

In dedicating this Issue to Professor Malinowski, we honor not only his memory but also the values, which he taught us: science and technology for meeting human needs.

Professor Stanisław Malinowski (1909–2001)

On 12 October 2001, at the age of 92, died Professor Stanisław Malinowski Professor at the Warsaw University of Technology (Politechnika), and member of the Polish Academy of Sciences, an outstanding technologist in organic chemistry and the Nestor of investigators on applications of heterogeneous catalysis in organic synthesis. He was an outstanding expert in the chemistry of flavors and fragrances and in the chemistry of cosmetics as also pharmaceuticals prepared from nitrocompounds. In 1954, he became interested in catalytic transformations of organic compounds. He conducted pioneering studies on the use of solid bases and also of homogeneous complexes of metals and organometallic compounds to catalyze these processes. He was the precursor of investigations on active sites present on the surface of ionic solids, and on their acid-base and radical properties. In these studies he was among the first to apply adsorption of probe molecules and to use infrared spectroscopy and electron spin resonance to study their adsorbed state. He is the co-inventor of solid superbases and of a series of solid superacids, possessing Lewis type acidic properties.

Professor Stanisław Malinowski was also an outstanding Lecturer in Chemical Technology at the Warsaw University of Technology. For several decades his appealing Lectures, full of humanistic substance, were a fascination for the successive generations of students. A man of great personal culture, making very easily contacts with people, he was an unrivalled inspirer and animator of scientific life. His personal charm and wisdom, his knowledge of worldwide literature and music, of national traditions and customs, helped him to overcome the political and financial barriers obstructing human relations. He was opening the Western World to his students and Collaborators. He initiated and, in cooperation with Professors Adam Bielański and Jerzy Haber, organized the Polish-French and the Polish-Czechoslovak Colloquia in catalysis for many years. To the young scientists in Poland these Colloquia made it possible to make first steps into the world of international contacts and gave an opportunity to confront themselves with the European level of chemical science and to self-evaluate one's own level on the European scale.

Professor's Malinowski last notes

The last months of Professor's Malinowski life were especially difficult for him. The periods of weakness when he could not leave his bed or his armchair alternated with the clear days, enabling him to take a stroll along the streets in the neighborhood and a lively contact with the nearest family. Despite his physical weakness he resumed his intellectual activities and came back to the problem which had attracted his interest in a couple of preceding years: the specific catalytic and physicochemical properties of alkaline earth metal oxides. In particular he was fascinated by the results described in the eighties and the nineties in the papers published by F. Freund in Germany and USA and saw vast perspectives for catalysis and geochemistry in the further development of the research in this field.

Freund had shown that when the proper conditions of sufficiently high temperature are fulfilled magnesium oxide can incorporate carbon dioxide and water, thus forming a number of crystal lattice defects such as vacancies, interstitial carbon atoms and even interstitial hydrogen atoms. On heating at temperatures 500–1000 K the gradual emission of gases from such samples occurs.

Mass analysis indicated the presence of not only H₂O and CO₂ but also of hydrogen, oxygen and even certain amount of different hydrocarbons. The latter are the products of the interactions of the lattice defects forming upon the incorporation of CO₂ and H₂O. The former supply carbon and the latter hydrogen for the formation of hydrocarbons.

Yet soon it was confirmed that other alkaline earth metal oxides such as SrO or BaO and also some silicates give similar effects. Professor Malinowski understood well the importance of all these investigations for the studies of the Earth's inner structure and some processes in tectonically active regions. He discussed the problem with his friends from the Institute of Geophysics of the Polish Academy of Sciences. The result of their collaboration was Malinowski's paper "Physical and Chemical Properties Related to Defect Structure of Oxides and Silicates Doped with Water and Carbon Dioxide" containing the critical review of the papers on defect structure of MgO published in the literature. It appeared as a chapter in the book "Earthquake Thermodynamics and Phase Transformations in the Earth's Interior" (Academic Press 2001) and was the last paper published during his life. Thanks to the courtesy of the Academic Press, the editors of the present issue can publish it again in the "Polish Journal of Chemistry", which is accessible to the polish chemical community.

