AD-A014 046

THE MECHANISM OF CATALYZER ACTION ON THE BURNING OF CONDENSED SYSTEMS

O. P. Korobeinichev, et al

Army Foreign Science and Technology Center
Charlottesville, Virginia

30 April 1975

247135

0

ADA014046

DEPARTMENT OF THE ARMY
U.S. ARMY FOREIGN SCIENCE AND TECHNOLOGY CENTER
220 SEVENTH STREET NE.
CHARLOTTESVILLE, VIRGINIA 22901

TRANSLATION

In Reply Refer to:
FSTC-HT-23- 148-75
DIA Task No. T741801

Date: 30 April 1975

ENGLISH TITLE: The Mechanism of Catalyzer Action on the Burning of Condensed Systems

SOURCE: Fizika Goreniia i Vzryva 8/1972, pp 511-517

AUTHOR: O. P. Korobeynichev, A. M. Viktorenko,
A. G. Tereshchenko, N. N. Kolomeychuk

LANGUAGE. Russian

COUNTRY: USSR

GRAPHICS NOT REPRODUCIBLE

REQUESTOR: AMXBR-XA-F1

TRANSLATOR: Leo Kanner Associates, Redwood City, CA. (BLT)

ABSTRACT: The burning surfaces of extinguished samples are studied using a scanning electron microscope and optical microscope. The effect of dispersion of a catalyst on the effectiveness of its action during the burning of a model mixture is discussed. It is concluded that the catalyst works very effectively in the c-phase.

SOURCE CIRC REFERENCE NO.

D D C
AUG 29 1975
D

NOTICE

NOT EDITED

15

A considerable number of works [1-6] have been devoted to a study of the catalysis mechanism in the burning of condensed mixtures on the base of ammonium perchlorate (PKhA). There is no single point of view on this question. The data of authors [2-4, 6] confirm the gas-phase mechanism for the action of the catalyst while experiments [1] indicate that the place of action of the catalyst is the condensed phase. The theory of the strongest possible catalyst in the gas phase [2] predicts the strong dependence of the catalyst's effectiveness on its dispersion. However, there are no data on the dependence of the effectiveness of the catalyst's action on its dispersion in the literature.

This work is devoted to an experimental study of the mechanism of the catalyst's action on the burning of condensed systems on the base of PKhA. The work presents the results of studies of catalysis of the burning of PKhA and mixtures on its base with the use of an optical microscope and scanning electron microscope and the results of studies of the effect of dispersion of a catalyst on the burning rate of PKhA and a model system of PKhA+polymethyl methacrylate (PMMA).

Study of the combustion surfaces of extinguished samples using a scanning electron microscope (SEM) and optical microscope. The extinguishing of samples burning at 1 atm was conducted by the sudden drop in pressure with the rupture of a diaphragm separating a large-volume evacuated vessel with a vessel in which the sample burned at 1 atm.

The surfaces of the extinguished fuel samples were studied using an optical microscope and electron scanning microscope (Cambridge Instrument Company Stereoscan) possessing high magnification with great depth of definition. These features which distinguish the SEM from an optical microscope made it a powerful tool for studying the burning mechanism of PKhA and fuels on its base. In American literature, a whole series of works have been published on the employment of the SEM for studying the structure of extinguished samples of PKhA and fuels on its base [7-9] which disclosed a number of facts important for an understanding of the burning mechanism of these fuels. The mechanism of action of the catalysts, however, was not studied in these works using an SEM.

As a result of the studies conducted the following was established.

The accumulation of particles of catalyst occurs on the surface of extinguished samples of a compound of a stoichiometric mixture of PKhA (2 μm)+PMMA (3 μm)+2.0% Fe_2O_3 (4 μm). As can be seen from Figure 1 (a, b) the fraction of the surface occupied by catalyst particles (on photos a, b -- black color) in the case of samples extinguished at 1 atm is an order greater than with the initial surfaces. The particles of catalyst (their average size 10-20 μm) are connected by their bases with the surface and project above it. On Figure 1 can be seen the fused upper parts of the catalyst grains (white). Their connection with the surface is accomplished through the connection of their base with other particles of the catalyst which are in the c-phase. The catalyst particles in the fuel form a framework within which the PKhA particles are arranged. If a tablet of PKhA is 100 percent decomposed (250-400 μm)+2.5% Fe_2O_3, then this framework of the catalyst is sufficiently strong and retains the shape of the tablet. During burning (in contrast to decomposition) the portion of the framework located above the combustion surface in the zone of the flame burns up and is destroyed (by means of the selection and analysis of combustion products of the compound PKhA+PMMA+1% Fe_2O_3 at 1 atm it was shown that ferric oxide burns up and is converted to ferric chloride) Formed on the surface of the burning fuel PKhA+PMMA+1% Fe_2O_3 are luminous foci which were also discovered in [6] and which move over the surface. The observations described above permit explaining the formation of these foci.

