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APPLICATION OF THE DTA METHODS TO INVESTIGATIONS ON THE CATALYTIC PURIFICATION OF GASES

The investigations of catalytic purification of gases require the information about the activity of catalysis, range of the working temperatures and activation stability. The usability of DTA method in such a process has been shown. This method makes it possible to take measurements in presence of catalyst and to obtain detailed characteristics of catalysts. Selection of catalysts, kinetic investigations, activity stability tests and analyses of gases have been discussed and the obtained results given.

1. INTRODUCTION

In recent years the catalytic purification of gases has become the subject of thorough studies. The investigations of this kind require the knowledge of some parameters of catalysts used, such as activity, poisoning and resistance to thermal deactivation, as well as the range of the working temperatures, and in particular the influence of chemical composition on the given properties.

The above data are usually obtained by the methods based on the analysis of the reaction products. These methods however, are time-consuming and require a considerable amount of the substance examined. Furthermore — because of their character — they exclude the automation of measurements and a simultaneous examination of many samples. Some difficulties in investigations of the gas purification processes can be also due to low concentration of the component examined, since in this case complex analytical methods must be applied.

In view of the above reasons it seems that a modified DTA method, enabling the measurement in presence of catalyst, and at the constant flow of the reaction mixture, can be successfully applied.

The suggested application of the DTA method is by no means new, having been proposed in the forties by PATRIKEYEV [1]. Later on attempts were made by various authors to apply this method in the solution of simple problems related to studies on catalysts. The adequate data are, however, scattered in the literature [2, 3]. Some papers in which the tests were performed on apparatus made by different firms have appeared quite recently [4, 5].

The modifications of DTA apparatus, made in our Institute in the course of investigations, allowed the measurements in the presence of catalyst [6, 8]. The purpose of the present paper is to show the possible application of DTA methods to the investigations on the catalytic purification of gases.

Two kinds of reactors have been used, i. e. the catalyst sample was placed either longitudinally or transversely with respect to the direction of the gas flow. Most measurements have been performed at a constantly increasing temperature of the reactor. Gas temperature, and the temperature difference between gas (treated as a standard) and the inside

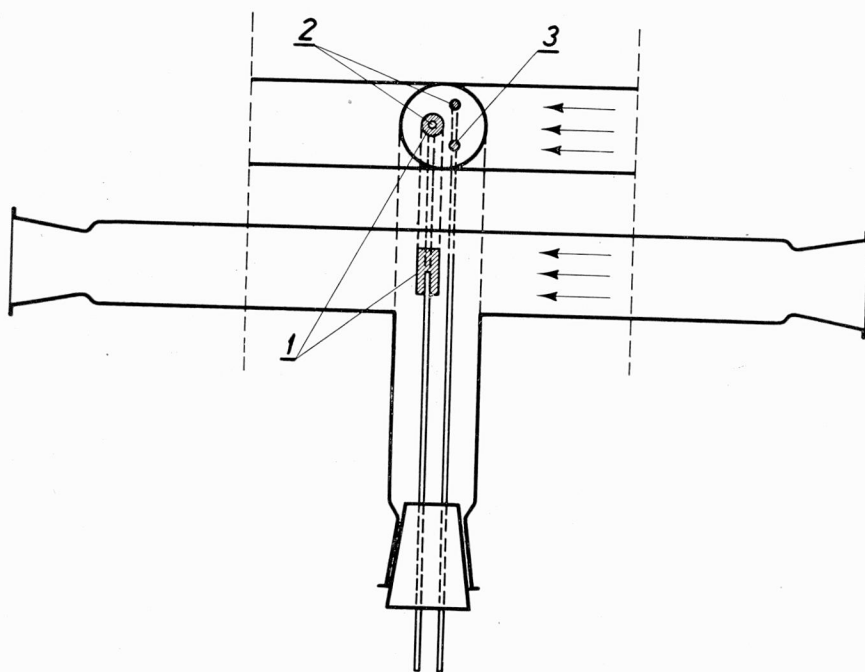


Fig. 1. Schematic representation of the reactor with catalyst sample placed transversely

- 1 - catalyst sample,
- 2 - differential thermocouple,
- 3 - thermocouple of the measurement of gas temperature

Rys. 1. Schemat reaktora z poprzecznym ułożeniem próbki katalizatora

- 1 - próbka katalizatora,
- 2 - termopara różnicowa,
- 3 - termopara do pomiaru temperatury gazu

of the catalyst sample have been determined by means of a simple and differential thermocouples, as well as by recorders, whose measuring range amounted to 1 mV. The gas temperature recording system has been additionally equipped with a compensation unit enabling to extend arbitrarily the scale recorded.

