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Catalytic science and technology for environmental issues

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Abstract: In the first part of this lecture it is demonstrated, how knowledge that comes from studies of catalysis at the molecular level helps to design new, more efficient catalysts and catalytic processes. In the second part the importance of catalytic technologies for solving environmental issues and providing sustainable development is discussed. It is demonstrated how catalysis helps to protect the ozone layer, to combat the greenhouse effect, to create environmentally safer transport, to solve environmental problems of energy production, to prevent pollution by H_2S in gas and oil mining and by CH_4 in coal mining, to purify exhausts of chemical and various other industries, to provide the highest energy efficiency and minimize consumption of raw materials in the chemical, petroleum and other industries, to process renewable raw materials, such as biomass, into valuable chemicals. In the third part, the role of the natural abiotic catalysis in the chemistry of the troposphere is discussed.

INTRODUCTION

Catalysis is the backbone of the chemical industry. It is also a fundamental feature of all life processes and of chemistry of the environment (1-3).

In the past three decades we have witnessed in the scientific study of catalysis a continuous shift from phenomenological approaches to structural and mechanistic investigations at the molecular level (1). Engineering of catalytic reactors has also become more based on a deeper understanding of reaction mechanisms, mass- and heat-transfer phenomena in catalyst pores, pellets and beds, and mathematical modelling of catalytic processes (1).

Catalysts, made by molecular design, already play an important role in the development of new environmentally friendly industrial technologies (1,2,4).

New catalytic technologies help to protect the ozone layer, to combat the greenhouse effect, to create environmentally safer transport, to solve environmental problems of energy production, to prevent pollution by H_2S in gas and oil mining and by CH_4 in coal mining, to purify exhausts of chemical and various other industries, to provide the highest energy efficiency and minimize consumption of raw materials in the chemical, petroleum and other industries, to process renewable raw materials, such as biomass, into valuable chemicals (2). Reactions over abiotic aerosol particles as catalysts play an important role in the global and local chemistry of the atmosphere (3).

1. MOLECULAR DESIGN OF CATALYSTS AND PROCESSES

Let us consider a few typical examples that illustrate how the principles of molecular design can be used to develop new industrial catalysts and catalytic processes.

1.1. Catalytic Systems Based on Palladium

Palladium is one of the most important elements for the preparation of catalysts. Methods of molecular design are used nowadays to develop both homogeneous and heterogeneous palladium catalysts, as well as anchored and giant cluster palladium catalysts that cover the gap between classical homogeneous and heterogeneous catalysts.

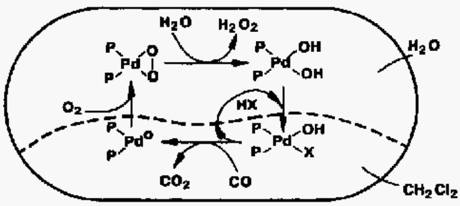
1.1.1. Homogeneous catalysis with Pd complexes

Many important features of homogeneous catalysis with metal complexes in solutions are quite well understood at the molecular level (4). Having at his disposal a list of known elementary reactions for complexes of various metals and estimates of thermodynamic and kinetic characteristics for these reactions, a researcher can design catalytic systems for selective transformations of various feedstocks into desired products (5).

By way of an example, in Scheme 1, the *a priori* expected pathway for synthesis of a valuable product H_2O_2, via conjugated oxidation of H_2O and such pollutant as CO

$$H_2O + O_2 + CO \xrightarrow[20^{\circ}C,\ 1\ atm]{H_2O/CH_2Cl_2} H_2O_2 + CO_2$$

is presented, from which the design of the really working catalytic system for this reaction has proceeded (1).



Scheme 1. Pathway for conjugated oxidation of H_2O and CO.