Through the entire visible range, the source of luminescence are the particles of catalyst which project 10-20 μm above the combustion surface. The framework (or skeleton) of the catalyst is especially clearly visible on the extinguished surfaces of fuel samples with large-dispersed PKhA (250-400 μm). In this case, the framework of catalyst particles with fused edges projects above the surface of PKhA particles several hundred microns forming honeycombs within which the PKhA particles are arranged. Apparently the ignition and combustion of these honeycombs which begins at a distance of several dozen microns above the surface of the c-phase is also the reason for the arising of the luminous foci. The formation of the framework of catalyst particles above the surface of the c-phase increases the effectiveness of its action since as a result of such an effect the concentration of particles of the catalyst in the gas phase above the combustion surface is substantially increased (by two to three orders).

Using the electron scanning microscope it was possible to disclose a number of features of catalysis in the c-phase which occur during burning, with p=1 atm, of a mixture of PKhA (2 μm)+ +2% CuO (the diameter of the catalyst particles was less than 40 μm, specific surface of catalyst $\sim 1\ m^2/g$). Figure 2 (a, b, c) with different magnification shows a section of combustion surface of a sample of PKhA (2 μm)+2% CuO extinguished at 1 atm.

From Figure 2 it follows: 1) the accumulation of catalyst particles 10-20 μm in size occurs on the combustion surface; 2) depressions are formed around the particles of catalyst in the PKhA in such a way that the catalyst particles are in craters whose diameter on the combustion surface is approximately