As it was already said, in the last months of his life Prof. Malinowski returned continually to this problem studying recent literature. He was also preparing a kind of expertise indicating how interesting and important is developing this line of investigation and

aimed to stimulate the research in Poland in a program the guide-lines, of which were sketched in his last note. The whole of his elaborate work needs some editorial preparation and I hope it will be published in the future. Here we present the English translation of the last chapter "Summary and Conclusions", the outline of the program. It is both very valuable proposal for scientific discussions and research, but also a testimony of Professor's Malinowski scientific passion and invention persisting to the last days of his life. I trust it will be at the same time a reminiscence of his unforgettable personality, a text read with emotion by his friends and students.

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Summary and Conclusions

This elaboration intended to find the answer whether the formation of hydrocarbons (in the Earth's crust) directly from CO₂ and H₂O as the sources of carbon and hydrogen is possible. When discussing this problem as the point of departure we should look for raw materials containing carbon and hydrogen present in sufficient amounts enabling the formation of mineral oil. It has been here assumed that such conditions are only fulfilled by carbon dioxide as the source of carbon and water as the source of hydrogen. Consequently the question arises whether these two compounds can react with the formation of hydrocarbons. In the light of the present review the answer is positive. It indicates that at the conditions of high pressure and temperature at which – as it is now assumed – mineral oil had been forming, and at the presence of different minerals, the formation of hydrocarbons of carbon dioxide and water was essentially possible. This conclusion is based on the results of laboratory experiments carried out in recent years (1978–1984) indicating that such reactions may occur at the presence of alkali earth metal oxides. Until now in literature magnesium oxide has been investigated extensively (8 papers) in this respect. Two papers were published concerning calcium oxide there were. Also strontium oxide has been mentioned a few times.

These oxides play the role of catalysts in the reactions between water and carbon dioxide or carbonates. Their products are saturated and non-saturated hydrocarbons of different chain length and structure; aromatic hydrocarbons of different number of rings are also forming as well as certain amount of elemental hydrogen and oxygen. At the pressure of 1 atm. some of these reactions occur already at 200°C, the others at 600–800°C.

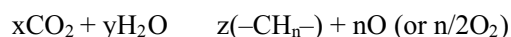
The main role as the reaction centers is played by the cationic vacancies of different types. They enable the dissociation of water into hydrogen and oxygen and carbon dioxide into atomic carbon and oxygen. Atomic carbon and hydrogen (atomic or molecular) migrate towards the surface of the CaO crystallites. Most probably reactions between carbon and hydrogen occur at the surface, thus giving a vast range of organic

compounds, mainly aliphatic hydrocarbons of different chain length and aromatic hydrocarbons exhibiting different number of aromatic rings.

The detailed mechanism of the formation of hydrogen and oxygen from water at the presence of alkali earth metal oxides, exhibiting defect structure, has been proposed by Freund. It has also been shown, that at the analogous conditions carbon dioxide can dissociate into atomic oxygen and atomic carbon. Such carbon atoms exhibit high mobility at the appropriate temperatures and accumulate in the next-to-surface layer. No detailed mechanism of the surface reactions leading to the formation of hydrocarbons has been proposed.

a)

The introductory thermodynamic analysis indicates that at temperatures of several hundreds to 1000°C the following reaction may occur



b)

Such conceived reaction, in the course of which elemental oxygen and hydrocarbons are forming, may occur under condition that electrons are supplied simultaneously i.e. at the presence of some reducing agent as *e.g.* Fe or other metals.

