

## Specific control parameters in the technology of aerosol nanocatalysis \*

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This article shows the benefits of new technology for the implementation of gas-phase chemical reactions by aerosol nanocatalysis. The influence of new managing factors such as the concentration of catalyst, frequency, amplitude of motion of catalyst particles, dispersive material, etc. This enhances the process management and increases the rate of reaction per mass of catalyst in the 104–106 times. The selectivity of chemical transformations increases by 10–20%. Sometimes, new valuable products of the reaction are formed.

### 1. INTRODUCTION

Generally here is need to apply catalytically active material in the catalysis of nanoparticles. However, the most common method is the use of catalysis in porous carrier. It has dominated the industry for over 130 years. There exist limitations and disadvantages of this technology of catalysis. The main of them include:

- carrier plugging deposits of carbon, salts, metal oxides, oligomers and polymers;
- impossibility of carrying out chemical processes with solid reagents;
- rapid loss of activity in the presence of solids in the raw material;
- lack of strength and heat resistance of carriers;

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\*This article is dedicated to Professor Roman Leboda on the occasion of his 65<sup>th</sup> birthday

– complexity of the production carrier with the desired porous structure.

The success of nanotechnology could be seen in the achievements of scientists, physicists as for the properties of nanoparticles in the late twentieth century. This has led researchers-chemists to draw attention to this work. Many scientists considered the problem. They found [1] that this is not about the viability of catalysis nanoparticles. The reason is the complexity of their production on a large scale.

The purpose of the study was to overcome the above-mentioned limitations of traditional catalysis on the carrier. The established technology of aerosol nanocatalysis (AnC) is an independent technology. The main provisions of AnC technology include:

- the use of only the catalytically active material without a carrier;
- aerosol synthesis of nanoparticles in the reactor during the reaction [2];
- the use of the basic theory of catalysis and the unique properties of nanoparticles.

AnC uses technology and equipment from chemical and petrochemical industries. At present time, we have completed the research work on the pilot plant technology AnC the reactor with a fluidized bed and developed technology AnC in the reactors with a vibrating bed.

The colleagues from the University of Duisburg (Germany) and the University of Delft (The Netherlands) for the installation of our measurements performed catalyst particles. They were carried out in a reactor AnC during the chemical interaction of reagents. As a result, there were recorded particles size 8–10 nm in the reaction zone, and 100–200 nm after the reactor. This ensures consistently high activity catalyst [3].

After our publications [3, 4] authors [5] studied the changes in activity of one nanoparticle of Ni in quartz. They studied using the example of the reaction methanation where nanoparticle of Ni remained in the reactor volume. They found that the time of high activity of nanoparticles is about 5 seconds, more rapidly reduced to the standard values.

The results of these studies confirm the correctness of our decisions on AnC - the continuous synthesis of nanoparticles in the reaction zone.

Currently, some researchers believe that they work in the field of nanocatalysis, as in polydispersive particles put on the carrier and detected the particles of nanosizes [6]. In literature a number of publications found the unjustified use of the term AnC. For example, in patent [7] the so-called process with a fluidized bed of inert particles passes through the flow of dust magnesium-chromium catalyst for aluminium oxide carrier. However, it is not a true copper.

## 2. THE THEORETICAL STATUS OF THE AEROSOL CATALYSIS

The results of the first work on the activity of aerosol particles of a catalyst for the unique catalysis are given in Table 1 (lines 5–7). A comparison with the results of the fluidized bed of the most active catalysts on the carrier is presented.

Tab. 1. The deep oxidation of acetic acid.

№	Catalyst	Regime	Porous bed of catalyst	Contents acid	Concentration of the active component of the catalyst	Limit load concentration in the reaction products CO <20 mg/m <sup>3</sup>			Productivity
				%mas.		kg/m <sup>3</sup> <sub>L.vol.</sub> *h	kg/m <sup>3</sup> <sub>cat.</sub> *h	kg/kg <sub>cat.</sub> *h	
1	Pt/γ-Al <sub>2</sub> O <sub>3</sub>	FB, catalyst on the carrier	0.6	98	4	1.5*10 <sup>3</sup>	1.5	1000	
2	CuCrO <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>		0.6	98	200	0.8*10 <sup>3</sup>	0.8	533	
3	CuCrO <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>		0.6	60	200	0.65*10 <sup>3</sup>	0.65	433	
4	CuCrO <sub>4</sub> /γ-Al <sub>2</sub> O <sub>3</sub>		0.6	30	200	0.37*10 <sup>3</sup>	0.37	247	
5	Fe <sub>2</sub> O <sub>3</sub>	AnCFB	~1	60	3.2*10 <sup>-3</sup>	1.7*10 <sup>8</sup>	3.6*10 <sup>4</sup>	115	
6	Fe <sub>2</sub> O <sub>3</sub>		~1	30	2.5*10 <sup>-3</sup>	1.3*10 <sup>8</sup>	2.6*10 <sup>4</sup>	65	
7	Fe <sub>2</sub> O <sub>3</sub>	AnCVB	~1	98	1*10 <sup>-5</sup>	5.3*10 <sup>8</sup>	1*10 <sup>5</sup>	1580	