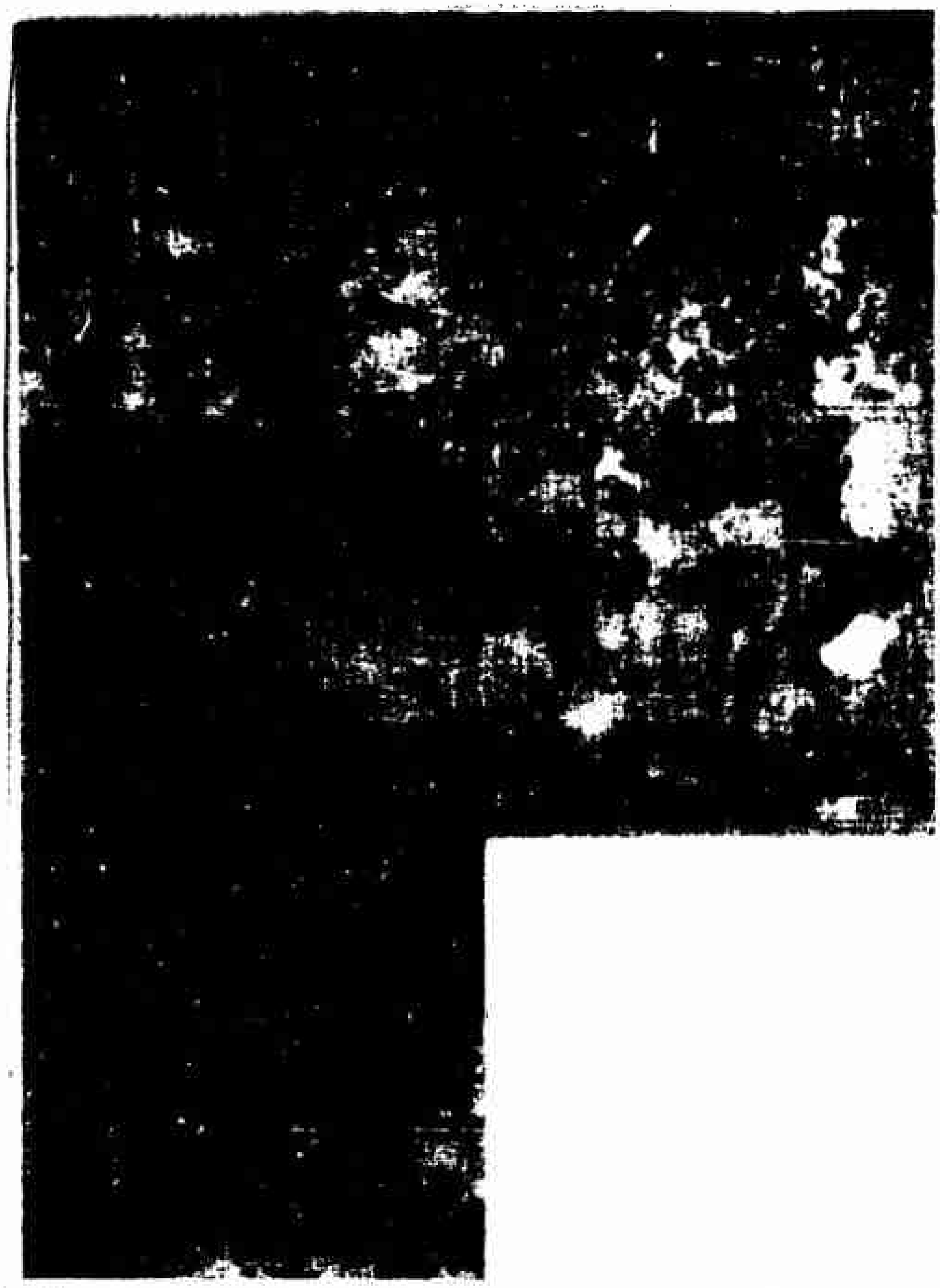

Fig. 1. Surface extinguished at 1 atm (a, c, d, e) and spalled surface (b) of sample of compound mixture. a, c) PKhA (2 μm)+PMMA (3 μm)+2% Fe_2O_3 (4 μm); d,e) without catalyst; a,b) obtained using optical microscope; c,d,e) obtained using SEM.

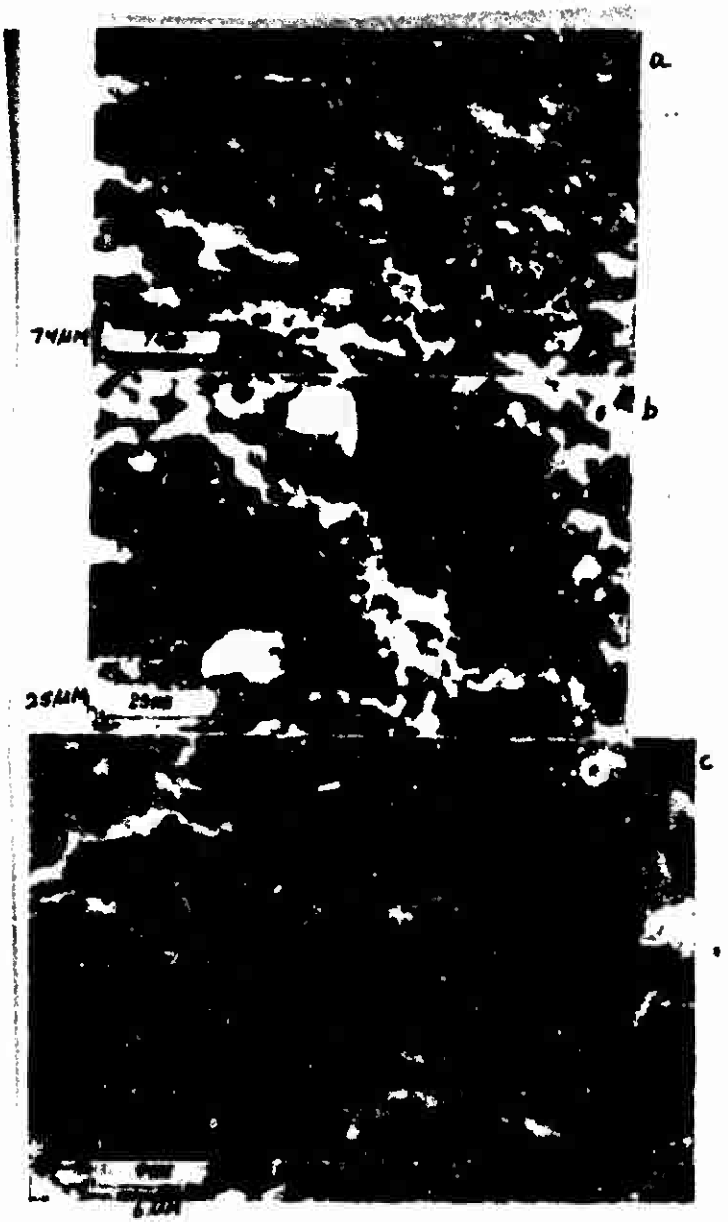

Fig. 2. Electron-microscope photos obtained with different magnification using SEM, of a section of surface of a sample of PKhA (2 μm)+2% CuO extinguished at 1 atm.