2. APPLICATION

2.1. SELECTION OF CATALYSTS

The selection of the catalyst calls for the knowledge of requirements concerning its properties. One of the most essential properties is the temperature below which the reaction rate on the catalyst is practically null. The accuracy with which this temperature is determined experimentally may depend on the sensitivity of the apparatus employed. To avoid this shortcoming another value, the so-called temperature of catalyst ignition is introduced. It is the temperature above which the reaction rate increases quickly until, in the given condition of gas flow and composition, the maximum value is attained.

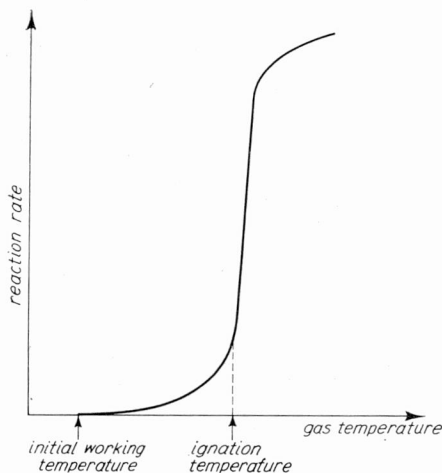


Fig. 2. Temperature at which the work is started and temperature of catalyst ignition

Rys. 2. Temperatura początku pracy i temperatura zapłonu katalizatora

Ignition temperature of a catalyst — because of the limited temperature of waste gases — is one of the parameters which decides upon its usage to purification of combustion gases. Therefore in many cases it is important to obtain catalysts characterized by low ignition temperatures.

The ignition temperature alone does not define explicitly the usefulness of a catalyst in the purification process since some catalysts may display different behaviour at temperatures exceeding that of ignition, and therefore the determining of the temperature optimal for the catalyst activity is indispensable.

In the case when a single component is to be removed from the gas the optimal temperature is equal to the temperature of the maximal reaction rate on the catalyst, provided however, that no undesirable phenomena, e. g. a quick deactivation of the catalyst, occur at this temperature. In a complex case, however, e. g. in the purification of combustion gas, the optimal temperature must be determined by taking account of the requirements referring to the contents of particular components after the purification process.

The data discussed above, and these concerning the activity of catalysts, in particular, can be obtained by applying the modified DTA method described earlier. This statement

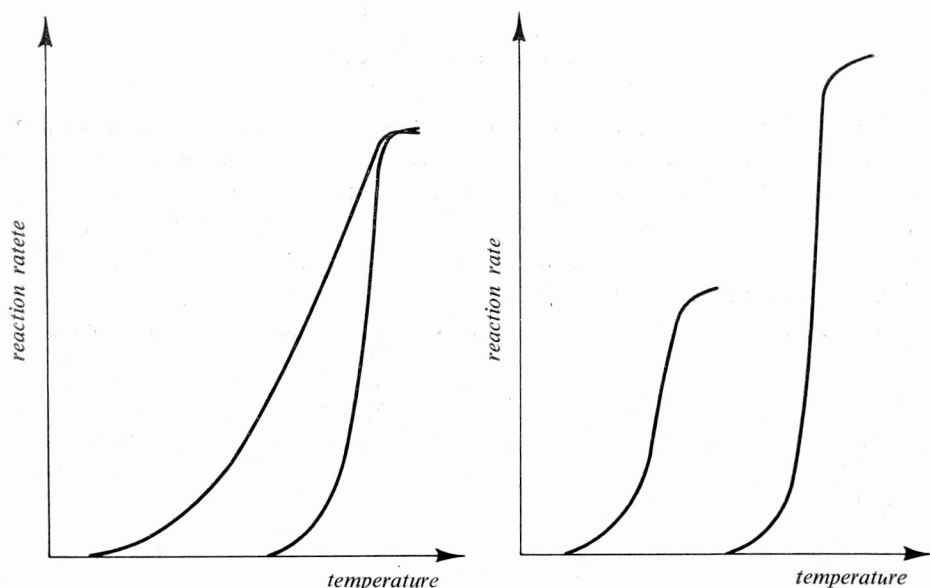


Fig. 3. Various behaviour types of catalysts at the increasing temperature

Rys. 3. Różne typy zachowania się katalizatorów podczas wzrostu temperatury

is justified by the reasoning given below. The amount of heat emitted on a catalyst sample in the flux of reaction mixture can be described by the formula [7]:

$$Q_1 = r \cdot (-\Delta H) \cdot v \cdot \eta, \quad (1)$$

where:

- $(-\Delta H)$ — thermal effect of reaction, cal/mol,
- r — reaction rate referred to the volume unit of the catalyst, mol/s · cm³,
- v — volume of catalyst sample, cm³,
- η — utilization factor of the catalyst inner surface.

The amount of gas abstracted heat equals

$$Q_2 = S \cdot \Delta t \cdot h, \quad (2)$$

where:

- S — external surface of the catalyst sample, cm²,
- Δt — stationary difference between the temperature of catalyst sample and gas, °C,
- h — coefficient of heat abstraction, cal/s · cm² · °C.

Hence, under stationary conditions, (easily obtained because of the low mass of the sample)

$$Q_1 = Q_2, \quad (3)$$

since — considering that usually the working temperatures of the catalysts discussed are

relatively low — the effect of radiation heat abstraction, essential at higher temperatures, can be neglected.

Then

$$\Delta t = \frac{(-\Delta H) \cdot v \cdot \eta}{h \cdot S} r, \quad (4)$$

or

$$r = \frac{h \cdot S}{(-\Delta H) \cdot v \cdot \eta} \Delta t. \quad (5)$$

Assuming a full utilization of the inner surface of the catalyst i. e. that $\eta = 1$ (this assumption being justified when thin layers of a catalyst are used), and comparing the reaction rates on two catalysts operating within similar ranges of temperature, i. e. when the value of h can be taken as invariant and S , v , $[-\Delta H]$ are constants, it can be stated that

$$\Delta t = k_1 \cdot r, \quad (6)$$

or

$$r = k_2 \cdot \Delta t, \quad (7)$$

where the value of k_1 and k_2 result from the equations (4) and (5).

If, however, the activity of the catalysts differing in the range of working temperatures, is to be compared, then the effect of temperature on the changes in values of the heat exchanger coefficient h cannot be neglected. Hence, we have

$$r = k_3 \cdot \Delta t \cdot h, \quad (8)$$

where the value of the constant k_3 results from (5).

The results obtained from the measurements performed on the air-methane mixtures, and given below justify the reasoning presented.

Since the gas temperature is given on the abscissa, the value of the catalyst temperature can be obtained by adding the temperature of gas and that of catalyst heating. The same measurements allow to obtain directly the value of gas temperature which is also the temperature of catalyst ignition.

If the equation (8) is applied then the values of the heat exchange coefficient h can be obtained from the following correlation

$$\frac{h \cdot d_p}{k} = 0.43 + 0.48 \text{ Re}^{1/2}, \quad (9)$$

where:

h — the heat exchange coefficient, $\text{cal/s} \cdot \text{cm}^2 \cdot ^\circ\text{C}$,

d_p — diameter of the cylinder (of sample), cm ,

k — thermal conductivity of gas, $\text{cal/s} \cdot \text{cm} \cdot ^\circ\text{C}$,

