

AN EFFECTIVE WAY OF THE REMOVING COMBUSTIBLE GASES

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Abstract

Certain environmental problems are solved through the use of new types of efficient industrial catalysts. This research are directed on figuring out new industrial technologies for high active of catalysts of oxidation (after burning) for combustible gases. The basic advantages of catalysis process is a high efficiency, profitability and absence of formation of secondary pollutants.

At present for combustion of exhaust gases of automobiles to use of the catalysts which are containing of the platinum or other metals of platinum group.

These catalysts are quite efficiently considerably reduce the pollution of the environment, but, certainly are very expensive. Besides if such element as platinum is put on aluminium oxide and the catalyst is used at temperatures about 800 °C there may be quite a negative phenomenon. The small and mobile ion of metal migrates in volume of aluminium oxide and hence, become catalytic inaccessible. Such effect was observed in particular, in the neutralizers of the exhaust gases of the automobiles applying at very high temperatures.

In these papers are submitted the results of the intensive researches directed on search of the "know-how" of catalysts of removing (after-burning) of combustible gases such as carbon monoxide which are not containing expensive metals of platinum group. The investigation has allowed to develop essentially new way of low temperature synthesis of an active component Co_3O_4 , and also way of putting active component of catalyst on a support $\alpha\text{-Al}_2\text{O}_3$ - fibre having the high specific area of a surface.

The variation of structures of an active component and supports has resulted in creation of the catalysts which have shown high efficiency during deep removing of combustible gases. The study of catalysis, and also of physical and of physical-chemical properties of the synthesised catalysts has shown, that the new way of low-temperature synthesis Co_3O_4 has allowed us to create high active catalysts with high permeation to gas level.

The research of creation of the put catalysts of removal of exhaust combustible gases (carbon monoxide) of has opened an opportunity to lower considerably or to exclude all influence of carbon monoxide on the environment.

The methods of atom adsorbed spectroscopy, photo electronic spectroscopy, X-phase and chemical analysis, and also method of thermal desorption of argon has allowed to carry out researches of a nature of an active component and support, structure and composition.

The investigation of kinetics of process of removing of combustible gases, has been carried out in gas dynamical installation in the flowing -through reactor with strict of the condition at the constancy of such parameters as rate of volume flow of a gas stream, mass of the catalytic agent, temperature of process.

Introduction

The research and development of active catalysts for after burning of combustible gases capable to replace precious metals and to make more cheaper manufacture of catalysts for waste recovery of exhaust gases of automobiles is conducted in all advanced countries of the world. The researchers is large interest caused by catalysts on a basis oxides of metals. The large group firm oxides of catalysts IV periods is investigated. Most perspective has appeared cobalt cobaltyt (Co_3O_4). In the Industry the cobalt cobaltyt turns out by decomposition of salts cobalt (nitrates) with the temperature 500- 700 ° C. The author was developed of the new method of low-temperature synthesis Co_3O_4 has allowed to create high active catalysts with high permeation to gas level.

The Problem of recycling of exhaust gases of automobiles is still actual. Significant difficulties are created with variability of structure of the exhaust gases, dependent on operating conditions of motor transport, nevertheless our investigation which have been carried out earlier, have shown high efficiency during reburning exhaust gases of catalysts on a basis low temperature cobalt oxide. The new method of low-temperature synthesis Co_3O_4 has allowed to create high active catalysts with high permeation to gas level and also moderate cost of catalysts on a basis low temperature cobalt oxide put on various carriers.

Necessity of use of the carrier has some reasons. Most essential of them are the following:

- ◆ The carrier allows to form the catalyst, making it mechanically strong.
- ◆ Except for that the carrier raises selectivity
- ◆ The carrier reduces difference of pressure
- ◆ The carrier reduces density catalytic an active phase and increases profitability

This last effect is achieved by drawing of the catalyst on the carriers having the form of cellular monoliths, rings. Last years significant the attention is given formation on metal carriers of a marked film from aluminium oxide., which has small diffused ability and increases thermostability of iron, nickel and other metals in an oxidizing atmosphere. Entered aluminium oxide renders positive influence on durability of coupling superimposed of active components with the carrier. Secondary oxide the carrier for metal carriers gets the big value: it carries out protective functions, the durability of the catalyst depends on durability of its coupling with metal.