twice as large as the diameter of catalyst particles. Since the catalyst particles are retained on the combustion surface, it can be assumed that the gap between the PKhA and catalyst particle, equal approximately to the radius of the latter on the combustion surface, decreases smoothly to zero in proportion to the advance beneath the combustion surface at a distance less than or equal to the diameter of the catalyst particle (on Figure 3c is shown the shape of the crater constructed on the basis of the facts mentioned above).

Hence, it follows that the thickness of the surface layer where the catalyst operates most effectively is less in this case or equal to 10-20 μm. Apparently, with the movement of the catalyst particles toward the surface of combustion a cavity is formed near it within which decomposition products from the PKhA accumulate, which leads to a considerable increase in the pressure within the cavity. This cavity opens when the wall thickness of the PKhA between the cavity and the combustion surface becomes less than the critical (at which the destruction of the wall occurs). The different phases of this process are shown in Figure 3a, b, c. Similar features (formation of craters around catalyst particles and so forth) were also observed in the combustion of a stoichiometric mixture of PKhA (2 μm) with PMMA in the presence of 2% copper chromite.

The effect of the dispersion of the catalyst on its action with the burning of a model compound mixture on a base of PKhA and PMMA. The rate of burning of compounds (procedure for preparing samples similar to [1, 5, 6]) was determined in a bomb of constant volume in an atmosphere of nitrogen with the recording of the burning time by recording the curve of pressure change caused by the burning of the sample. Catalysts of different dispersion were obtained as a result of the calcination, in the air, of ferric oxide at various temperatures of 350-1000°C.

Fig. 3. Different phases in the growth of a cavity near a particle of catalyst of CuO moving toward the combustion surface.

During the calcination of the catalyst the sintering of its particles occurred. The dispersion of the catalysts was determined, on the one hand, from the data on the specific surfaces of the catalysts and, on the other, from electron microscopic studies of the average dimensions of catalyst particles in a powder and in the fuel. These data agree for particles with $r_c > 0.1$ μm. Only in the case of highly-dispersed samples of catalysts with a specific surface of ∿100-30 m^2/g did the conglomeration of primary particles with a size of ∿0.01 μm occur with the formation of bigger agglomerates of these particles of ∿0.1 μm (and in some cases even bigger). In the case of some samples of Fe_2O_3 (r_c∿0.1-0.2 μm) the uniform distribution of catalyst particles in the c-phase was recorded.

Figure 4 presents the results of measurement of the dependence of the effectiveness of action of the catalyst $z-1=\frac{u_c\ \ u_0}{u_0}$

(where u_c and u_0 are the rates of burning of a compound with a catalyst and without it) on the average radius of the catalyst r_c calculated from the formula

$$r_c = \frac{3}{S_{sp}},$$

where S_{sp} is the specific surface of the catalyst determined by the method of thermal desorption of argon. As can be seen from the figure, the shape of curves z-1 from r_c has a different nature for PKhA and the mixture compound and also depends on the dispersion of the PKhA. The dependence of z-1 on r_c is different from that forecast by the theory of maximum strong catalysis in the gas phase ($z-1 \sim r_c^{-1}$). It corresponds more to that dependence which follows from the model developed in [10] where the action of the catalyst is considered both in the gas and in the condensed phase. This model, initially developed for catalysis of the combustion of a monofuel (as applicable to PKhA) can also be employed for the combustion of "homogeneous" mixtures on the base of PKhA (when the dimensions of the oxidizer particles and particles of the fuel are rather small so that the diffusion mixing of the primary products of pyrolysis of the oxidizer and binder is not the limiting stage). The calculation performed in [10] shows that with the operation of the catalyst in a diffusion region the effectiveness of its action in the c-phase is more than an order superior to the effectiveness of action in the gas phase. This also follows from the following elementary estimates. The relation of the stay times τ_c and τ_{gas}

of the particles of the catalyst in the effectively operating c-phase layer near the surface (with width L_c) and in the zone of heating in the gas phase (with width L_g) equals