TABLE 1. Catalytic properties of palladium particles of various size anchored on the surface of Sibunit

Pd particle size/Å	Activity/g TFMNB · (gPd · min · atm)$^{-1}$	Selectivity (yield of TFMAB)
ca.10	6.9	99.98
10-30	12.0	98.8
60-120	3.0	99.0
ca.1000	1.3	80

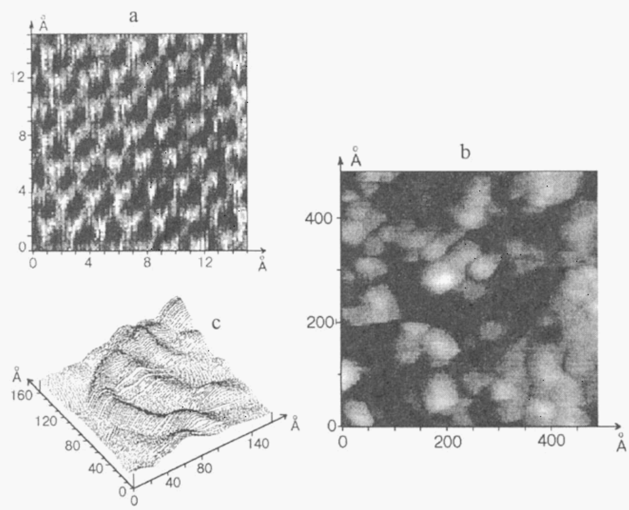


Fig. 1. STM images of: (a) - the basal surface of graphite; (b) - the surface of Pd/Sibunite catalyst with highly dispersed Pd particles; (c) - the surface of a large Pd particle in Pd/Sibunite catalyst.

1.1.2. Heterogeneous catalysis with supported Pd metal

An impressive example of taylor-made commercial heterogeneous catalysts is a new family of Pd/C (palladium supported on carbon) catalysts proposed for hydrogenation processes at the Boreskov Institute of Catalysis (6). For these new catalysts the size of supported palladium particles can be controlled rather precisely (2).

Particles of different size demonstrate differing activity and selectivity. As an example, in Table 1 the data are presented on hydrogenation of trifluoromethylnitrobenzene (TFMNB) to the corresponding amine (TFMAB). Based on these data, the catalyst with the particle size of 10-30 Å was chosen for commercial production.

The Scanning Tunneling Electron Microscopy (STM) data of Fig. 1 (7) explain why selectivity of Pd decreases with the increase of its particle size. As seen from Fig. 1c, the surface of a big Pd particle is rather rough, which implies different chemical properties of Pd atoms located at different spots of the surface.

Note that in these catalysts a new carbon support (so-called Sibunit) is used (2, 6). This support is non-pyrophorus, has a unique crushing strength (up to 500 kg/cm^2) and attrition stability, high thermal stability as well as porous structure and adsorption properties optimal for catalysis. Pd/Sibunit catalysts are efficient in slurry, fixed bed and fluidized bed processes. They have such advantages as high activity and selectivity, mechanical and thermal stability. All these properties are very important for making hydrogenation technologies more friendly to the environment. Sibunit and Pd/Sibunit catalysts for various hydrogenation processes are commercially produced in Russia by KALAN Ltd.

1.1.3. Catalysis with anchored Pd complexes

By anchoring metal complexes to the surface of a support one can prepare taylor-made heterogeneous catalysts with the intentionally designed composition and structure of the active sites (8).

As an example, in Fig. 2a the active site is presented of the bimetallic (Pd+Co)/SiO_2 catalyst for hydroformylation of olefins, designed by V.A. Likholobov with co-workers (5). This site was assembled by anchoring carbonylphosphine palladium and cobalt complexes to the surface of SiO_2. The mechanism of hydroformylation of ethylene over this bimetallic site is shown in Fig. 2b.

