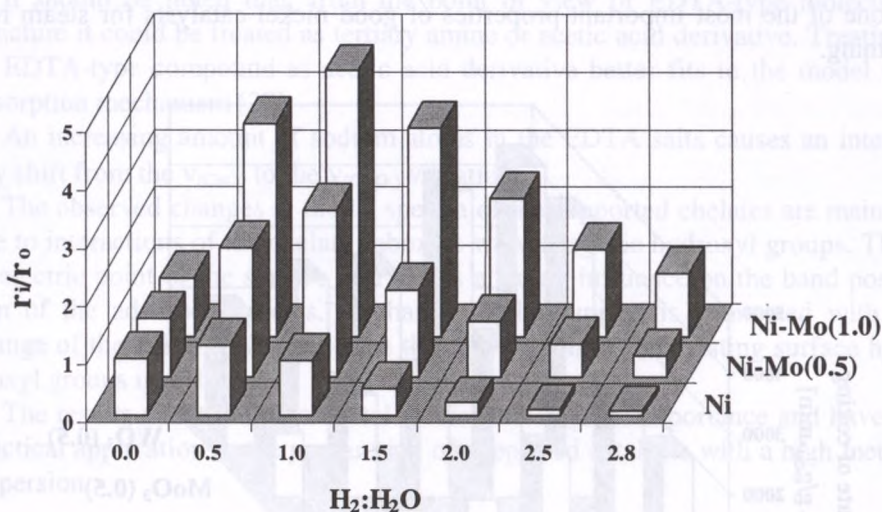


Figure 5. Influence of hydrogen on relative coking rates at various ratio $H_2:H_2O$ [33] (r_o - rate of coking in mixture $H_2:H_2O = 0$; r_i - rate of coking in mixture $H_2:H_2O > 0$)

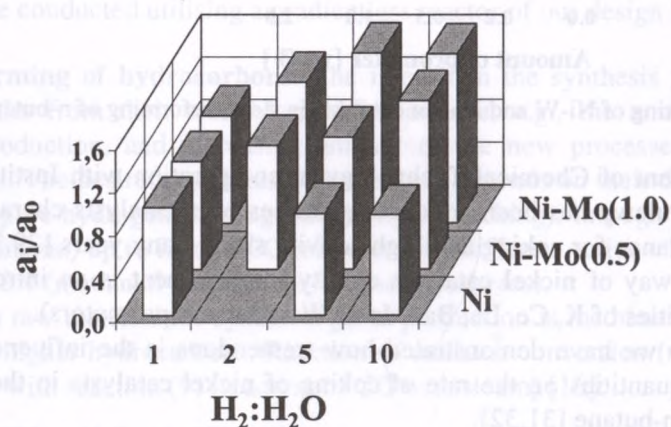


Figure 6. Influence of hydrogen on the relative activity of catalysts ($H_2:H_2O$ ratios ≤ 10) [33] (a_o - activity of catalysts in mixture $H_2:H_2O = 1$; a_i - activity of catalysts in mixture $H_2:H_2O > 1$)

Cerium additives appear as an interesting texture promoter of the nickel catalysts [34]. The experimental results show that the cerium promoter has very favourable influence on the nickel dispersion and its resistance for sintering. On the contrary the cerium promoter does not have the influence on the decrease of the rate of carbon formation in the steam reforming of n-butane.

Table 2. Main properties of the promoted catalysts examined [34]

Catalysts	Surface area ($\text{m}^2 \text{g}^{-1}$)				d_x^a (nm)		Coking rate ^b ($\mu\text{g g}_{\text{cat}}^{-1} \text{min}^{-1}$)	
	Total		Active		R^c	$(R+PH)^d$	$\text{H}_2\text{O}:\text{C}=0.5$	$\text{H}_2\text{O}:\text{C}=2.0$
	R	(R+PH)	R	(R+PH)				
Ni	3.8	3.8	2.0	0.9	42	90	10667	2000
Ni-Ce (0.5)	6.2	4.9	3.4	3.4	52	56	19513	4557
Ni-Ce (1.0)	6.5	5.2	3.9	4.0	34	-	18962	4503
Ni-Ce (2.0)	5.5	5.0	3.3	3.5	39	54	-	4212
Ni-Mo (0.5)	3.5	4.3	1.8	1.1	27	-	644	13
Ni-W (2.0)	3.3	3.9	1.8	1.1	31	-	6667	1053

a. from X-ray broadening data ($\text{CuK}\alpha$ radiation)

b. rate of coking at 20 wt. % C on the catalysts (R+PH)

c. samples after reduction (R) at 800 °C

d. samples after reduction and pressurised heating (R+PH) at 800°C in $\text{H}_2\text{O}+\text{H}_2$ mixture

Oxidative coupling of methane into ethylene. Direct conversion of methane into ethylene is a desirable way of industrial applications of natural gas and other high-methane gases. One of the considered and most promising methods of such process is the oxidative coupling of methane (OCM). The OCM leads to the formation of C_{2+} hydrocarbons (i.e., hydrocarbons C_2 and higher) and it takes place in the presence of oxides of alkaline earth metals as the catalysts, usually promoted with alkaline metal compounds [35-55].