$$\frac{\tau_c}{\tau_{gas}} = \frac{\rho_c}{\rho_{gas}} \frac{L_c}{L_{gas}},$$

where ρ_c and ρ_{gas} are the densities of the condensed and gas phases. If we accept L_c=5-10 μm and L_{gas}=10-50 μm, then with a pressure of 40 atm τ_k/τ_{gas} =100-40. Since the distance between the particles of the catalyst in the c-phase is less than the distance between the catalyst particles in the gas phase by ρ_c/ρ_{gas} times, in the diffusion region the ratio of the times of diffusion of the gas to the particle of the catalyst connected with the c-phase and to the particle of the catalyst which is in the gas phase will be no greater than ρ_{gas}/ρ_c. The ratio of the stay time to the diffusion time also determines the effectiveness of the catalyst's action in the diffusion mode. As can be seen, this ratio is considerably greater for catalyst particles connected with the c-phase than for particles which are in the gas phase.

The microscopic and electron-microscopic studies presented above confirm the point of view in accordance with which the catalyst works extremely effectively in the c-phase (presence of craters around the catalyst particles in the case of cupric oxide). The formation of a framework of catalyst particles (in the case of Fe_2O_3) which projects 10-20 μm above the burning

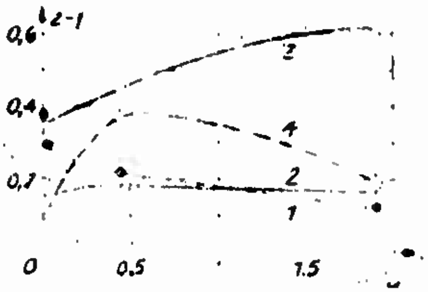

Fig. 4. Dependence of the effectiveness of action of catalyst z-1 on its dispersion with the burning of PKhA and a stoichiometric mixture compound. 1- PKhA (2 μm)+PMMA (3 μm) + +1% Fe_2O_3 at 60 atm (u_0=14.3 mm/s); 2- PKhA (200 μm)+PMMA (3 μm)+1% Fe_2O_3 at 60 atm (u_0=6.5 mm/s); 3- PKhA (2 μm)+ +1% Fe_2O_3 at 80 atm (u_0=7.9 mm/s); 4- PKhA (200 μm)+1% Fe_2O_3 at 80 atm (u_0=8 mm/s).

surface also should lead to an increase in the effectiveness of its action near the surface of the c-phase (due to an increase in the effective concentration of the catalyst in this region of the gas phase in comparison with that which is found at distances greater than 10-20 μm from the surface of the c-phase). If the distance from the surface of the c-phase to the flame zone is 50-100 μm, it can be considered that the catalyst works effectively near the c-phase, which can also be recorded using measurements of the effective zones of heat release with thin thermocouples. If the flame zone is at a distance of 10-20 μm from the surface of the fuel, then the c-phase (in which we can include the framework of catalyst particles) is in the flame zone. Consideration of this circumstance should reconcile investigators who have opposing points of view in their quarrel about the place of action of the catalyst in the burning of condensed systems.

The authors express their gratitude to F. L. Eydel'man for assistance in studies on the SEM and to N. N. Surkov for assistance in measuring burning rates.

Received by editors 18 August 1972

Bibliography

1. Zenin, A. A., Leypunskiy, O. I., and Puchkov, V. M., Dokl. AN SSSR, 198, 361 (1971).
2. Leypunskiy, O. I. and Istratov, A. G., II vsesoyuznyy simpozium po goreniyu i vzryvu (2nd All-Union Symposium on

Combustion and Explosion), Author's abstract of report, Chernogolovka, p 24 (1969).

3. Pittman, I. U., Raketnaya tekhnika i kosmonavtika, 2 (1969).
4. Bakhman, N. N., Lobanov, P. N., et al., Dokl. AN SSSR, 202, 1107 (1972).
5. Abdyunin, V. I., Bakhman, N. N., Nikiforov, V. S., et al., Izv. vyz. Khimiya i khim. tekhn., 5, 666 (1971).
6. Bobolev, V. K., Gen, M. Ya., et al., FGV, 3, 366 (1971).
7. Hightower, J. D. and Price, E. W., Astronautica Acta, 14, 11 (1968).
8. Boggs, T. L. and Kraeutle, K. J., Comb. Sci. and Techn., 1, 75 (1969).
9. Derr, R. L. and Boggs, T. L., Comb. Sci. and Techn., 1, 369 (1970).
10. Korobeynichev, O. N., Shmelov, A. S., and Tatevosyan, A. V., FGV, 8, 3 (1972).