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Translated from *Uspekhi Khimii* **60** 649–652 (1991)

Development and introduction of catalytic methods for the detoxification of industrial and automobile transport waste emissions

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New technologies based on the use of chemical catalysis should play an important role in the solution of acute ecological problems. Firstly, these are the catalytic technologies for the detoxification of the largest amounts of waste emissions from industry and automobile transport. Secondly, these are new technologies, producing little waste, for the manufacture of chemical products and based on the use of more selective catalysts.

The catalytic technologies for the detoxification of gases and liquid waste from various branches of industry and automobile transport, developed by the "Katalizator" Interbranch Scientific-Technical Complex, will be examined below. Their wide scale employment in the existing undertakings and in transport could even today improve significantly the ecological situation in our country.,

1. Elimination of sulphur dioxide from the waste gases in non-ferrous metallurgy

The emission of sulphur dioxide by non-ferrous metallurgical industries is one of the principal sources of the formation of acid rain. The "Katalizator" Scientific-Technical Complex is developing, jointly with the organisations of Ministry of Metallurgy of the USSR, several technologies for the removal of sulphur dioxide from such gaseous emissions with the simultaneous manufacture of valuable products — sulphuric acid or elemental sulphur. Some of these developments are significantly superior to those abroad as regards the level of their sophistication.

A non-stationary method (the flow reversal process) for the removal of sulphur dioxide with the simultaneous manufacture of sulphuric acid has been developed. This new technology is suitable for the majority of regions in the USSR. It is applied on an industrial scale in a number of factories. With the aid of this technology, more than 300 000 tonnes of sulphuric acid annually is already being produced† and is finding useful applications in the national economy. Licences for the flow reversal process for the oxidation of sulphur dioxide have been taken up by firms in Japan and Bulgaria.

Catalysts and processes for the conversion of sulphur dioxide into sulphur are being developed for the detoxification of the waste gases from the Noril'sk Mining-Metallurgical Industrial Unit. The conversion of sulphur dioxide into sulphuric acid under the conditions of the Noril'sk establishment is not appropriate because of the difficulties in transporting it away. Sulphur can be obtained by the partial reduction of sulphur dioxide to hydrogen sulphide, after which the catalytic Claus process is carried out. This process can be achieved in the presence of both heterogeneous and homogeneous catalysts. Both heterogeneous and homogeneous catalysts of the Claus process, specially developed for the Noril'sk Mining-Metallurgical Industrial Unit, have already been tested experimentally in the latter. The characteristic features of the new heterogeneous catalyst are improved activity (as a result of this, it is possible to reduce significantly the size of the catalytic apparatus) and also resistance to the oxygen present in the waste gases from the unit. The manufacture of a large batch of this catalyst for experimental-industrial tests is being prepared.

A method for the removal of sulphur dioxide from waste gases is being developed on the basis of the new homogeneous catalyst — the so called LES‡ (liquid-phase elimination of sulphur) process. At the present time this method is being tested on a large scale experimental apparatus in Noril'sk.

2. Elimination of nitrogen oxides from the waste gases from chemical industries and thermal electric power stations

A new catalytic method is being developed for the reduction of nitrogen oxides by ammonia under artificially created non-stationary conditions (a variant of the flow reversal process). An experimental-industrial apparatus with an output of 10 000 $m^3\ h^{-1}$ has been constructed and has been working successfully.

A variant of the flow reversal process for the selective catalytic reduction by ammonia of nitrogen oxides in the waste gases from thermal electric power stations is being developed.

3. Elimination of hydrogen sulphide from natural gas

The natural gas from a number of large deposits in the USSR contains considerable admixtures of hydrogen sulphide. The method for its elimination used at present is fairly complex. It is based on the partial oxidation of hydrogen sulphide to sulphur oxides followed by the multistage Claus process. The "Katalizator" Interbranch Scientific-Technical Complex has been developing jointly with the organisations of the Ministry of the Gas Industry of the USSR a fundamentally new single-stage purification technology involving the catalytic oxidation of hydrogen sulphide to elemental sulphur. The method has passed an experimental test in the detoxification of the so called blow-off gases from bore holes.

4. Elimination of carbon monoxide and organic substances from industrial waste gases

An appreciable amount of carbon monoxide and a wide variety of organic compounds is present in the waste gases from ferrous metallurgical and chemical industries. Harmful organic substances

† February, 1989.

‡ SOZh in Russian (Ed. of Translation).

are also present in the emissions from a number of other undertakings employing solvents, varnishes, etc.