The degree of interaction of a covering with the cellular carrier is defined by temperature of subsequent processing, and durability of interaction of the catalyst with a carrier it is caused next factors:

- In temperature of holding
- Degree of crushing
- Uniformity of hashing
- Relationship of the sizes of particles.

One of the most successful forms of the carrier are “beer honecombs”. In their structure as a rule enter refractory materials. Catalysts with cellular structure on the basic parameters:

- Efficiency
- Weight
- Resistance to gas stream
- Strength of coalescence of an active component with carrier

do not concede to catalysts on cellular ceramic carriers, and in mechanical strength surpass them. As a rule, it is necessary to take into account requirements of a surface suitable for the catalyst and thus to not complicate impregnation and a covering “honecombs” and also to not exceed allowable difference of pressure.

In our research work the aluminium oxide with an advanced surface had been rendered on the cellular nickel carrier by hydrothermal method. After drying and incineration on the surface of "honeycombs" the thin layer aluminium oxide with an advanced surface and big adsorptive ability has been formed. The catalyst has been applied on the covering of thin layer aluminium oxide.

The Investigation of kinetics of process of recovery of combustible gases.

At present in the theory of active ensembles metal carriers of the applied catalysts may carry out a role of a trap of energy of activation with the subsequent transfer of this energy to the active centre of the catalyst for excitation, remaining an inert carrier.

As the carrier we offered blocks from frothed nickel on which it is put aluminium oxide by a hydrothermal method. The surface of this block carrier determined on a method thermal desorption of argon made $100 \text{ m}^2/\text{g}$. Then on it rendered the catalyst cobalt cobaltyt synthesized at low temperature.

In the apply of oxides carriers for oxidic catalysts probably chemical interaction between a carrier and the catalyst that results in increase of adhesion of the catalyst and the carrier. Author did research of possible interaction catalytically an active phase of cobaltyt cobalt with a substrate from aluminium oxide by methods thermogravimetry, differential-thermal and X-ray analyses are carried out. The method X-ray analysis confirms formation of the compound of aluminate of cobalt CoAl_2O_4 in interaction cobalt cobaltyt with the carrier from aluminium oxide. Thus loss of weight in 2 % is marked on a curve thermogravimetry the analysis.

The result of X-ray diffraction data has shown that the ion of cobalt has tetrahedral structure in the compound of the following type CoAl_2O_4 which has structure of the normal spinel. In the oxide Co_3O_4 there is a cobalt both tetrahedral and octahedral. Thus compound of cobaltyt cobalt has a structure of the following type: $\text{Co}^{+2}(\text{Co}^{+3}\text{O}_2)_2$.

For catalysts of the applied on carriers the problem of the account of a share oxide, entering in interaction with a carriers is characteristic. It is known, that products of interaction between aluminium oxide and cobalt cobaltyt are characterized by more difficult reducibility than pure cobaltyt cobalt. The investigation of comparative experimental data of a degree of reducibility pure oxides and oxides of the applied on carriers have shown, that on the carrier $\alpha\text{-Al}_2\text{O}_3$ remains free 95 % of a surface from put cobalt cobaltyt. Thus, application as the carrier $\alpha\text{-Al}_2\text{O}_3$ provides a high degree of use of an active component of the catalyst. The study of kinetics of process of recycling of exhaust gases on catalysts consisting of an active component of cobalt cobaltyt, put on carrier $\alpha\text{-Al}_2\text{O}_3/\text{Ni}$ have been made in gas dynamical installation of a flowing type in flowing reactor.

The analysis of gas before and after plug flow reactor carried out by gas adsorption chromatography method. The general schematic of gas-dynamical flowing installation is submitted in a figure 1.