Re — Reynold's number

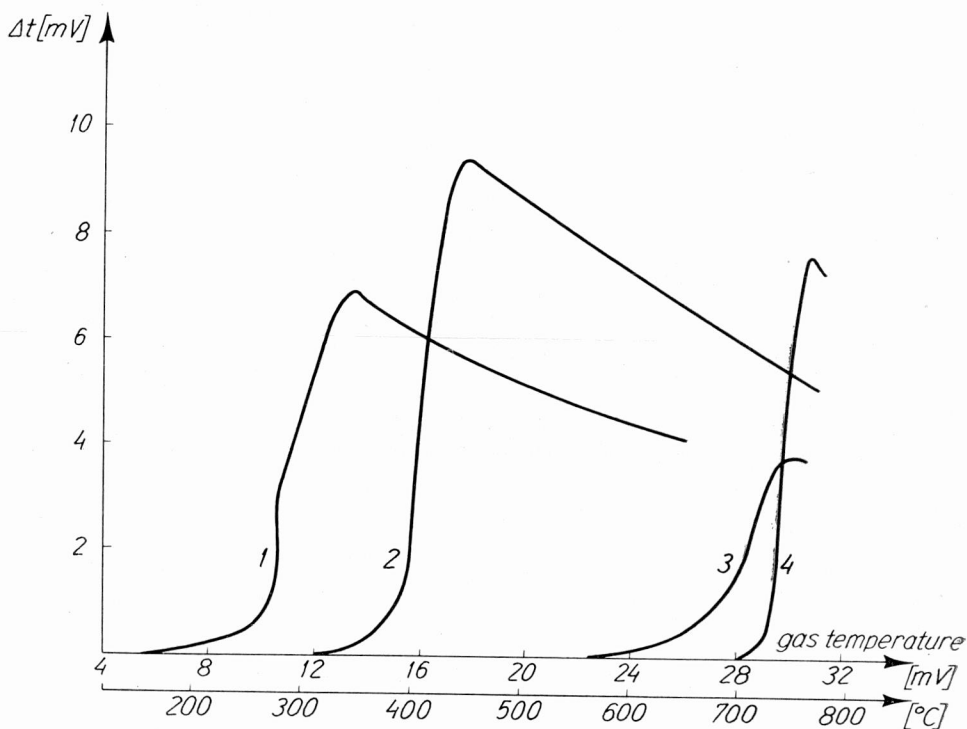


Fig. 4. Heating temperature curves of catalyst in methan-oxygen reaction

1 - Co_2O_3 , 2 - Fe_2O_3 , 3 - Sm_2O_3 , 4 - CaO

Rys. 4. Krzywe rozgrzania katalizatorów w reakcji metan-tlen

This correlation is used when the sample is placed transversely with respect to the direction of gas flow. If, however, the sample is placed parallelly, (9), (10) then the correlation

$$\frac{h \cdot d_e}{k} = 2.0 + 0.6 \text{Re}^{1/2} \cdot \text{Pr}^{1/3} \quad (10)$$

is used, where:

d_e — equivalent diameter, i. e. the diameter of sphere in which the external surface is the same as that of the cylinder tested, cm,

Pr — Prandtl's number.

When the values h are calculated for the appropriate temperatures and compositions of gas mixture, the maximum value of the product $\Delta t \cdot h$, and the corresponding value of gas temperature are to be found according to (8). At this temperature of gas and the corresponding temperature of catalyst, i. e. at $t_g + \Delta t$, the reaction rate is maximal. This follows from the equation (8).

The calculations of the values h can be avoided by a direct calibration of the measuring device with the heat of a microheater of a known power [11].

It should be borne in mind that the determined value of optimum (maximum) temperature corresponds exclusively to the working conditions of a single catalyst pellet for a given linear velocity of gas mixture flux, and therefore it cannot be employed directly in design of a reactor with a catalyst bed.

3. KINETIC TESTS

The method described may be easily used if the dependence of reaction rate on the concentration of separate compounds of the reaction mixture is to be determined. Fig. 5 illustrates the case when hydrogen is polluted with oxygen.

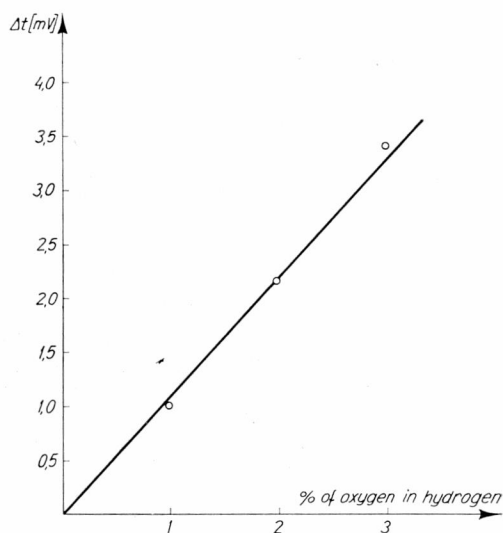


Fig. 5. Heating temperature of the catalyst PtRh vs. the concentration of oxygen in mixture with hydrogen

Rys. 5. Zależność rozgrzania katalizatora PtRh od stężenia tlenu w mieszaninie z wodorem

The data obtained by applying the above method allow to write kinetic equations and determine the value of the reaction activation energy. It is also possible to study the reaction rate at the given degree of conversion obtained in the integral reactor placed in front of the DTA apparatus.

