Catalyzed Burning Rates of Ammonium Perchlorate and Polymethylmethacrylate Mixtures

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The catalytic effect of Fe_2O_3, carbon black and SiO_2 ("Aerosil") on the burning rates, u, of ammonium perchlorate (AP) and AP-polymethylmethacrylate (PMMA) mixtures was studied. An increase in the catalyst weight percent, C, in the mixture caused a significant increase in u only at $C \leq$ 5–10% (in some cases even at $C \leq$ 1–2%). Dependence of the burning rate on the catalyst specific surface area, S, is slight (if S is not too small). Strong catalyst agglomeration (especially for Aerosil) was observed in the burning zone. The rate of catalytic reaction, W, in the burning zone was calculated. The comparison of W with catalytic reaction rates measured in conventional chemical reactors leads to the conclusion that the weight part of the mixture reacting on catalyst under the burning condition is very small. A heterogeneous–homogeneous mechanism of catalysis in flames is suggested.

NOMENCLATURE

C	Weight percent of catalyst in the mixture
$d = 6/\rho \cdot S$	Effective particle size
l	Burning zone width
n	The number of molecules impinging on the surface per second
p	Pressure
p_f	Partial pressure of fuel gas
R	Gas constant
S	Specific surface area
S_z	Total catalyst surface area per gram of mixture
T	Temperature
u	Burning rate
v	Gas velocity
W	Rate of catalytic reaction, grams of oxidizer–fuel mixture per square centimeter of catalyst surface area per second
$\dot{x}$	Catalyst particle velocity

$\alpha = \dfrac{m_{ox}/m_f}{(m_{ox}/m_f)_{stoich}}$	Oxidizer-fuel ratio (m_{ox}, m_f — weight fractions of oxidizer and fuel in the mixture)
ϑ	Weight fraction of oxidizer–fuel mixture reacting on catalyst
η	Molecular weight
ρ	Density
τ	Residence time of a catalyst particle in the burning zone
τ_b	Burning time of a strand

INTRODUCTION

Catalysis of the burning of gaseous and condensed systems is of great practical interest.

For solid propellants (where ammonium perchlorate is used as an oxidizer and various polymeric binders serve as fuels) catalysts are used to obtain a predetermined value of the burning rate and to modify the dependence of burning rate on pressure.

It was found in Refs. (*1–16*) that the

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addition of several percent of various compounds of Fe, Co, Ni, Cr, Mn, V, or Si may increase (up to 2–3 times) the burning rate of AP or AP-fuel mixtures.

The addition of compounds of Cu, Mn, Co, Cr, Ni, Zn, or Fe enhanced also the thermal decomposition of AP (1, 8, 17–22). The catalysts were mixed with AP powder or placed (e.g., on petri dish) in the gas decomposition products of AP, the catalyst effectiveness was different in the two cases.

Moreover, the effectiveness of the set of catalysts with respect to burning differs considerably from that for thermal decomposition.

Many authors suggested (6, 22, 24) that in AP based systems the catalytic effect on thermal decomposition and burning is due to acceleration of $HClO_4$ decomposition.

It was demonstrated in Refs. (20, 22, 23) that compounds of Cr, Co, Ni, Cu, and Fe accelerate $HClO_4$ decomposition. The effect of these catalysts on thermal decomposition of $HClO_4$ is similar to that of AP in the gas phase. However, this correlation is not complete [e.g., Al_2O_3 and TiO_2 are effective for $HClO_4$ but not for AP decomposition (23)].

The conditions of catalyst action in the burning zone are much more severe than those in industrial reactors. Simple theoretical models taking into account the conditions specific for the burning zone, have been proposed by Bakhman and Kondrashkov (25) and by Leipunskii and Istratov (26). It was assumed in both models that catalysts act in the gas phase. In the model of Ref. (26) the rate of a homogeneous reaction was taken to be low compared to that of a heterogeneous catalytic reaction. On the contrary, it has been suggested in Ref. (25) that a homogeneous reaction in the gas phase and a heterogeneous reaction on catalyst particles occur simultaneously. The competition of these two reactions is considered to be essential for understanding of experimental data.

The purpose of this study was further investigation (both experimental and theoretical) of the mechanism of catalytic activity in the burning zone.