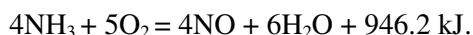
FB – fluidized bed

AnCFB – aerosol nanocatalysis with the fluidized bed

AnCVB – aerosol nanocatalysis with the vibrating bed

Table 1 shows that the use of an aerosol without the carrier with the increase of the active surface 10<sup>4</sup>–10<sup>5</sup> times. Technology AnC reduces the cost of the catalyst by 5–7 orders of magnitude and dimensions of equipment. The technology AnCVB is particularly effective. Its application reduces the volume of the reactor up to ~ 3 times.

The reaction of the high-temperature oxidation of ammonia on a platinum grid is as follows:



Time of contact is greater than 2\*10<sup>-4</sup> sec. Currently, platinum is the only industrial catalyst. It losses 0.2–0.5 g/tonne of nitric acid. This is a problem for plants producing nitric acid.

We performed a study in the reactor AnCFB in aerosols Fe<sub>2</sub>O<sub>3</sub>. The high speed of reaction and selectivity of nitrogen oxides are shown in Figure 1. It is higher than on platinum. The project of reconstruction of the production of nitric acid was carried out according to our data for one of the Ukrainian firms, but it has not been implemented yet.

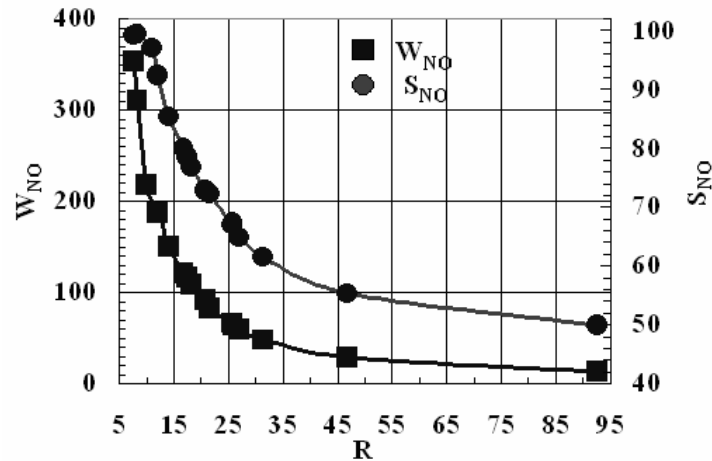


Figure 1. Dependence of reaction rate ( $W_{NO}$ , mmol/(g<sub>cat</sub>\*sec)) and selectivity ( $S_{NO}$ ,%) oxidation of ammonia to NO by diluting the mixture to Fe<sub>2</sub>O<sub>3</sub> as a catalyst by the technology AnCFB.

The selectivity and rate of NO<sub>x</sub> is dependent on dilution of the mixture (R). In the interval of values of R from 7.7 to 25 a sharp decrease in selectivity from 99% to 65% is observed. With the increasing dilution rate up to 50 a slow decrease in selectivity up to 50% is found. With further increase in R a slight decrease in selectivity occurs.

Prior to our studies an attempt was made to replace the platinum catalyst. This comprises a process in reactors with the fixed catalyst bed and the FB, including  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [8, 9]. At 750–800°C and time  $(1-5) \cdot 10^{-2}$  seconds selective oxidation of ammonia to nitrogen monoxide amounts to 89–90% at the beginning. But several hours later, that figure drops to 70%. This is unacceptable in the industry. The sharp drop in activity is associated with the restoration of Fe<sub>2</sub>O<sub>3</sub> to FeO. In the technology AnCFB selectivity for nitrogen oxides increases up to 95–96.7% without time limitation [10].

Investigation of n-pentane cracking in AnCVB showed that the aerosol catalyst and the frequency determine the selectivity of the process. The results are presented in Figure 2. Upon reaching the frequency of vibration of the catalytic system of 5 Hz in the cracking products, ethylene evolved along with hydrogen and carbon.