4. ACTIVATION STABILITY

The most interesting parameter, apart from the ignition temperature and activity of the catalyst, is the activation stability. The lack of stability can be due to the presence of catalytic poisons or to the change occurring in the catalyst itself.

The stability of activation is a particular problem when the catalysts are used for combustion of waste gases. These catalysts are exposed to the presence of poisons as well

as to frequent and quick changes of temperature resulting from the changes in the action of the engine, (stoppage and various driving conditions).

The application of the method described to a quick activation stability test of a catalyst is shown in Fig. 6.

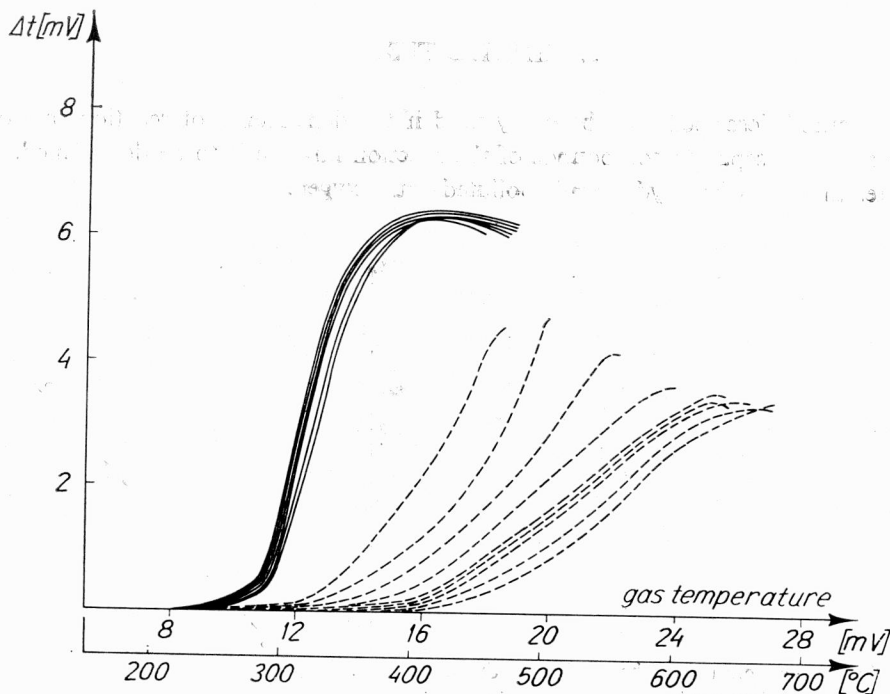


Fig. 6. Heating curves of 2 catalysts obtained in consecutive measurements in methan—oxygen reaction. Continuous line denotes the catalyst with a higher activity stability

Rys. 6. Krzywe rozgrzania 2 katalizatorów otrzymane w kolejnych pomiarach w reakcji metan—tlen; linią ciągłą oznaczono katalizatory o wyższej stabilności aktywności

This method allows moreover, investigations on the resistance to poisoning at a constant temperature, as well as on the effect of working temperature exceeding the optimal one (overheating) on the activation stability.

5. APPLICATION TO GAS ANALYSES

The application of the method described to analytical purposes is a separate problem. The investigations on gas purification require that the process be controlled by the measurement of the component being removed. Although some special apparatus, the so-called

thermocatalytic analysers produced by industry, are known in the literature, nevertheless the apparatus described in the present paper, can be used as a gas analyser.

The application of this apparatus is conditioned by the catalyst whose reaction with a given component should be sufficiently high, as the sensitiveness of the method depends on the catalyst's activity, and the latter is correlated with its heating temperature.

The stability of the catalyst is the second parameter on which its application depends, since the heating of the catalyst should depend exclusively on the concentration of the given component.