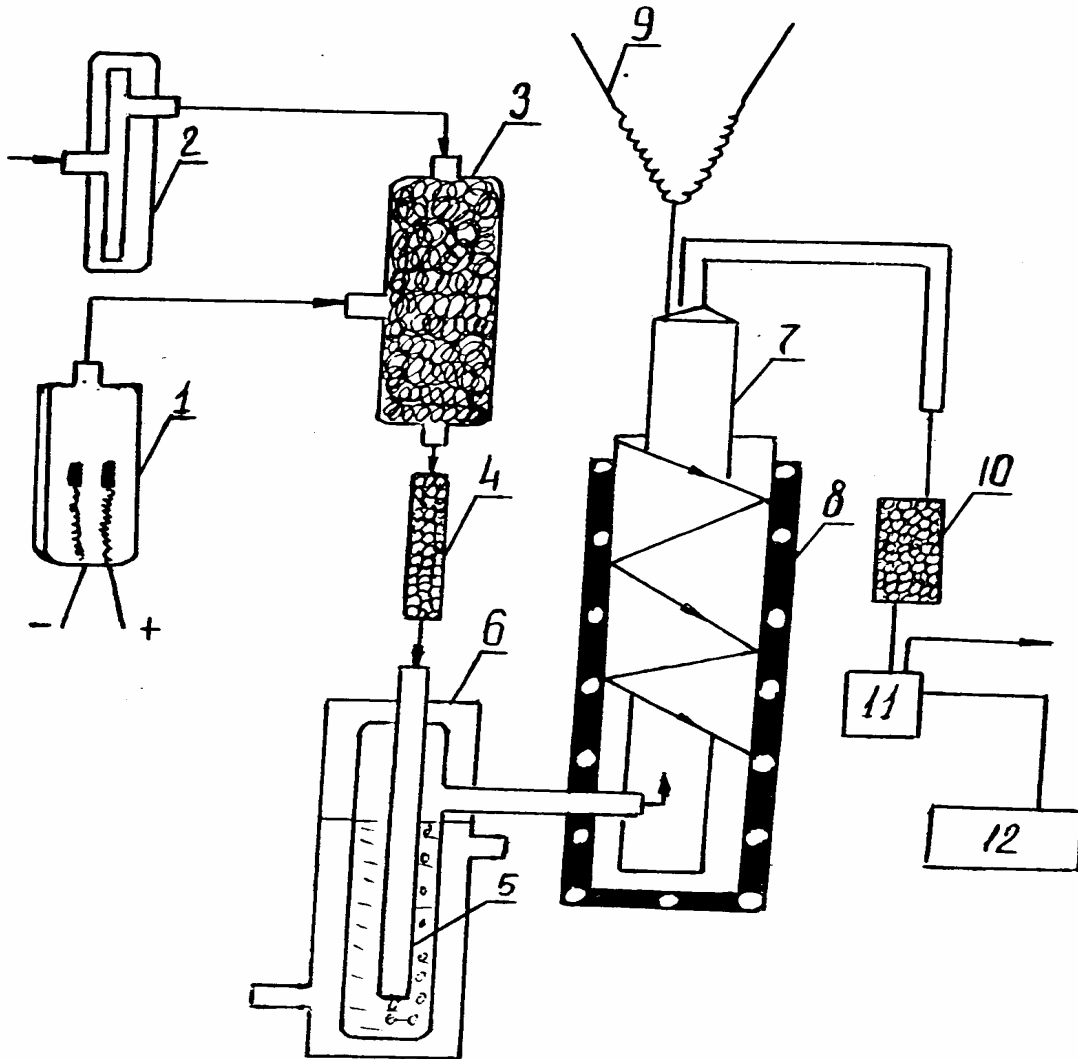
Though cross-flowing systems demand more complex equipment, their applying eliminates an opportunity of distortion actually speeds of reaction due to the slowed down movement of reacting substances to a surface.

The flowing reactor was graduated on temperature. The reactor has been executed with such proportions l/d which are provided for reactors of ideal replacement:

$$\frac{l}{d} \geq 20$$

Speed of a gas stream varied in an interval from 3.2 l / hour till 24.0 l / hour.