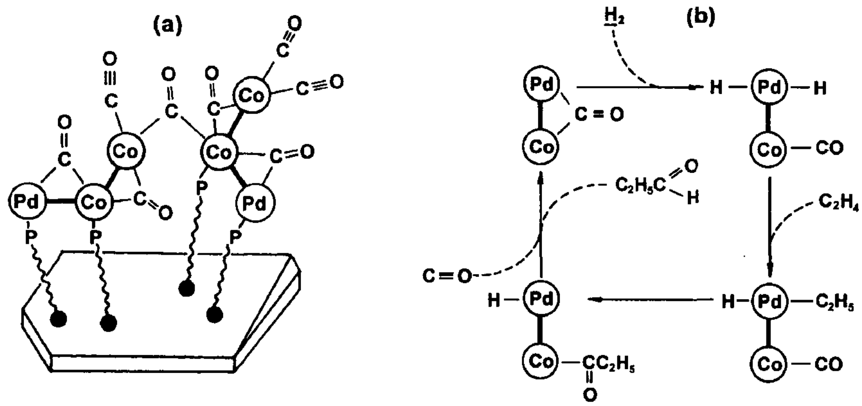


Fig. 2. Active site of the bimetallic (Pd+Co)/SiO_2 catalyst (a) and the mechanism of hydroformylation of ethylene over this site (b)

Pd is more active than Co in the steps of activation of H_2 and insertion of C_2H_4 into the metal-hydride bond, while Co is more active than Pd in the insertion of CO into the metal-alkyl bond. As a result, Pd and Co work together in the bimetallic site much more efficiently than each of them works alone in similar monometallic sites that contain only Pd or only Co.

1.1.4. Catalysis with giant Pd clusters

New recently designed catalytic materials are soluble giant palladium clusters containing more than 500 metal atoms (9). Among reactions catalyzed by giant Pd clusters very selective oxidation of olefins should be mentioned (reactions 1):

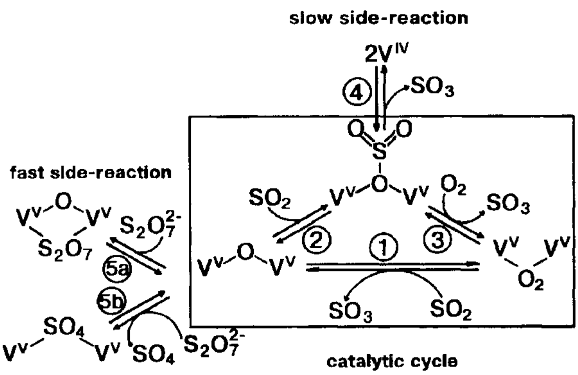
1. $C_2H_4 + 1/2O_2 + AcOH \longrightarrow CH_2 = CHOAc + H_2O$
   $C_3H_6 + 1/2O_2 + AcOH \longrightarrow CH_2 = CHCH_2OAc + H_2O$ } Yield 95-98%
   $PhCH_3 + 1/2O_2 + AcOH \longrightarrow PhCH_2OAc + H_2O$
2. $2RCH_2OH + O_2 \longrightarrow RCOOCH_2R + 2H_2O$
3. $(CH_3)_2CHOH + 1/2O_2 \longrightarrow CH_3COCH_3 + H_2O$ Yield 100%

Note also a 100% (within the accuracy of GC analysis) selectivity of reaction 3. This is the value of selectivity that is nowadays achievable and must be accepted as a standard for commercial catalytic processes, if we want to make chemical industry of the XXI century environmentally friendly.

1.2. Redox Catalysis by Oxides

An excellent example of an industrial oxide catalyst that has been substantially improved using molecular design is the vanadium catalyst for the oxidation of SO_2 to SO_3 in the production of sulfuric acid, developed by G.K. Boreskov with co-workers (10). Its distinct feature is a combination of a detailed (at the level of elementary steps) investigation of reaction kinetics with the thorough examination of the catalyst states at various stages of its preparation and process performance, using a combination of spectroscopic techniques. The insight into the mechanism of this heterogeneous reaction is almost as deep as that traditionally available for only homogeneous catalysis.

The mechanism of SO_2 oxidation to SO_3 over industrial vanadium catalysts, as elucidated with various spectroscopic methods as well as relaxation and steady-state kinetic methods, is presented in Scheme 2.



Scheme 2. The mechanism of SO_2 oxidation to SO_3 over industrial vanadium catalysts.