EXPERIMENTAL METHODS

The burning of AP and AP + PMMA mixtures was studied. SiO_2 ("Aerosil"), carbon black, and Fe_2O_3 were chosen as catalysts. AP, PMMA, SiO_2, and soot were technical grade; Fe_2O_3 ($S = 6.6$ m^2/g) was reagent grade; Fe_2O_3 ($S = 20, 83, 202$, and 253 m^2/g) was obtained by pyrolysis of ferrous oxalate. A fine polymodal fraction of AP was obtained by grinding. The effective particle size of AP ($d \approx 10$ μm) and PMMA ($d \approx 3$ μm) was calculated from the specific surface area measured by drawing air through a layer of powder. The specific surface area of SiO_2, soot, and Fe_2O_3 was measured chromatographically by the technique of thermal argon desorption.

Powders of AP, PMMA, and catalysts were mixed for 30–40 min. Cylindrical strands 8 mm diam and ≈ 10 mm long were pressed. The burning time τ_b of inhibited strands was measured in a nitrogen-pressured bomb (at $p \leq 100$ atm) by a piezoelectric pressure transducer, and the mean burning rate $u = h/\tau_b$ (where h is the strand length) was calculated.

Investigation of catalysts before and after burning was conducted by means of a BS 513A Czech electron microscope of the transmission type. The catalyst particle sizes were determined by a MIR-2 microscope from the negatives obtained.

The ratio of phases was measured by an X-ray apparatus URS-5 01. The phase composition of individual catalyst grains or of their small agglomerates was determined from microdiffraction in the electron microscope.

EXPERIMENTAL RESULTS AND DISCUSSION

Under conditions typical for industrial reactors the catalysts operate in the kinetic region, and the reaction rate is proportional to the total surface area of the catalyst, S_Σ.

For solid propellants the total surface area of catalyst per gram of propellant is $S_\Sigma = C \cdot S$. Thus, S_Σ may be varied by varying C at $S = $ const or S at $C = $ const.

An increase in C (at $S = $ const) caused a significant increase in the burning rate only

TABLE 1
EFFECT OF CATALYST CONTENT ON THE BURNING RATE

| | u (mm/sec) | | |
| | p (atm): | | |
% SiO_2	10	40	100
0	5.0	5.5	8.2
0.05	5.4	8.0	11.3
0.1	6.3	10.0	16.1
0.3	6.1	13.9	20.0
0.5	6.5	12.6	22.0
0.7	6.3	14.5	24.7

at small C. At $C = 5–10\%$ (and, in some cases, even at $C = 1–2\%$) the burning rate ceased to rise. For instance, the burning rate of the mixture $(100 - C)\%$ (AP + PMMA, $\alpha = 0.61$) + $C\%$ SiO_2 increased noticeably with C increasing only at $C \leq 0.5–0.7\%$ (Table 1).

Further increase in the catalyst content caused a gradual decrease in the burning rate.

The effect of S (at C = const) on the burning rate is rather weak* (if S is not too small)—see Table 2.

It is worth noting that some increase in the burning rate with increasing S was observed by Boldyrev and co-workers (4) for mixtures 80% AP + 20% binder with 1% CuO or 1% NiO added.

The fact that the catalytic effectiveness depends only slightly on the catalyst specific surface area is quite unusual for heterogeneous catalysis. Two factors (acting in the same direction) seem to be responsible for the paradoxical dependence $u(S)$.

Firstly, the rate of a catalytic reaction on catalyst particles must be diffusion limited, and strong agglomeration of the catalyst takes place in the burning zone.

Indeed, the residence time of catalyst

* However, it has been demonstrated (28) that thermal decomposition of AP catalyzed with Fe_2O_3 accelerates considerably with increasing C (over the range 2.5 to 50%) at S = const or with S increasing (over the range 1.7 to 110 m²/g) at C = const.

particles in the burning zone is very small $(10^{-5}–10^{-1}$ sec), and the thermal gradient in this zone is very steep (up to $10^5–10^6$ grad/cm). Therefore, catalytic reactions may proceed only on the outer surface of catalyst particles. The surface of pores (both inside of single particles and their agglomerates) may have no effect on the catalytic reaction rate.

Our experiments show that catalyst agglomeration in the burning zone may be very significant. For instance, the specific surface area of SiO_2 collected from combustion products of AP + PMMA + SiO_2 mixtures (at $p = 1$ atm) was 10–15 m²/g at $C = 1\%$ and ≈ 0.8 m²/g at $C = 10\%$, whereas the specific surface area of virgin SiO_2 (before mixing with AP and PMMA) was 290 m²/g. Thus, the value of S diminished by one (at $C = 1\%$) or two (at $C = 10\%$) orders of magnitude. The following data were obtained for Fe_2O_3 collected on porcelain dishes (Table 3).