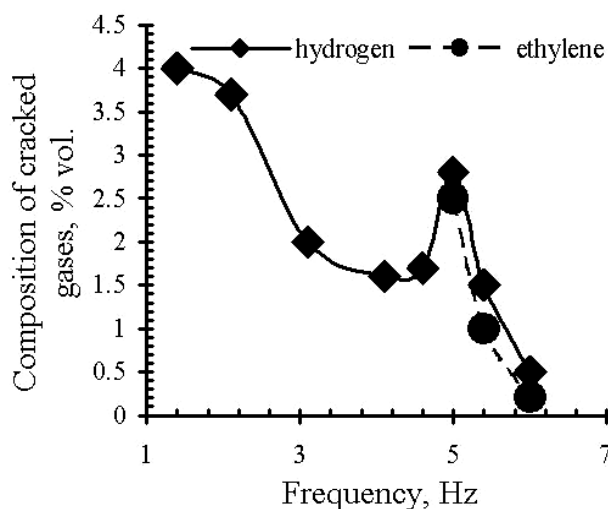


Fig. 2. Dependence of the output gas cracking of n-pentane at 450°C of the oscillation frequency of the reactor on iron oxide (III) catalyst.

### 3. NEW FACTORS MANAGEMENT

Study of the oxidation of ammonia, acetic acid and active silt showed the influence of the reaction rate of the catalyst. This is specific to AnC. This phenomenon is shown in Figure 3.

In the studies dried active silt biologically and chemically treated was used. It should be noted that the active silt contains a solid phase and in spite of this oxidation reaction takes place. However, the rate compared to other reagents is below ~ 2. In the catalysis on the carrier, this reaction does not proceed.

The effect of catalyst concentration is specific for each reaction. We offer this option to be included in the mathematical description of chemical reactions. This can be attributed to other specific parameters of the AnC technology, for example, the frequency of catalytic systems (AnCVB). The results of the processes of deep oxidation of natural gas and oxidation with dehydrochlorination of 1,2-dichloroethane are shown in Figure 4. We show that the first increase in frequency reduces the reaction speed. For some processes at a certain frequency the reaction rate may increase. This is of practical interest.

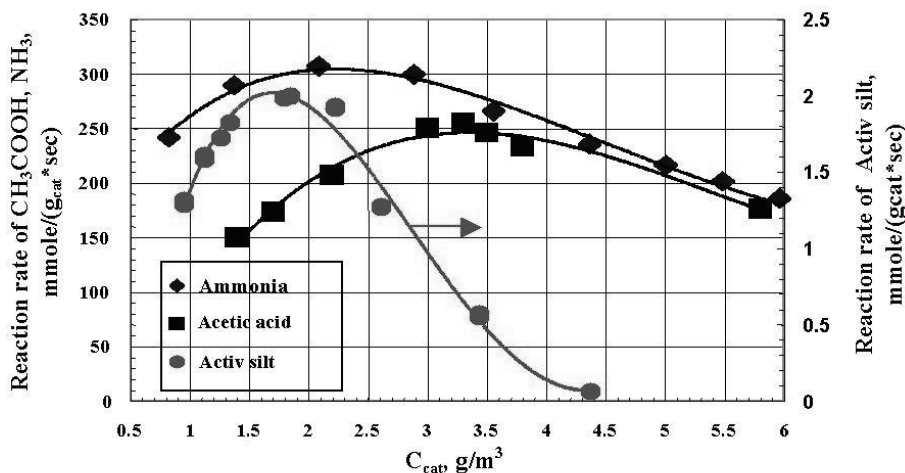


Fig. 3. Dependence of oxidation rate of gaseous, liquid and solid substances of the concentration of Fe<sub>2</sub>O<sub>3</sub> as a catalyst in the fluidized bed for the technology AnCFB (temperature 600<sup>0</sup>C).

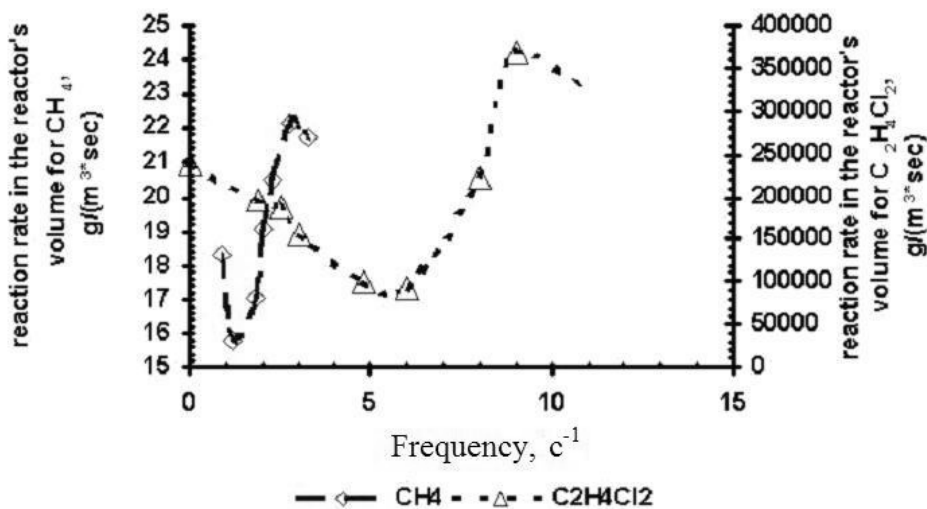


Fig. 4. Dependence of the reaction rate on the frequency of oscillations for different processes.