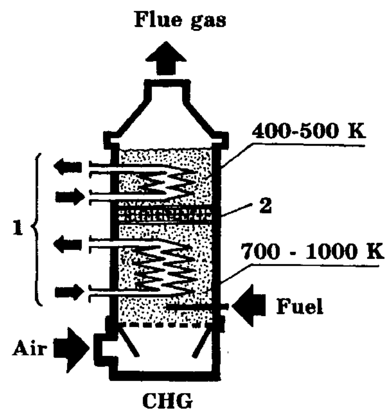


Fig. 3. A Catalytic Heat Generator (CHG) for heating/evaporation of liquids: 1 - heated liquid; 2 - temperature regulating grid.

Based on the knowledge of the kinetics and mechanism, substantial improvements were proposed at the Boreskov Institute of Catalysis for both the composition of the vanadium catalysts and the operation of catalytic reactors for SO_2 oxidation (*vide infra)*.

2. CATALYTIC TECHNOLOGIES FOR ENVIRONMENTAL ISSUES

2.1. Role of Catalysis in Protection of the Ozone Layer

It is known that some of synthetic products nowadays introduced to meet the requirements of modern civilization (for example, fully haloidated chlorofluorocarbons CFCs), deplete the ozone layer (11). New catalysts play an important role in the development of technologies for obtaining ozone friendly alternatives (such as hydrochlorofluorocarbons (HCFCs) (11).

Table 2 presents the list of HCFCs alternatives to the ozone depleting CFCs obtained with various catalysts. The data are taken from the review by L.E. Manzer (11).

2.2. The Importance of Catalysis in Decreasing the Greenhouse Effect

The so-called greenhouse effect, which produces extremely unfavourable ecological consequences, may be decreased by development of:

a) energy-saving technologies on the basis of environmentally more friendly catalytic combustion of fuels (12); b) new catalysts for high output fuel cells (12); c) catalysts and processes for solar energy conversion and hydrogen energetics (12); d) catalysts and processes for synthesis from CO_2.

TABLE 2. Ozone friendly HCFCs alternatives to ozone depleting CFCs

Market	Current CFC	HCFC-Alternative
Refrigerants	CF_2Cl_2	CF_3CFH_2 CHF_2Cl Blends/Azeotropes
Blowing Agents	$CFCl_3$	CH_3CFCl_2 CF_3CHCl_2 CHF_2Cl Blends/Azeotropes
Cleaning Agents	$CF_2ClCFCl_2$	New Compounds

2.2.1. Technologies based on catalytic combustion

The main contributor to the greenhouse effect is known to be CO_2. Considerable reduction of the CO_2 emission into the atmosphere can be achieved by carrying out combustion processes in a more economic way in the so-called Catalytic Heat Generators (CHGs) that were designed and commercialized by the Boreskov Institute of Catalysis (13). CHGs (Fig. 3) are devices, where the highest energy efficiency is achieved by combining in one reactor various energy-consuming processes (such, e.g., as heating or evaporation of water and other liquids, drying and thermal treatment of solid powders, detoxication of waste water from organics etc.) with catalytic oxidation (i.e. combustion) of fuel with the stoichiometric amount of air at the desired temperature in a fluidized bed of special catalysts.

Catalytic combustion in CHGs is much more economic with respect to the consumption of fuel and energy efficiency and much more friendly to the environment than a conventional non-catalytic combustion in furnaces. In particular, the emission of CO_2 is reduced and the formation of nitrogen oxides is crucially suppressed with combustion in CHGs.

Various technologies based on CHGs have been commercialized in Russia and Kazakhstan.

2.2.2. Catalysts for high output fuel cells

Another route to reduce CO_2 emission into the atmosphere is to generate electricity via electrocatalytic oxidation of hydrocarbons in high output fuel cells (Fig. 4). Such fuel cells demonstrate notably higher efficiency of conversion to electricity of the chemical energy of hydrocarbon fuels than conventional thermal electric power plants (12).