These two points a) and b) need detailed elaboration. The present conclusions concerning the formation of hydrocarbons from CO₂ and H₂O are based mainly on the experimental results, which were presented in the main part of present review. Although the mechanism of the reactions is not fully understood, the formation of hydrocarbons is confirmed. Partially known is the composition of the mixture of products and conditions of their formation, their amount and formation rate. Basic role is played by the alkali earth metal oxides, acting as catalysts or perhaps as reagents.

Conclusions

Basing on the description of experiments and results obtained by Professor's Freund team related in my review, a number of indications and proposals concerning further studies can be formulated in both theoretical and practical aspects.

Theoretical problems

1)

A theoretical study of thermodynamical aspects of well chosen reactions between water, carbon dioxide and carbonates, aiming to determine temperature effect on the equilibrium constants and reaction yield. Such data would give information concerning the possibility of realizing particular reactions at the laboratory conditions. A seminar concerning this topic should be organized.

2)

A theoretical study of the possibility of the formation of earth gas and coals from inorganic material, using calcium and strontium oxides as the catalysts (other oxides

should be taken into account if the appropriate investigations would be published). A seminar concerning this subject should be organized.

3)

Further literature studies, which would answer the following questions:

a)

are there in the literature publications concerning the effect of defect structure on physical and chemical activity of other oxides than magnesium, calcium and strontium

b)

physical and chemical properties of the compounds other than oxides containing carbon in their crystal lattice. Is this kind of carbon also mobile?

4)

Can the crystalline systems composed of more than one oxide (*e.g.* such as MgO-SiO₂) incorporate carbon atoms into the interstitials in a similar way as it occurs in the case of alkali earth oxides (MgO).

5)

As it was reported in my review, magnesium oxide is the catalyst of the reaction between water and carbon dioxide, which consists in fact of the surface reaction between atomic carbon and hydrogen. This indicates that the earlier research on catalytic properties of MgO surface should be again discussed and analyzed from that point of view. Such papers are numerous. However, there are no papers in which reactions between atomic carbon and hydrogen or water were studied on the surface of magnesium oxide. Similarly no studies of the well known formation of synthesis gas from solid carbon and water vapour were undertaken at the presence of MgO. This is in fact a new and interesting problem from both scientific and technological perspectives.

6)

One needs also some orientation and analysis from the point of view of the present report, which were the rocks and sediments accompanying – according to the present opinions – the formation of rock oil and similar products. What was their chemical composition and crystal structure? What were the reactions of the formation of such rocks? From which substrates and under which conditions? These latter questions should be answered by geologists and their interest in this field should be attracted.

Practical problems

Continuation in Poland of the further research on the possibilities of using carbon dioxide as the source of carbon in the synthesis of organic compounds. Utilization of water as the direct source of hydrogen in the formation of hydrocarbons and other organic compounds. The answer for this question – I think – will be found in the analysis of the work of Freund's team (and partially of Derouane) described above in my report and also in those theoretical studies suggested in the preceding section of this summary.

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**Physical and Chemical Properties Related to Defect
Structure of Oxides and Silicates Doped with
Water and Carbon Dioxide***

Stanisław Malinowski

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Acido-Basic Properties of Selective Oxidation Catalysts – an Overview

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Various aspects of acido-basic properties of transition metal oxides – catalysts for selective oxidation processes – are reviewed. The acido-basic properties of these catalysts may depend on coordination of the component ions, morphology of oxide crystals and the dispersion of an active oxide phase on a support. The methods for their determination are briefly described and the role of acido-basic properties in controlling the activity and selectivity of selective oxidation reactions is considered.