It follows from Table 3 that a significant agglomeration of particles of Fe_2O_3 occurs in the course of burning. Note that the ratio of various allotropic Fe_2O_3 forms suffers essential changes and the partial reduction of Fe_2O_3 to FeO occurs.

Very interesting data were obtained for AP + PMMA mixtures with 1 or 3% ferrocene. The latter is known (6) to be a good catalyst of AP based systems. For AP + PMMA mixtures ferrocene provides nearly the same burning rate as Fe_2O_3 does. The data listed in Table 4 provide a simple explanation to this phenomenon. Indeed, the specific surface area and phase composition of the solid products of ferrocene decomposition are very similar to those of solid products for AP + PMMA + Fe_2O_3 mixtures (see Tables 3 and 4).

The second factor suggested to be responsible for the weak dependence $u(S)$ is the complication of heterogeneous catalysis by heterogeneous–homogeneous processes.

Let us evaluate the weight fraction of oxidizer–fuel mixture which may react on catalyst surface in the burning zone.

There is strong evidence that in many cases catalysts (especially ferrocene and other organometal compounds) act in the

TABLE 2

Effect of Catalyst Specific Surface Area on the Burning Rate of the Mixture AP + PMMA, $\alpha = 0.61$

Catalyst	S (m²/g)	u (mm/sec) p (atm):				
		10	20	40	70	90
1% Fe₂O₃	7		10.5	13.0		
	20		11.0	11.2		
	83		11.0	11.3		
	202		11.0	10.3		
	253		9.0	10.5		
No catalyst	—		6.0	5.8		
1% Carbon black	26	6.0			10.7	9.4
	91	5.2			10.9	9.8
	267	6.0			8.2	9.2
No catalyst	—	5.0			6.8	7.5

gas phase where particles of catalysts (or their decomposition products) are suspended in the gasification products of AP and fuel.

The residence time of the catalyst (particles) in the burning zone is $\tau = l/\dot{x}$. The rate of catalytic reaction per unit of surface area of catalyst is:

$$W = \vartheta \cdot \frac{100 - C}{C} \cdot \frac{1}{S} \cdot \frac{\dot{x}}{l} \qquad (1)$$

Consider now two extremes: (a) catalyst particles are small enough so that their velocities nearly equal that of the gas ($\dot{x} \approx v$), and (b) catalyst particles are large enough so their velocities are zero in the laboratory coordinate system or $\dot{x} = u$ in the coordinate system connected with the burning zone. According to Ref. (29) a

particle is "small enough" if its diameter does not exceed several decimal fractions of micron and "large enough" if its diameter is equal to dozens of microns or more. Particles having a specific surface area 10 m²/g and 0.3 m²/g are denoted as "small enough" and "large enough," respectively. Provided these particles have no inner surface (no pores) and the particle density is $\rho = 2$ g/cm³, their effective sizes are 0.3 and 10 μm, respectively.

Let us compute the magnitude of W at $C = 1\%$, $p = 1$ atm, $u = 0.1$ cm/sec. The following estimate can be given for the burning zone width at $p = 1$ atm: $l \approx 10$–1000 μm $= 10^{-3}$–10^{-1} cm. The temperature range of the catalysts action may be estimated at $T = 500$–1500°C. The density ρ_g of gasification products ($\eta = 30$) is $\rho_g = p\eta/RT = (2.06$–$4.73) \times 10^{-4}$ g/cm³, and

TABLE 3

Specific Surface Area and Phase Composition of Solid Particles Collected from Combustion Products of 99% (AP + PMMA) + 1% Fe₂O₃ Mixtures ($p = 1$ atm)

α	S (m²/g)[a]	Phase composition
0.6	1.2	52% α-Fe₂O₃; 43% γ-Fe₂O₃; 5% FeO
1.0	1.2	80% α-Fe₂O₃; 20% γ-Fe₂O₃
2.0	2.7	55% α-Fe₂O₃; 45% γ-Fe₂O₃
Virgin Fe₂O₃	5.3	100% α-Fe₂O₃

[a] Measured from negatives obtained by an electron microscope.

TABLE 4

SPECIFIC SURFACE AREA AND THE PHASE COMPOSITION OF SOLID PARTICLES COLLECTED FROM COMBUSTION PRODUCTS OF AP + PMMA + FERROCENE MIXTURES

α	C (%)	S (m^2/g)	Phase composition[a]
0.61	1	5.1	α-Fe_2O_3; Fe_3O_4; FeO
1.0	1	1.9	α-Fe_2O_3; Fe_3O_4; FeO
2.0	1	4.9	α-Fe_2O_3; Fe_3O_4
0.61	3	1.6	α-Fe_2O_3; Fe_3O_4

[a] From microdiffraction data.

the gas velocity is $v = \rho u/\rho_g = 380\text{--}875$ cm/sec (taking for solid AP + PMMA mixture $\rho = 1.8$ g/cm^3).