Note that value added products such as ethylene can be formed from CH_4 in the fuel cell simultaneously with electricity, given appropriate choice of catalytic material for the anode.

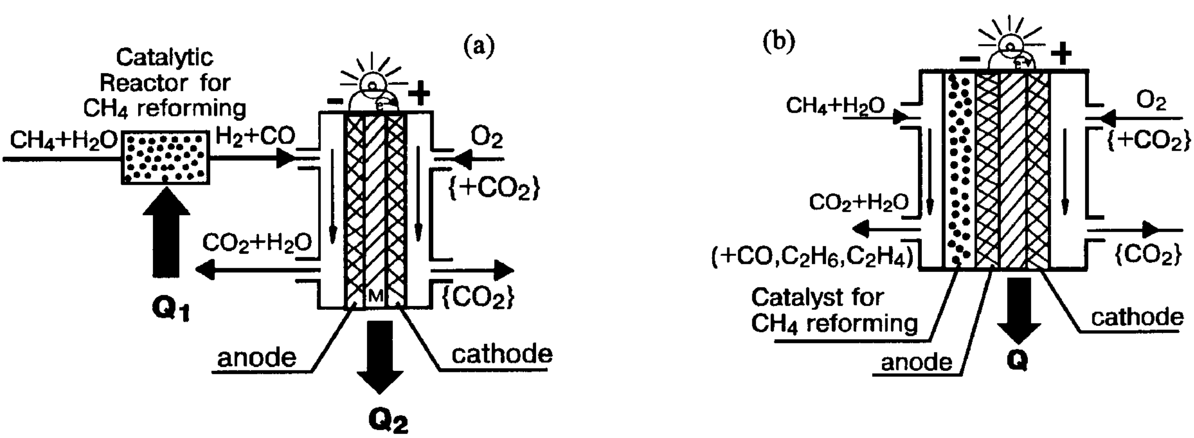


Fig. 4. High output methane fuel cells with the external (a) and internal (b) reforming of CH_4. Thick arrows indicate heat fluxes. M is the high-temperature oxygen conducting membrane or molten carbonate.

2.2.3. Catalytic devices for solar energy conversion

Solar light is an alternative source of energy that is quite friendly to the environment. In particular, it emits neither CO_2 nor other greenhouse gases into the atmosphere. Moreover, solar energetics produces no acid rains.

The most attractive method for solar energy utilization seems to be its direct conversion to the energy of chemical fuels, thereby allowing it to be accumulated so as to smooth the supply (12).

In Fig. 5 is presented a photograph of a working pilot plant for thermocatalytic conversion and utilization of solar energy, based on a closed thermochemical cycle. At the first stage of the process solar energy is converted into the chemical energy of syngas (i.e., $CO+H_2$ mixture) via the endothermal reaction of methane reforming with steam

$$CH_4 + H_2O \longrightarrow CO + 3H_2 .$$

This reaction is provided by heating of the catalyst bed for CH_4 reforming with the concentrated solar flux. The obtained syngas can be stored for a long time. When needed, the stored energy can be released via the reversed exothermal methanation reaction

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

which restores the initial chemical composition of the circulating reaction mixture.

The pilot plant of Fig. 5 has been built at the Boreskov Institute of Catalysis and installed in the Crimea (Ukraine). An efficiency ca. 43% at the useful power of 2 kWt has been achieved for the thermocatalytic solar-to-chemical energy conversion. Recently an efficiency as high as ca. 70% has been achieved for this process under laboratory conditions at the Institute.

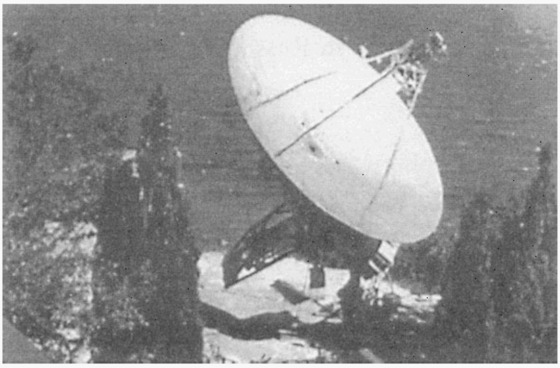


Fig. 5. A working pilot plant for thermocatalytic conversion and utilization of solar energy.