We have found [39,41,52] that sodium promoter increases the specific activity of the Na^+/CaO catalysts, but not to the same extent for various products (Figure 7).

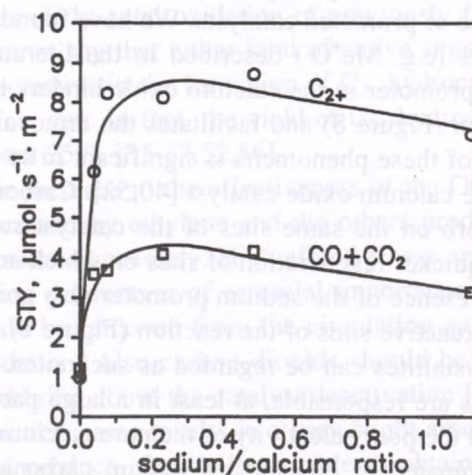


Figure 7. Dependence of the space time yield (STY) of the main groups of the OCM products on the Na/Ca ratio in the Na^+/CaO catalysts (catalyst weight = 0.5 g, 800 °C, methane/air = 1, flow rate of feed gas = 50 cm^3/min ., total pressure = 1 atm.) [47]

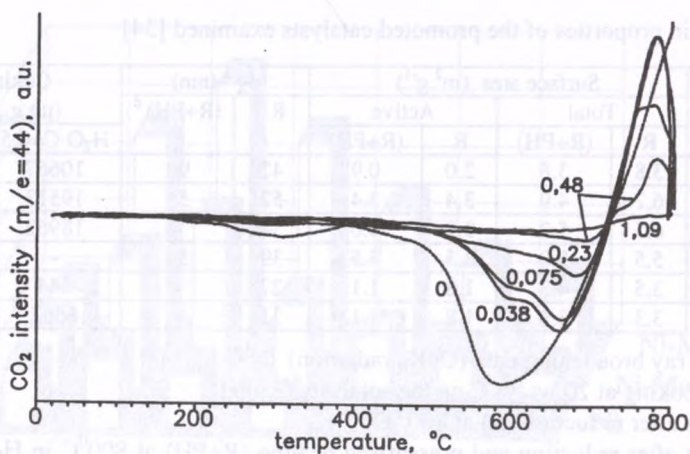


Figure 8. Temperature-programmed reaction of the Na^+/CaO catalysts in carbon dioxide (numbers indicate the Na/Ca ratio, catalyst weight = 0.1 g, heating rate 25 °C/min., 4.73 mol% of carbon dioxide in helium, flow rate 50 cm³/min.) [47]

The greater increase in the rate of C_{2+} hydrocarbons formation than of the rate of carbon oxides formation over promoted catalysts results in improvement of their selectivity as compared with pure CaO. Changes in the specific activity of the catalysts resulting from their promoting signify that there occurs a change in the rate of the limiting step of the whole process, i.e., in the rate of hydrogen abstraction from the methane molecule and formation of methyl radicals. This step occurs with the participation of active oxygen from the catalyst surface. The increase in activity may indicate an increased amount of active oxygen on the surface of promoted catalysts. We have found that apart from the creation of new sites (e.g. Me^+O^-) described in the literature [35-37,52], the presence of sodium promoter in the calcium oxide hinders its carbonation during the OCM reaction (Figure 8) and facilitates the removal of carbon dioxide (Figure 9). The role of these phenomena is significant in so far as carbon dioxide is a poison of the calcium oxide catalyst [40,52]. Carbon dioxide competes with oxygen to adsorb on the same sites of the catalyst surface, thus sodium promoter enables a quicker regeneration of sites on which active oxygen can be chemisorbed. The presence of the sodium promoter also greatly diminishes the number of the most reactive sites of the reaction (Figure 8). Corners and edges of calcium oxide crystallites can be regarded as such sites. It seems that these low-coordinated sites are responsible, at least in a large part, for the formation of carbon oxides and the poor selectivity of the pure calcium oxide in the OCM. These sites are eliminated or blocked by sodium carbonate, which is stable under the conditions of the OCM process. Still, the other type ("selective") of active sites, which leave in promoted catalysts and which enable the formation