Figure 1. The schematic of gas- dynamical flowing installation



1-electrolyze
2-rheometer
3- mixer
4,10- drier
5-humidifer
6-thermostat

7- plug flow reactor
8- electric furnace with regulator to a high precision
9- termocouple
11-gas chromatograqph
12- recording apparatus
13- termocouple wire

The investigation of kinetics of process carried out in an interval of temperatures 456-513 K. At strict maintenance of parameters of process:

- ◆ Temperature of catalysis
- ◆ Speeds of a gas stream
- ◆ Weights of the catalyst
- ◆ Volumetric parity of exhaust gases and gas of a thinner.

With processing experimental data was used of the equation of a efficient constant of speed of heterogeneous chemical process of the first order, when a product of reaction adsorb is strong:

$$K = n_0 \frac{B}{b \cdot l} [-\ln(1-x) - x]$$

Where: n_0 - initial number of moles of substances, taking place through the given section in unit of time

x - share of the reacted substance

K - constant of speed of reaction

B - sum of products adsorbed of factors on stoichiometric factors for products of reaction

b - adsorbed of factor.

l - length of a hot zone of plug flow reactor

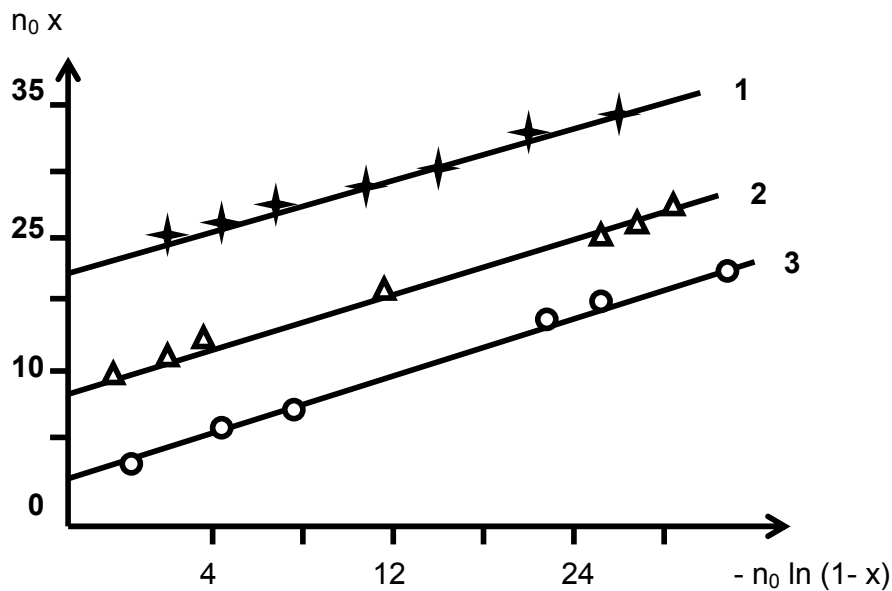
After transformation the equation has a kind:

$$n_0 x = -n_0 \ln(1-x) - K \frac{b \cdot l}{B}$$

If for variable to accept $y = n_0 \cdot x$ and $z = n_0 \cdot \ln(1-x)$, to this equation will correspond a direct.

Experimental data of change of structure of a gas mix during reaction of removing of combustible gases, with temperatures 456; 474; 513 K are submitted in a figure 2.

Figure 2. The kinetics of process recovery of combustible gases.



1. T = 456 K

2. T = 474 K

3. T = 513 K

As shown in figure 2 with magnification of temperature of process the effective constant of velocity grows from 2.0 c^{-1} at the temperature 456 K up to 23.0 c^{-1} at the temperature 513 K. It has allowed to consider high efficiency of the block catalyst $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3/\text{Ni}$.

Conclusions.

For the decision of problems of catalytic removing after burning of combustible gases (exhaust gases of automobiles) precious metals of platinum group nowadays are used. Instead of platinum of catalysts for process after burning of combustible gases it is offered to use oxide cobalt of the catalyst, which cost by far is lower.

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