In order to achieve the detoxification of such emissions, the "Katalizator" Scientific-Technical Complex has proposed several technologies based on catalytic extensive oxidation reactions. The usefulness of a particular technology is determined by the nature and concentration of harmful impurities, the degree of saturation of the emission with dust, etc. For high concentrations of the substances being oxidised, one can employ the oxidation method in additional reactors with a stationary catalyst bed. At lower concentrations (down to 0.5–0.8 g m^{-3}), the flow reversal process is effective. This new energy-saving method has already been introduced in seven§ undertakings in different cities. At still lower concentrations, it is possible to use the adsorption-catalytic method. Finally, the method involving oxidation in a fluidised catalyst bed is promising for the detoxification of dust–gas mixtures. In particular, studies are being prosecuted on the introduction of this method for the purification of gaseous emissions from the Coke-Chemical Industry and plants for the dry quenching of coke.

5. Catalytic combustion of liquid organic waste

A method has been developed for the combustion of liquid organic waste in compact reactors with a fluidised catalyst bed (catalytic heat generators). The procedure makes it possible to burn the waste at comparatively low tempereatures, i.e. under conditions which rule out the formation of toxic nitrogen oxides, and at the same time it permits the utilisation of the heat evolved.

6. A catalytic method for the detoxification of waste water

This technology is also based on the use of catalytic heat generators. It has passed an experimental-industrial test and is applicable to the purification of salt-free waste waters containing organic substances at concentrations sufficient to vaporise water by the heat of their combustion.

A similar technology is being developed also for the detoxification of the solid waste present as admixtures in waste waters.

7. Block catalysts for the purification of the exhaust gases from internal combustion petrol engines

The exhaust gases from automobile transport constitute one of the main sources of the pollution of the atmosphere by carbon and nitrogen oxides. Specimens of block and granulated catalysts of different kinds have been produced for the elimination of these oxides from the exhaust gases. Experimental tests of catalysts based on metallic blocks and alumina grains have been carried out with positive results.

The data presented below concerning the catalytic technologies for the detoxification of the gaseous and liquid emissions from industry and automobile transport, being developed at the "Katalizator" Interbranch Scientific-Technical Complex, are summarised in Table 1, which also indicates the level (i.e. the degree of completion) of each development. About half of them have been introduced into industry or are at the stage of experimental-industrial tests.

Table 1. Catalytic technologies for the detoxification of the waste emissions from industry and automobile transport developed at the "Katalizator" Interbranch Scientific-Technical Complex.

Type of pollutant	Source of pollution	Type of development	Level of development
Sulphur dioxide	Waste gases from metallurgical and chemical industries; natural gases; concomitant gases in petroleum processes; gaseous emissions from heat and power generating plant	Non-stationary method for the processing of sulphur oxides with formation of sulphuric acid	Industrial apparatus
		Liquid-phase purification method with formation of commercial sulphur	Experimental-industrial apparatus
		New catalysts of the Claus process	Experimental apparatus
		Claus method in a non-stationary regime	Research stage
		Catalytic procedure for the purification of waste gases from the Claus process	Experimental apparatus
Hydrogen sulphide	Waste gases from metallurgical and chemical industries; concomitant gases in petroleum processing	Liquid-phase purification method with formation of commercial sulphur	Experimental-industrial apparatus
		New catalysts of the Claus process	Experimental apparatus
		Claus method in a non-stationary regime	Research stage
		Catalytic procedure for the purification of waste gases in the Claus process	Experimental apparatus
		Plants for the detoxification in a fluidised bed of the hydrogen sulphide-containing blow-off gases from bore holes	Experimental apparatus
Nitrogen oxides	Technological gases and gaseous emissions from industrial undertakings; spent gases from internal combustion engines; gaseous emissions from heat and power generating plant	Non-stationary purification method	Experimental-industrial apparatus
		Development of block catalysts for converters	Experimental-industrial apparatus
		Development of granulated catalysts for converters	Experimental-industrial apparatus
		Method of involving selective catalytic reduction by ammonia	Research stage
Carbon monoxide	Technological gases and gaseous emissions from industrial undertakings; spent gases from internal combustion engines	Non-stationary purification method	Experimental-industrial apparatus
		A fluidised bed catalytic purification method	Experimental apparatus
		Adsorption-catalytic purification method	Experimental-industrial apparatus
		Development of block catalysts for converters	Experimental apparatus
Organic compounds	Technological gases and gaseous emissions from industrial undertakings; waste water; products of the incomplete combustion of organic fuels	Non-stationary purification method	Industrial apparatus
		A fluidised bed catalytic purification method	Experimental apparatus
		Detoxification plant used on catalytic heat generators	Experimental-industrial apparatus
		The use of mixed catalytic air heaters for combustion	Experimental-industrial apparatus

However, the rate of introduction of the new developments is clearly unsatisfactory. They have been applied in a comparatively small number of undertakings and have not so far led to a

§ By February, 1989.

significant alteration of the ecological situation in our country. The main reason for this unsatisfactory situation is inadequate interest in industrial undertakings in measures for the protection of nature. In my view, there is only one solution to the problem which has arisen: the universal introduction of fines for exceeding the level of harmful emissions above the permitted limit. A reasonable approach is necessary both to the selection of the initial magnitude of the fines and to the dynamics of their increase as a function of time. Both these parameters must be chosen so that industrial undertakings are encouraged to introduce more rapidly nature-protecting technologies without going at the same time beyond the limits of realistic possibilities.