Catalysis on Bifunctional Pt Acid Zeolites. A Route to Cleaner Processes

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The large benefit brought by the association of hydrogenating sites (Pt or Pd) with the protonic acid sites of a zeolite is shown here on three examples of reactions related to Refining, Petrochemicals and Specialty Chemicals processes: n-alkane hydroisomerization and hydrocracking, ethylbenzene (EB) isomerization, synthesis of methylisobutylketone (MIBK) from acetone. Whatever the reaction, the bifunctional catalysts are more stable than the purely acidic catalysts. They are able to catalyze certain reactions, which cannot occur through acid catalysis (*e.g.* EB isomerization). They allow the synthesis in one apparent step of products, which requires several successive steps catalyzed by metallic and acidic sites (*e.g.* synthesis of MIBK). Their selectivity can be directed to the desired products (*e.g.* monobranched alkanes in isodewaxing, xylenes in EB isomerization). Moreover, the semi-quantitative relations, which were established between their physico-chemical properties, especially the balance between hydrogenating and acid functions and the zeolite pore structure, and their catalytic properties constitute guidelines for a scientific design of optimal catalysts and for the development of economic and environmentally friendly processes.

Temperature-Programmed Techniques in Catalysis

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The possibilities of application of TPR, TPO, TPD and TPSR techniques in the studies of catalysts as well as in the study of acidity of catalysts' surface are discussed.

Catalytic Combustion of Trichloroethylene over Pd-Doped Ti-Pillared Montmorillonites

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Palladium (0.8 wt.%) was introduced onto Ti-pillared montmorillonite samples by means of incipient wetness technique either before or after calcination of the pillared matrix. Combustion of trichloroethylene (TCE) has been chosen to test the catalytic properties of clay catalysts in deep oxidation of chlorinated volatile organics. The results were referred to the performance of a commercial catalyst. Both materials based on pillared clays were more active than the reference sample. The clay sample doped after calcination was better of the two and gave complete combustion of TCE at temperature by 100 K lower than the commercial catalyst. This material showed also the highest selectivity to HCl at maximum TCE conversion. Further improvement of the clay catalyst performance in terms of the HCl yield and suppression of chlorine evolution was achieved by addition of the methanol vapour to the reaction mixture. The results are discussed in terms of textural and acidic properties of the investigated catalysts.

Physicochemical Properties of CuAlMCM-41 and CuNbMCM-41 Mesoporous Molecular Sieves

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The texture and surface properties of copper-containing aluminosilica and niobiosilica mesoporous molecular sieves of MCM-41 type, in which all elements were introduced during the synthesis, have been studied by means of XRD, N₂ adsorption, H₂-TPR, FTIR combined with pyridine and NO adsorption as well as in the skeletal region, and the test reaction. The results were compared with those obtained earlier for Cu post synthesis exchanged AlMCM-41 and NbMCM-41. All the results and this comparison allow the suggestion that copper is partially located in the skeleton of both MCM-41 materials, which exhibit redox and acidic properties.

Nickel Mediated Coupling of Organic Ligands

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Reactions of nickelocene, NiCp_2 , with organolithium compounds RLi ($\text{R} = -\text{C}\equiv\text{CPh}$; $-\text{CPh}=\text{CPh}_2$; $-\text{CPh}_3$, $-\text{CPh}_2\text{SiMe}_3$), where R does not contain α - and β -hydrogen atoms, have been studied. It was found that $\{\text{CpNiR}\}$, formed in the first step of the reaction, underwent coupling with the formation of $\{(\text{NiCp})_2\}$ and R-R . As organolithium substrates are readily available, and yield of coupling products was high (from over 60% to ~90%), the studied reactions could be applied as synthetic methods for preparation of wide range of R-R type organic compounds. In order to improve yield of the products and to prevent very active $\{(\text{NiCp})_2\}$ species from further reactions, NiCp_2 and LiR were reacted in the presence of $\text{PhC}\equiv\text{CMe}$, what led to the formation of only two products: $(\text{NiCp})_2 \cdot \text{PhC}\equiv\text{CMe}$ complex and R-R . These products were easily separated by column chromatography on neutral alumina, leading to the isolation of R-R in high yield.