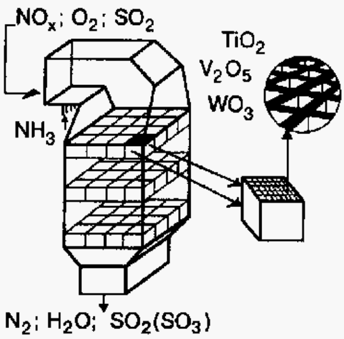


Fig. 6. Reactor and honeycomb catalyst for the catalytic reduction of NO_x in flue gases of power plants.

2.2.4. Catalytic processes for syntheses from CO_2

Catalysis can help to combat the greenhouse effect by using CO_2 emitted at power and steel plants as a feedstock for syntheses of various chemicals. At elevated temperature, CO_2 reacts with coal to produce CO

$$CO_2 + C \longrightarrow 2CO .$$

When mixed with H_2, the obtained CO makes the syngas - a famous feedstock for catalytic organic syntheses. However, for large-scale organic syntheses based on CO_2 feedstock to become actually feasible, new processes must become available for production of H_2. These processes must be based on decomposition of H_2O with alternative (other than oil, coal or natural gas) sources of energy, such as nuclear or solar.

2.3. Catalysis in Creation of Environmentally Safer Transport

Catalytic technologies help to substantially reduce pollution of the Earth atmosphere with transport vehicles by: (a) production of unleaded gasoline (14a), (b) production of motor fuels with still lower sulfur content (14b), (c) production of automobile catalytic converters (15), (d) development of anew generation of engines on the principles of catalytic fuel combustion (15).

2.4. Role of Catalysis in Solution of Environmental Problems of Energy Production

Catalytic technologies help to solve eenvironmental problems of energy production by: (a) catalytic removal of NO_x from flue gases of power plants (see Fig. 6) (16); (b) development of environmentally safer catalytic combustion processes (12); (c) development of catalytic heat generators (CHGs) and technological processes on their basis (13).

2.5. Catalysis in Purification of Industrial Exhausts

Catalysis helps to purify industrial exhausts by: a) development of technologies for purification of industrial flue gases from CO, NO_x, SO_2, H_2S, COS, hydrocarbons and other organics; among them are unique unsteady-state technologies (17) and one-step selective oxidation of H_2S into sulfur (18); b) development of technologies for catalytic recycling or incineration of solid and liquid wastes (19); c) development of technologies for catalytic incineration of pesticides and poisonous organic substances containing Cl, F, P, S, N, etc; d) replacement of conventional liquid acids by solid superacids in organic syntheses (20).

2.5.1. Catalytic technologies for purification of industrial flue gases

As the first example, Fig. 7a exhibits the technological scheme of the unsteady-state catalytic process of SO_2 removal from flue gases of non-ferrous metallurgy plants via its oxidation and conversion to sulfuric acid. This technology has been designed and commercialized by G.K. Boreskov and Yu.Sh. Matros with co-workers at the Boreskov Institute of Catalysis (17). Its advantages compared to conventional steady-state technology (Fig. 7b) are significant simplification of the reactor unit and cut in capital investments, decrease of energy consumption and possibility to process diluted (with respect to SO_2) gases and gases with a variable concentration of SO_2.

Similar, very efficient unsteady-state technologies have been commercialized by the same Institute for detoxication of flue gases from CO and various organics, as well as from NO_x (17).