From statements made by the leaders of the State commission on Nature in the USSR, we known that the inevitable introduction of fines is expected at the beginning of the next five year plan and that proposals for the appropriate resolutions are being prepared. They suggest that it would be right to publish these proposals as quickly as possible, so that they can be discussed in good time and also to make sure that workers of the industrial undertakings and in transport should be convinced of the reality of the coming fines.

Translated from *Uspekhi Khimii* **60** 653–658 (1991)

Ecological aspects of the production and consumption of hydrogen

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The world annual production of hydrogen is about 50–60 million tonnes, including that of the USSR which is about 6 million tonnes. Natural gas is the major raw material for the production of commercial hydrogen; the amount of hydrogen obtained by electrochemical methods is not greater than 1–2% of the total.

Virtually all hydrogen produced is consumed within the chemical industry, in particular for the production of ammonia and nitrogeneous fertilisers. In the decades ahead, it is expected that not only will hydrogen production increase (to 80–100 million tonnes annually), but also the structure of its consumption will change. It is also predicted that the use of hydrogen in the national economy will increase in an effort to create ecologically clean power generation and fuel technology for transportation facilities, to increase substantially the efficiency of oil refining and to use coal as the raw material for the production of synthetic fuel. Even nowadays, a small admixture of hydrogen to motor fuels would assist in overcoming a number of regional environmental problems, primarily those of increasing pollution of the atmosphere by carbon monoxide and carcinogenic products from the combustion of organic fuels, prevalent in large cities and opencast mines, which produce ore, coal, and other minerals.

Hydrogen is assuming special importance in low-volume high-technology branches of industry, such as electronic and pharmaceutical, in the production of high-purity metals and alloys, composite materials, chemically highly active substances, catalysts, and the like.

In the mid-1970's, the possibilities of the widespread use of hydrogen in the national economy as an alternative fuel or energy carrier were considered in the context of the so-called "energy crisis". At that time, however, various approaches to energy problems, based on the concept of hydrogen energy system, despite its apparent logic and attraction, were not supported by the necessary volume of research and development work. What is more, in engineering and economical respects the above approaches lost the competition with alternative ideas for the development of power engineering complexes based on high-performance energy-saving technologies.

At present, owing to the worldwide deterioration of the ecological situation, hydrogen is again actively considered as an alternative fuel and hopes are being placed on it. This feeling was expressed by the US participant at the 7th International Conference on Hydrogen Energy Systems, held in Moscow in October 1988. The use of hydrogen "gives humanity a unique change to survive in the world, rescued from ecological and social disasters", he said in his concluding remarks.

It is worth quoting some figures which illustrate how acute is the ecological problem associated with the combustion of organic fuel. In recent years, the industrial emission of carbon dioxide has been in excess of 5 billion tonnes annually, while that of carbon monoxide was in the range of 100–200 million tonnes annually. The emissions increased by a factor of 3.5 compared with their level in the 1950's and the tendency to increase is continuing: by the year 2000, the amount of carbon dioxide entering the atmosphere will rise to 6.0–6.5 billion tonnes annually, whilst that of carbon monoxide will rise to 250–300 million tonnes annually. Motor transport is responsible for up to 20% of CO_2 and (depending on the region) for 60–90% of CO emissions. For example, during the period 1985–1988, 800 000 trucks and diesel buses, which formed part of the Moscow fleet, ejected into the atmosphere about 200–250 thousand tonnes of carbon monoxide annually, excluding carcinogenic smoke resulting from incomplete combustion and pyrolysis of organic fuels.

However, in order to pave the way for hydrogen energy systems, including ecologically clear transport, we must solve a number of complex technical problems, relating to chemistry and to hydrogen technology, or at least in the next few years get this process going.

The first problem is due to the fact that hydrogen is currently too expensive as a fuel and is produced in amounts that are too small to satisfy the demand for it in the new branches of the national economy, which include not only power generation, but also chemical technology and materials science applications mentioned earlier.

Furthermore, current production of hydrogen from natural gas is itself not ecologically clean and not only leads to the consumption of nonrenewable resources of this valuable raw material, but is also accompanied by the generation of a considerable amount of carbon dioxide as a by-product. In the USSR alone, the emission of carbon dioxide into the atmosphere caused by hydrogen production, is about 18–20 million tonnes annually.

In view of this, improvement of the existing processes for electrochemical production of hydrogen by the electrolysis of water and water vapour is acquiring paramount importance along with the reduction in the associated energy consumption which may be achieved through the use of radically new materials and nonconventional chemical processes, primarily those based on renewable energy sources, such as solar energy, wind power, geothermal and hydrothermal processes, etc.

In the late 1970's a concept was promoted which is currently acquiring practical importance, namely that not only water and