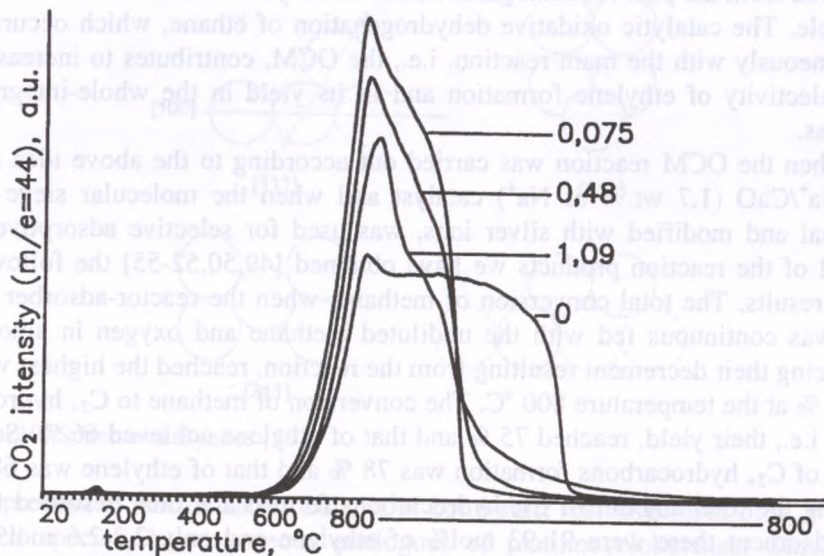


Figure 9. Amount of carbon dioxide released during temperature-programmed decomposition of the carbonate precursors of the Na^+/CaO catalysts (numbers denote the Na/Ca ratio, catalyst weight = 0.5 g, heating rate $25\text{K}/\text{min.}$, helium as a carrier gas, flow rate $50\text{ cm}^3/\text{min.}$) [47]

of C_{2+} hydrocarbons, fails to ensure a 100% selectivity of hydrocarbons formation. The same “selective” sites may also be responsible for the formation of methoxide ions from methyl radicals, further oxidised to carbon oxides and for secondary processes of the total oxidation of previously formed C_{2+} hydrocarbons. Thus, one cannot say that either kind of active sites present on the catalyst is completely selective in the formation of C_{2+} hydrocarbons from methane in the presence of oxygen. In fact, the yield of C_{2+} hydrocarbons is limited, in the best case, to about 25 % [35-37,52,56].

For considerable increase in the effectiveness of the OCM, recycle of unreacted methane processed by ethylene and the others products separation from the post-reaction gases is necessary. High effectiveness and selectivity of separation of the reaction products is of essential importance. The already formed hydrocarbons should be removed from the circulating gas in order to prevent their complete oxidation. Also carbon dioxide should be removed because its accumulation could bring about the catalyst deactivation [40,52]. If the separation of the post-reaction gases results in a very slight amount of methane present in the removed products then it is possible to obtain the high conversion degree of methane and high yield of the reaction products. The only small amount of ethane, the second (besides ethylene) main product of the OCM,

removed from the post-reaction gases makes its recycle with unreacted methane possible. The catalytic oxidative dehydrogenation of ethane, which occurs simultaneously with the main reaction, i.e., the OCM, contributes to increase in the selectivity of ethylene formation and in its yield in the whole-integrated process.

When the OCM reaction was carried out according to the above idea over the Na^+/CaO (1.7 wt.% of Na^+) catalyst and when the molecular sieve 5A, original and modified with silver ions, was used for selective adsorptive removal of the reaction products we have obtained [49,50,52-55] the following good results. The total conversion of methane, when the reactor-adsorber system was continuous fed with the undiluted methane and oxygen in amounts balancing their decrement resulting from the reaction, reached the highest value of 96 % at the temperature 800 °C. The conversion of methane to C_{2+} hydrocarbons, i.e., their yield, reached 75 % and that of ethylene achieved 66 %. Selectivity of C_{2+} hydrocarbons formation was 78 % and that of ethylene was 68 %. Among the total amount of C_{2+} hydrocarbons formed and then desorbed from the adsorbent there were 91-93 mol% of ethylene and only 2.2-2.6 mol% of ethane. Besides C_2 hydrocarbons, in the products of the OCM there were also propene, propane and C_4 hydrocarbons. These hydrocarbons constituted 4-8 mol% of the total amount of obtained hydrocarbons and the ratio of propene to propane was not much greater than one.