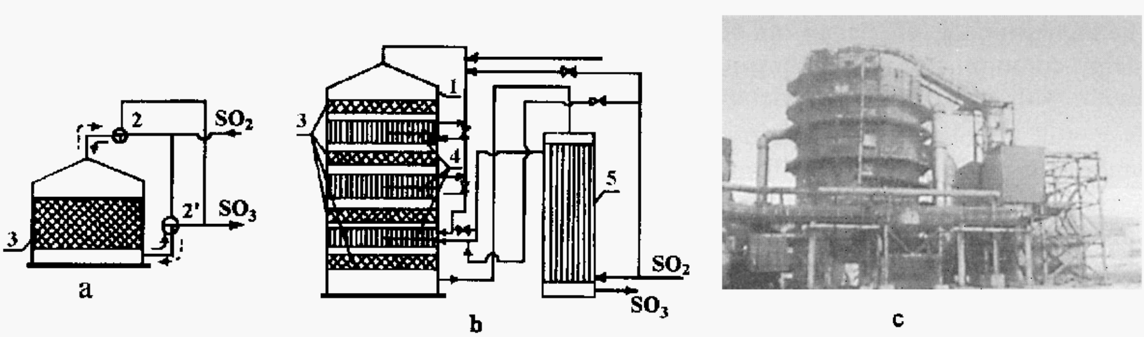


Fig. 7. Schemes and relative sizes of catalytic reactor and heat exchanger units for unsteady-state (a) and traditional steady-state (b) performance of SO_2 removal from flue gases of non-ferrous metal plants (1 - reactor, 2 and 2' - three wày valves; 3 - catalyst beds; 4 and 5 - heat exchangers). Photograph of the industrial unit for unsteady-state SO_2 removal (c).

As the second example, in Fig. 8 the scheme is presented of the one-step removal of H_2S from flue gases via selective oxidation to sulfur in a fluidized catalyst bed. This technology has been proposed recently at the Boreskov Institute of Catalysis by Z.R.Ismagilov with co-workers (18).

This technology is much simpler than the conventional multi-step Claus process. It can be used to remove H_2S from flue gases of refineries, streams of natural gas, hot waters of geothermal power stations, etc.

2.5.2. Technologies for catalytic recycling or incineration of solid and liquid wastes

T. Ono, K. Saito and A. Kobayashi have described a catalytic technology for recycling plastics via their liquification into motor fuels (19a).

Another example in this area are catalytic technologies for environmentally safer catalytic incineration of solid and liquid wastes in Catalytic Heat Generators (13).

A special note should be made about technologies for incineration of pesticides and toxic organic substances, containing Cl, F, P, S, N, etc. Non-catalytic combustion of these compounds in a furnace is often accompanied by emission of such harmful pollutants as dioxines, as well as SO_2, NO_x, etc. Therefore, work is under way on catalytic technologies that convert burnt compounds selectively into harmless products. For example, combustion catalysts have been designed that convert organic nitrogen mainly to N_2 rather than NO_x (12).

2.6. Role of Catalysis in Preventing Pollution of the Atmosphere by H_2S in Gas and Oil Mining and by CH_4 at Coal Mining

Catalysis helps to prevent pollution of the atmosphere by H_2S in gas and oil mining and by CH_4 in coal mining by: processing H_2S into sulfur in a traditional multi-step Claus process (21); processing H_2S into sulfur in a new one-step process of selective oxidation (Fig. 8) (18); as well as oxidation of CH_4 in diluted mixtures with air using unsteady-state technology (17).

In the latter process substantial amount of energy can be produced simultaneously with the elimination of CH_4.

2.7. Catalysis in Providing Highest Energy Efficiency and Minimizing Consumption of Raw Materials in Chemical, Petroleum and Other Industries

In the coming years, energy efficiency is expected to be substantially improved and consumption of raw materials minimized with the use of new catalytic technologies. The chemical and petroleum industries are expected to be revolutionized by a coming new generation of tailor-made catalysts, that will accomplish multi-step reactions in one step and provide selectivity with respect to the desired product close to 100%, thus minimizing the consumption of raw materials.

The highest energy efficiency can be achieved using Catalytic Heat Generators, where various energy-consuming processes (heating, evaporation, drying, etc.) can be combined in the same reactor with environmentally friendly catalytic combustion at a desired temperature.