From Eq. (1) the rate of catalytic reaction on catalyst particles is:

tion rates of hydrocarbons, ammonia, and hydrogen at $p_f = 0.1\text{--}1$ atm do not exceed 10^{20} molecules/cm^2 sec or $\approx 10^{-3}$ g of fuel/cm^2 of catalyst surface per second. Thus, the rate of catalytic reaction computed from Eq. (1) at $\vartheta = 1$ is by 3 to 6 orders of magnitude (for "small" particles $S = 10$ m^2/g) or by 1–4 orders of magnitude (for "large" particles, $S = 0.3$ m^2/g) higher than those listed in Table 5. Hence, comparison of $W_{Eq.\ 1}$ and catalytic reactions rates in conventional chemical reactors (as well as the aforementioned comparison of of $W_{Eq.\ 1}$ and n) allows one to draw the conclusion that $\vartheta \ll 1$ in the burning zone.[†]

Agglomeration of catalysts in the burning zone must lead to further decrease in ϑ with decreasing S [see Eq. (1)].

Since the weight fraction of oxidizer–fuel mixture reacting on catalyst must be small,

S (m^2/g)	0.3	10
W (g/cm^2 sec)	$(3.33 \times 10^{-2}\text{--}3.33) \cdot \vartheta$	$(3.76\text{--}865) \cdot \vartheta$

If the weight fraction of the oxidizer–fuel mixture reacting on catalyst, ϑ, were close to unity, the magnitude of W would be too high. Indeed, the number of molecules impinging on the catalyst surface per second is $n = p(2\pi mkT)^{-0.5}$ where m is the mass of molecule; k, the Boltzmann constant. For ammonia at $T = 1000°C$ we obtain n (g/cm^2 sec) $= 5.1$ p (atm). Thus, if ϑ were close to unity, the rate of catalytic reaction W on "large" particles would be nearly equal to n (at the right boundary of the W range). This result seems to be unrealistic.

For "small" particles the magnitude of W at the right boundary of the W range would be even greater than n. Certainly, such a result would have no physical meaning.

Thus, comparison of W and n leads to the conclusion that the weight fraction of oxidizer–fuel mixture reacting on the catalyst under burning conditions must be small compared to unity.

Consider now the data from available literature concerning the rates of catalytic oxidation reactions (Table 5).

It follows from Table 5 that the oxida-

it is reasonable to suggest that heterogeneous–homogeneous catalysis occurs under burning zone conditions. Some active species formed on the catalyst surface diffuse in the gas phase and promote (even in very small concentrations) the main homogeneous reaction.

There is direct experimental evidence that total oxidation of hydrocarbons and organic oxygen compounds over certain catalysts occurs by the heterogeneous–homogeneous mechanism. However, only few papers give data permitting comparison

[†] Zenin, Leipunskii and Puchkov (11) calculated the residence time, τ, of a catalyst particle in the burning zone and the time interval τ_{df} for diffusion of a gaseous oxidizer–fuel mixture [$(100 - C)$ grams of mixture per each C grams of catalyst] to the catalyst particle. For particles 3 μm in diameter τ_{df} was by two orders of magnitude higher than τ (at $\dot{x} = v$). The conclusion was drawn from this comparison that only a small weight fraction of the mixture can react on the catalyst. However, it will be noted that τ_{df} decreases with decreasing d ($\tau_{df} \sim d^2$) whereas $\tau \neq f(d)$ at $\dot{x} = v$. Thus, at $d < 0.3$ μm we must obtain $\tau_{df} < \tau$ and the above conclusion can not be deduced from comparison of τ with τ_{df}.