Phase Transfer Catalyzed Reactions of Chloroform with Methacrylic Esters

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Chloroform reacts with an excess of methyl methacrylate in the presence of 50% aq NaOH and benzyltriethylammonium chloride (TEBA) as a catalyst (phase transfer catalysis, PTC) to give a mixture of dichlorocarbene and trichloromethyl anion adducts, **1** and **2**, respectively. These additions proceed as parallel processes, there is a slow conversion of **2** → **1**, which proceeds as an intramolecular process.

Alkylpyridines Transformations over Acidic Catalysts. An Example of Radical Reactions on Ionic Surfaces

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4-Methyl-, 4-ethyl-, and 4-isopropylpyridine, ethyl-, and isopropylbenzene transformations were studied over the series of amorphous silica-aluminas. The main reactions of alkylpyridines were the transformations of the alkyl side chain. The crucial role of one-electron donor (radical) centres in the mentioned reactions was evidenced by the physicochemical characterization of the catalyst surfaces, the apparent correlation of activity vs. active centres concentration, and the dependence of product composition upon reaction conditions.

Pentane Transformation over Silicaalumina/ BCl_3 Solid Superacid

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Pentane transformation over $\text{SiO}_2(87\%) - \text{Al}_2\text{O}_3/\text{BCl}_3$ superacid was studied. It was found that Brönsted superacid centres formed in the reaction between the carrier and BCl_3 vapours are active in n-pentane low temperature transformation. Pentane is converted over them into carbenium ion (through intermediate carbonium ion), which either undergoes isomerization to form 2-methylbutane or reacts with a second molecule of the reactant forming 2-methylpropane and a longer surface carbenium ion. The latter acts as a secondary active centre for 2-methylpropane formation and also undergoes further transformation leading finally to coke.

Rhodium Complexes with HP(O)R_2 ($\text{R} = \text{Ph, OPh}$) Ligands – Structure and Catalytic Reactions with Phenylacetylene

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In the reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ with HP(O)(OPh)_2 the hydride rhodium(III) complex, $\text{HRh}\{\text{P(OPh)}_2\text{O}\}_2\text{H}$ (**1**), was obtained. Complex (**1**) at room temperature catalyzes dimerization of phenylacetylene to *trans*-diphenylbutenyne ($\text{PhCH}=\text{CHC}\equiv\text{CPh}$). The reaction of $[\text{RhCl}(\text{cod})]_2$ with HP(O)Ph_2 and PPh_3 led to the following new rhodium complexes: *trans*- $\text{RhCl}[\text{P(OH)Ph}_2]_2(\text{PPh}_3)$ (**2**), *trans*- $\text{RhCl}[\text{P(OH)Ph}_2](\text{PPh}_3)_2$ (**3**), $\text{HRh}[\text{P(OH)Ph}_2]_3$ (**4**) and $\text{RhCl}_2\{[\text{PPh}_2\text{O}]_2\text{H}\}_2[\text{P(OH)Ph}_2]_2$ (**5**), characterized by ^1H and ^{31}P NMR spectra. The hydride complex (**4**) catalyzes a coupling of HP(O)Ph_2 with $\text{PhC}\equiv\text{CH}$ (phosphorylation reaction) to 1-(diphenylphosphiny)-2-phenylethene ($\text{PhCH}=\text{CHP(O)Ph}_2$). In the first step of this reaction (**4**) reacts with $\text{PhC}\equiv\text{CH}$ forming alkene complex $\text{Rh}(\text{CH}=\text{CHPh})[\text{P(OH)Ph}_2]_3$ (**6**).