Even well established branches of the chemical industry, e.g., production of sulfuric acid, synthesis of ammonia and methanol, steam reforming of methane, sulfur recovery from H_2S and SO_2 as well as detoxication of exhaust gases from various industries, can be revolutionized with respect to energy efficiency by new catalytic technologies, such as unsteady-state reverse processes or one-step selective oxidation of hydrogen sulfide to sulfur.

2.8. Role of Catalysis in Processing Biomass into Valuable Chemicals

In future, biomass may become an important feedstock for chemical industry. Using catalytic technologies, it is possible to convert biogas into syngas, that can be further converted into various valuable chemicals over appropriate catalysts. In this way, liquid hydrocarbon fuels and various chemicals can be produced from biomass (22).

Pyrolysis of biomass into the so called bio-crude-oil with the subsequent catalytic upgrading of the latter is yet another way to produce liquid fuel (23).

Catalytic technologies can be used also to convert components of biomass selectively into various valuable products (24).

3. THE ROLE OF NATURAL ABIOTIC CATALYSIS IN THE GLOBAL CHEMISTRY OF ATMOSPHERE

Recently an expected important role of catalysis in the global (and local) chemistry of the Earth atmosphere has been reported (3). In particular, a possible role of heterogeneous photocatalysis over dust aerosol particles was estimated to be nonnegligible (3). Photocatalytic processes may occur in the troposphere on aerosol particles containing Fe_2O_3, TiO_2 and ZnO (Fig.9) under the action of the near ultraviolet, visible and near infrared solar light.

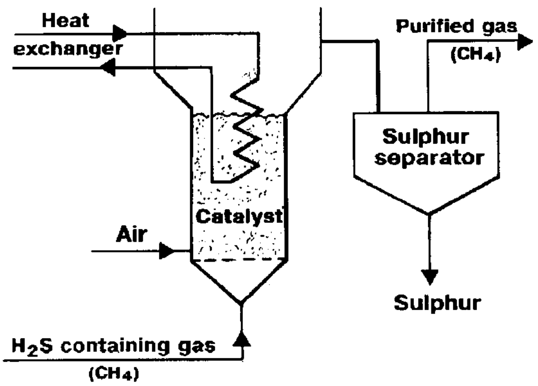


Fig. 8. Reactor with fluidized catalyst bed for selective oxidation of hydrogen sulfide.

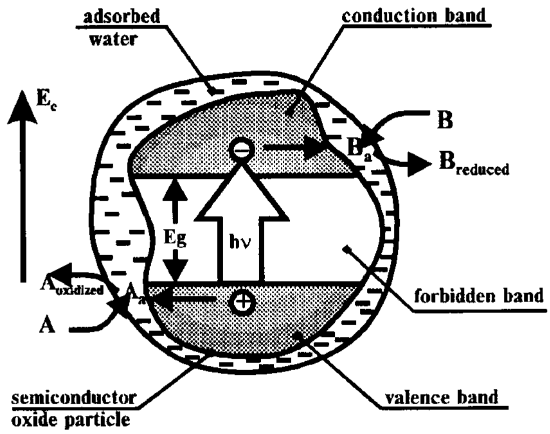


Fig. 9. Photogeneration of the holes and electrons at the aerosol semiconductor particle under light with $h\nu > E_g$ and subsequent redox processes that provide the overall reaction: $A + B \longrightarrow A_{oxidized} + B_{reduced}$.

Photocatalysis is anticipated to affect the intensity of acid rains, concentration of some "greenhouse gases" and clean the atmosphere from harmful compounds. Thus, desert areas where continental dust is generated, perhaps, may serve as "kidneys" of the Earth.

CONCLUSION

The examples presented above suggest that the innovations which will come from catalysis are indeed likely to make the industry of the future much more friendly to the environment, much more efficient with respect to the consumption of energy and raw materials, susceptible to the use of alternative feedstocks of raw materials and energy. Through this catalysis will help to provide a sustainable development of mankind and improve the quality of life worldwide.

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