These results demonstrate that it is possible to achieve high methane conversion and high yield of C_{2+} hydrocarbons among which ethylene clearly predominates in the process of catalytic oxidative coupling of methane.

Hydrogenolysis of hydrocarbons on metals and alloys. Metals of the VIII group of the periodic table are utilised in such reactions as dehydrogenation, dehydrocyclization, hydrogenolysis and isomerization. Fundamentally, metals are divided into [57,58]:

- hydrogenolysing – i.e., elements from the nickel group,
- isomerizing – i.e., elements from the platinum group.

Works explaining the properties of these metals are carried out for several years [58]. At present stage of investigations, it is assumed that the hydrogenolysis reaction requires a set of active centres which is composed of a great amount of surface atoms, including low coordinated ones [7,10-11,58]. On the other hand, the isomerization reaction requires only a single surface platinum atom. However, in the work [58], it was established that the isomerization can proceed as well on a single platinum atom, as on a big set of surface atoms, “provided” with B_5 or B_4 centre, but the mechanism of the process changes.

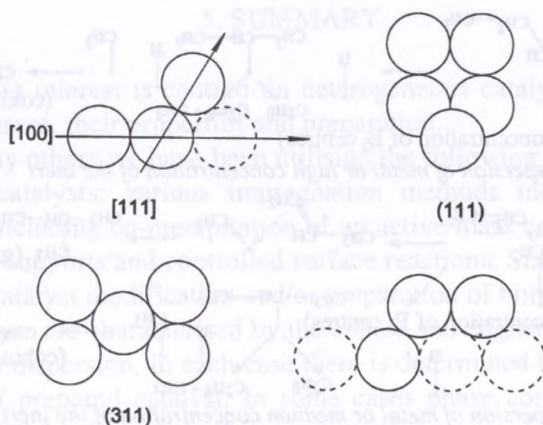


Figure 10. Scheme of B_5 sites [59]

The process of isomerization consist of bond-shift rearrangement of α , γ – adsorbed species, heterogeneous analogues of platinocyclobutanes, which are stabilised by multicenter bonds and partial charge transfer from the adsorbed species to the metal [60].

Bimetallic and multimetallic catalysts have been widely investigated in recent years [58].

Pt-Rh, Pt-Sn and Pt-Re are used quite widely in oxidation of ammonia or naphtha reforming, respectively. From a fundamental point of view, the Pt-Cu, Pt-Au and Pt-Ag combinations are also interesting. The introducing of Cu, Au and Ag modifier into platinum catalyst can cause geometric changes such as site blocking and ensemble formation responsible for isomerization and hydrogenolysis reaction [15].

Hydrogen activated by platinum can be accepted by the second metal through "spillover" effect. In this case platinum atom could be active in an isomerization reaction of hydrocarbon. Decreasing in the ratio of the reaction rate of propane towards i-butane (in studied range of modifiers concentration) suggests the above described presumption probable. It seems that Ag_3Pt structure [61] could be formed by the transformation of the existing B_5 centre (primary composite only with platinum atoms). Similar to B_5 centre this new structure consists with low coordinated atoms which could exhibit an increased activity in the "spillover" effect. The Pt-Me catalysts characterised by high selectivity towards propane exhibit also high selectivity towards i-butane and low selectivity towards ethane and methane.