Temperature Programmed Desorption of Triethylamine from Differently Pretreated Pd/Al₂O₃ Catalysts

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The temperature programmed desorption (TPD) of triethylamine from alumina and two alumina-supported palladium catalysts of different metal loadings (0.3 and 2.77 wt.% Pd) confirmed the presence of strong Lewis acid sites in the samples subjected to high temperature reduction at 600°C. With increasing temperature during thermodesorption, triethylamine adsorbed on Lewis acid sites of alumina undergoes transformation, leading to desorption of several products, among which hydrogen, ethylene and acetonitrile predominate. However, introduction of increasing amounts of palladium to alumina makes the acidity probing difficult, because a considerable part of adsorbed triethylamine is decomposed on metal sites. Temperature programmed oxidation (TPO) shows that the organic coke left after TPD of triethylamine is associated with acid sites of alumina, not with palladium sites. Another observation that pure alumina and 0.3 wt.% Pd/Al₂O₃ retained larger amounts of coke than the 2.77 wt.% Pd/Al₂O₃ catalyst reveals a beneficial role of palladium in desorbing organic material in the course of TPD runs.

MoO₃/Al₂O₃ Catalyst: Comparison of Catalysts Prepared by New Slurry Impregnation with Molybdic Acid with Conventional Samples

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Alumina-supported molybdena catalysts were prepared by conventional impregnation with (NH₄)₆Mo₇O₂₄ (CIM) and by a new slurry impregnation method (SIM). SIM is the reaction of alumina support with the slurry of MoO₃ in water. Two commercial supports were used and the commercial MoO₃/Al₂O₃ catalyst was included for comparison. Maximum amount of MoO₃ deposited by SIM was about 19–20% MoO₃ with the surface area of the support of 260–280 m² g⁻¹ and this corresponded to saturation monolayer of similar density as described in literature for CIM catalysts. At the ratios of MoO₃ to Al₂O₃ in the impregnation slurry below saturation monolayer, the pH of the slurry was 3.5–6 (depending on loading) and chemical erosion of alumina was negligible. However, using the large excess of MoO₃ (35% MoO₃), the pH was 2.4–3.4 and chemical erosion of alumina occurred. Silica contained in alumina supports was partly extracted as soluble silicomolybdic anions during SIM. The catalysts were characterized by BET, IR, DRS (UV-vis and NIR), TPR, and catalytic activity in hydrodesulfurization of thiophene. Calcination had no significant effect on the properties of SIM catalysts and this proved that calcination is not needed in that method. All catalysts exhibited features of high monolayer dispersion of molybdena and no significant difference in structure and catalytic properties was observed between SIM and CIM catalysts. This confirmed that SIM is a simple, clean and reliable method of preparation of monolayer type MoO₃/Al₂O₃ catalysts.

Catalytic Performance of CuO/ZnAl₂O₄–Al₂O₃ Catalysts in *n*-Hexanol Conversion

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A series of CuO/ZnAl₂O₄-Al₂O₃ catalysts with various CuO loading were prepared by an impregnation method. The effect of copper oxide addition for the reaction of *n*-hexanol was examined. The reactions were carried out at atmospheric pressure in a fixed bed reactor in the temperature range of 533–663 K. Experimental data show that the addition of copper oxide into studied catalysts does improve the activity in dehydrogenation of alcohol. Catalysts containing CuO have both dehydration and dehydrogenation properties, whereas ZnAl₂O₄-Al₂O₃ carrier only dehydrates alcohol. Obtained results indicate that the dehydrogenation of *n*-hexanol over CuO/ZnAl₂O₄-Al₂O₃ catalysts proceeds *via* carboxy intermediate.

Hydrosulfurization of Methanol on Y₂O₃–TiO₂–ZrO₂ Catalysts

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Y₂O₃-TiO₂-ZrO₂ catalysts, where the contribution of oxide components ranges from 0 to 100 mol %, have been studied for their catalytic performance in methanol hydrosulfurization. Their activity and selectivity have shown a strong dependence on acid-base properties which, in turn, changed with catalyst composition. High yttria content favors selectivity to methanethiol, while catalysts highly active for the formation of dimethylsulfide were those containing 8 mol % Y₂O₃. The latter composition, which boosted selectivity to (CH₃)₂S, has created favorable conditions for the generation of acid centers in chemically mixed oxides as concluded on the ground of ESR studies and acidity measurements.