A determined effect of the component investigated on the heating value of the catalyst (which is equivalent to calibration of the analyser) allows a direct application of the apparatus to the analysis of gases containing the above component. If the mixture analysed

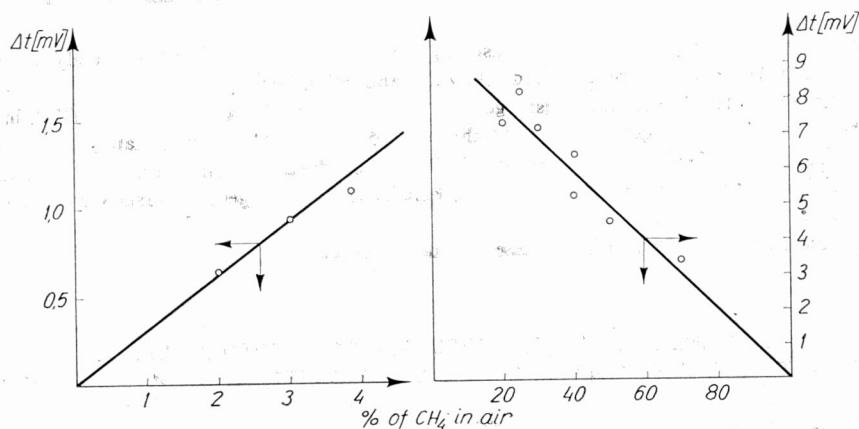


Fig. 7. Heating temperature of the catalyst Co_2O_3 vs. methane concentration in the air
Rys. 7. Zależność rozgrzania katalizatora Co_2O_3 od stężenia metanu w powietrzu

contains several components which can react simultaneously, the problem may be solved by choosing the catalyst whose selectivity in separate reactions [14] is sufficiently high. The application of this method in the case of methane—air mixtures is shown in fig. 7.

CONCLUSIONS

From the results presented it follows that various investigations conducted with the help of the DTA apparatus, allow to obtain a multi-aspect characteristic of the catalyst used in reactions important for gas purification process.

The details concerning the construction and the possible application of the described method to investigations of other types of catalysts will be given in the next paper.

ZASTOSOWANIE TERMICZNEJ ANALIZY RÓŻNICOWEJ (DTA) W BADANIACH PROCESÓW KATALITYCZNEGO OCZYSZCZANIA GAZÓW

W badaniach procesów katalitycznego oczyszczania gazów potrzebne są informacje o aktywności katalizatorów, ich zakresie temperatur pracy, stabilności i aktywności.

W niniejszej pracy pokazano możliwości wykorzystania metody termicznej analizy różnicowej (DTA) w procesie katalitycznego oczyszczania gazów. Umożliwia ona pomiary w obecności katalizatora przy ciągłym przepływie mieszaniny reakcyjnej i uzyskanie wielostronnej charakterystyki katalizatorów.

Omówiono: selekcję katalizatorów, badania kinetyczne, badania stabilności aktywności i analizę gazów. Badania zilustrowano wynikami.

ANWENDUNG DER TERMISCHEN DIFFERENTIALANALYSE (DTA) IN PROZESSUNTERSUCHUNGEN KATALYTISCHER GASREINIGUNG

In Prozessuntersuchungen katalytischer Gasreinigung werden Informationen über Katalysatorenaktivität, ihren Bereich der Arbeitstemperatur und Aktivitätstabilisation benötigt.

In der Arbeit werden die Ausnutzungsmöglichkeiten termischer Differentialanalyse DTA in Prozess katalytischer Gasreinigung dargestellt. Diese Methode ermöglicht die Messung in Katalysatoranwesenheit bei stetiger Strömung des Reaktionsgemisches und die Gewinnung der allseitigen Charakteristik der Katalysatoren. Es werden besprochen: Katalysatorauswahl, kinetische Forschungen, Untersuchungen der Stabilität, Aktivität und Gasanalyse.

Die Untersuchungen wurden in Ergebnissen wiedergespiegelt.

ПРИМЕНЕНИЕ РАЗНОСТНОГО ТЕРМИЧЕСКОГО АНАЛИЗА ПРИ ИССЛЕДОВАНИИ ПРОЦЕССОВ КАТАЛИТИЧЕСКОЙ ОЧИСТКИ ГАЗОВ

Для исследования процессов каталитической очистки газов необходимы данные об активности катализаторов, их температурном интервале работы и устойчивости активности.

В работе показаны возможности использования метода разностного термического анализа при процессе каталитической очистки газов. Благодаря этому методу возможны измерения в присутствии катализатора при постоянном протекании реакционной смеси, а также получение многосторонней характеристики катализаторов. Обсуждены селекция катализаторов, кинетические исследования, испытания устойчивости активности и анализ газов. Приведены некоторые результаты.

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