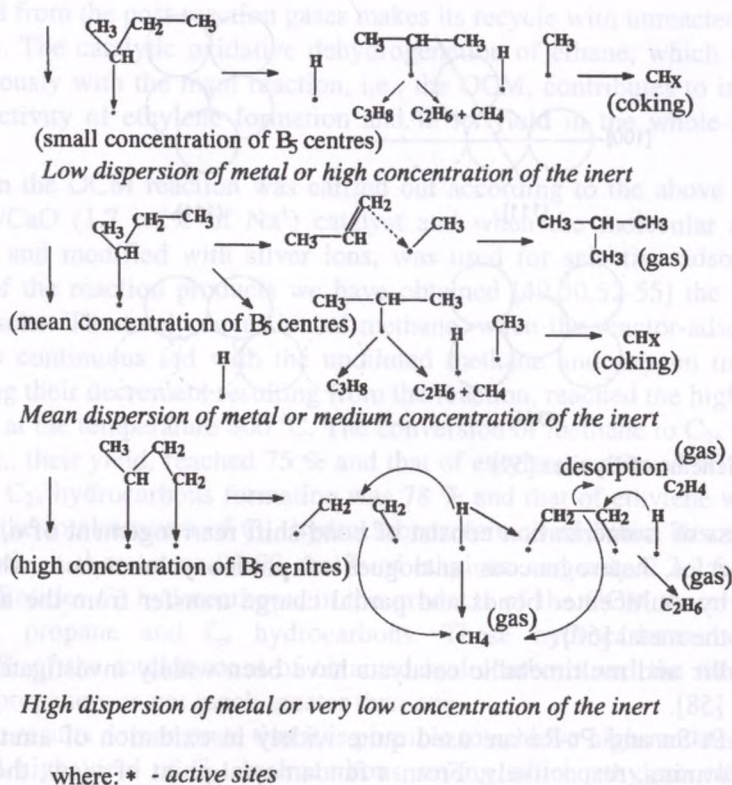


Figure 11. The influence of the quantitative and qualitative sites of the existing on the surface alloys on the course of n-butane hydrogenolysis [15]

The analysis of data included in paper [15] leads to the conclusion that the Pt-Me system formed actually involves another system of active centres on the surface than pure platinum does. Slight decrease of the total reaction rate on those catalysts suggests that carbon deposit on the active surface is lower than on the others. From the proposed scheme is resulted that „dilution” of ensembles causes changes in n-butane chemisorption on the alloyed surface of catalysts, decrease of the total catalytic activity connected with an increase towards isomerization as well as carbon deposition. The number of the new active centres formed (or modified existing sites) is regulated by the presence of Cu, Ag or Au contained in the catalysts, giving a constant change in quality, but different overall activities.

5. SUMMARY

Our scientific interest is centred on heterogeneous catalysts used for technological processes, their properties and preparation.

Among many others we have been utilising the following preparation procedures of the catalysts: various impregnation methods including DIM, co-precipitation (including co-precipitation of an active mass concentrates), deposition on alkali supports and controlled surface reactions. Similar methods have been used for catalyst modification and/or preparation of bimetallic systems. Prepared catalysts are characterised by the course and degree of an active phase reduction, their dispersion. In each case there is determined the total and active surface area of prepared catalyst. In some cases phase composition is determined (e.g., NiO-MgO-Al₂O₃). Temperature Programmed Desorption (TPD) and Reduction (TPR) are used very often.

Prepared catalytic objects are studied and utilised in the reactions with hydrocarbons or carbon oxides with a particular interest in studying the deactivation processes (coking, sintering, poisoning) of catalysts applied to obtain synthetic gas from hydrocarbons (steam reforming, low temperature partial oxidation), hydrogenolysis of simple hydrocarbons as well as to investigate oxidative coupling of methane.

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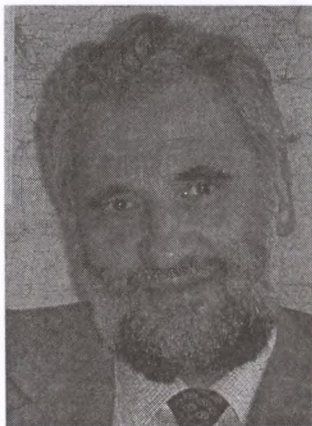
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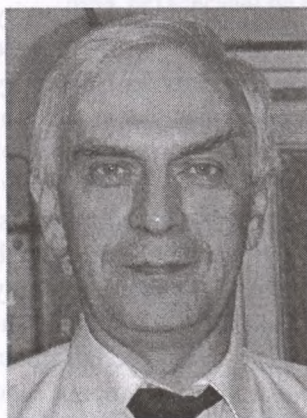
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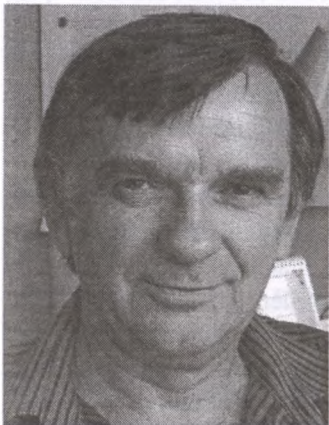
CURRICULA VITAE



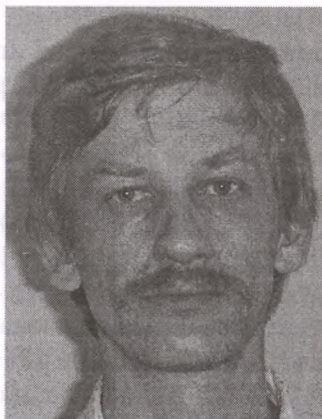
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