The reaction rate affects the amplitude of motion of particles in the reaction volume. This influence is shown in Figure 5 for the oxidation process with dehydrochlorination of chlorobenzene and varying frequency of oscillation. The nature of dependence is not changed, but the best apparent vibration amplitude is

equal to 27 mm. A similar phenomenon is observed in the study of 1,2-dichloroethane. This option should also be included in a mathematical equation.

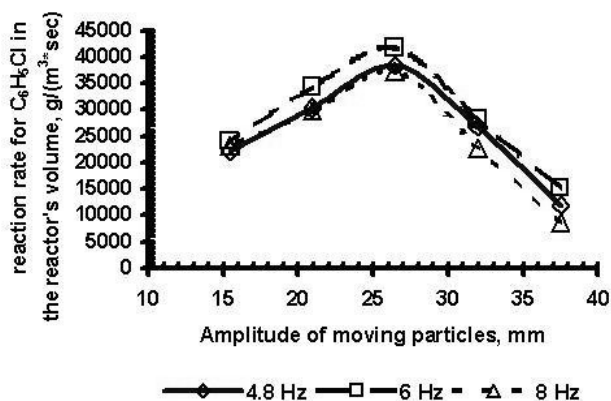


Fig. 5. Dependence of reaction rate of chlorobenzene oxidation with dehydrochlorination of amplitude of particle motion.

Our studies with the replacement of dispersive material also showed specific dependence on the contact time (Figure 6). It turns out that it is necessary to select dispersing material. Roughness of the surface and non-standard shape of particles give the effect of increasing the reaction rate. Presumably this is possible thanks to the changing mechanical influences.

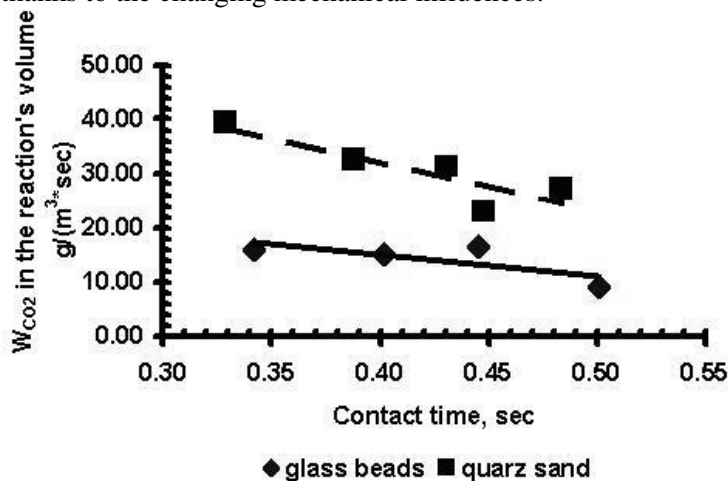


Fig. 6. Dependence of the reaction rate of deep oxidation of natural gas on the contact time with different dispersive materials.

#### 4. CONCLUSIONS

As follows from the experimental research it is necessary to adopt the following assumption. In the technology of the aerosol nanocatalysis there is a number of parameters that specifically affect the reaction rate. They should be taken into account in mathematical equations. In the classical equation of the reaction rate  $W = k \cdot C$  the constants of the concept should be expanded. After the substitution of new control parameters the equation takes the following form:

$$W = k_1 \cdot C \cdot C_{cat}^{n_1} \cdot f^{n_2} \cdot A_{particle}^{n_3}$$

where  $W$  – the rate of reaction,  $g/(m^3 \cdot sec)$ ;  $k_1$  – the constant rate;  $C$  – the initial reagent concentration,  $g/m^3$ ;  $C_{cat}$  – the catalyst concentration,  $g/m^3$ ;  $f$  – frequency, Hz;  $A_{particle}$  – the amplitude of particle motion, m;  $n_1, n_2, n_3 \dots$  – the order of the reaction of the corresponding parameter.

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#### CURRICULA VITAE



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