TABLE 5

RATES OF SOME CATALYTIC OXIDATION REACTIONS IN CONVENTIONAL CHEMICAL REACTORS

Fuel	P_f (atm)	Catalyst	T (°C)	W_{exp} molecule/ cm² sec	W_{exp} g/cm² sec	Refs.[c]
Methane	1	Pd/Al_2O_3	450	$\approx 10^{17}$ [a]	$\approx 3 \times 10^{-6}$	(30)
Isooctane	0.02	Pt	400	10^{17} [a]	2×10^{-5}	(31)
Propylene	0.1	SnO_2	470	6×10^{13}	4×10^{-9}	(32)
	0.1	$Bi_2O_3 \cdot MoO_3$	470	10^{14}	7×10^{-9}	(32)
Ammonia	0.1	Co_3O_4	700	$\approx 10^{17}$	3×10^{-6}	(33)
	0.1	Pt–Rh (grid)	860	10^{20}	3×10^{-2}	(34)
Hydrogen	0.008	Co_3O_4	63	10^{11} [b]	3×10^{-13} [b]	(35)

[a] Initial rate corresponding to $\approx 1\%$ conversion.

[b] Extrapolation to $T = 525°C$ and $P_f = 0.1$ atm gives $W \approx 10^{17}$ molecules/cm² sec.

[c] A pulse microreactor (30), a flow reactor (31, 33, 34), a nongradient method (32), and a static circulating apparatus (35) have been used.

of the reaction rate for a strictly heterogeneous and that for a heterogeneous–homogeneous reaction. One of these (36) describes propene oxidation on a copper oxide catalyst. At a constant reaction time the degree of propene oxidation by a heterogeneous–homogeneous mechanism was by about an order of magnitude higher than for a strictly heterogeneous reaction.

The homogeneous reaction contribution can be seen from the results obtained by L. A. Nersesyan (37). Methane oxidation over silica gel was investigated by differential calorimetry in a flow (27). The reaction products contained CO, H_2, CH_2O. Table 6 lists the experimental results obtained from the temperature difference of a differential thermocouple and correlation of experimental and calculated results. Com-

parison of theoretical and experimental results obtained from the temperature dependence of a differential thermocouple (Table 6) shows that methane oxidation over silica gel at 650°C follows the heterogeneous–homogeneous mechanism, the heterogeneous contribution is 17% and the homogeneous, 83%.

Dependence of burning rate on C provides further evidence confirming the heterogeneous–homogeneous mechanism of catalysis during burning. We have seen that the burning rate ceased to increase with increasing C at $C = 5$–10% and even at $C = 1$–2%. It is quite unlikely that all the mixture reacts on catalyst particles [a dependence $u \sim C^{0.5}$ was obtained in Ref. (26)]. On the contrary, this phenomenon would seem to be rather natural if only a

TABLE 6

DATA OF METHANE OXIDATION OVER SILICA GEL OBTAINED BY DIFFERENTIAL CALORIMETRY

Temp (°C)	Initial content (%)	Δt_{exp} (°C)	Δt_{theor} (°C)	Heterogeneous part of the reaction (%)	Homogeneous part of the reaction (%)
650	CH_4, 20 O_2, 20 N_2, 60	1.3	7.5	17	83

small quantity of active species were generated on the catalyst surface.

Further, it will be noted that in some cases small additives exert a strong catalytic effect on burning of AP-fuel mixtures at $\alpha = \alpha_1$ and an inhibiting effect at $\alpha = \alpha_2$. For example, Aerosil significantly promotes the burning of rich AP-fuel mixtures ($\alpha < 1$), but behaves as a strong inhibitor with lean AP-fuel mixtures ($\alpha > 1$) and especially with pure AP:

% SiO_2	0	0.001	0.01	0.05	0.1	0.2	0.5	1.0
$u_{100\ atm}$ (mm/sec)	10.0	9.1	5.8	3.6	3.5	2.5	2.4	1.9

This fact cannot be understood if one supposed that all the mixture reacted on the catalyst surface. On the other hand, it does not conflict with the heterogeneous–homogeneous mechanism of catalysis.

CONCLUSIONS

Experimental data and theoretical considerations lead to the conclusion that catalyst effectiveness (as well as the effect of catalyst surface area on catalyst effectiveness) under the burning zone conditions is very different from that in conventional chemical reactors.

For solid propellants an increase in the weight percent of catalyst, C, caused a steep increase in burning rate, u, only at low C.

An increase in the catalyst specific surface area, S, at $C = $ const slightly affects the burning rate.

Two factors seem to be essential for the weak $u(S)$ dependence. Firstly, a catalytic reaction is diffusion-limited (due to the very short residence time of catalyst particles in the burning zone), and strong catalyst agglomeration observed in the burning zone for Fe_2O_3 and especially for Aerosil.

However, the main reason responsible for the peculiar irregularities of burning catalysis (in particular, the weak dependence of the catalysis activity on its specific surface) seems to be the heterogeneous–homogeneous processes and the competing homogeneous reaction occurring in the absence of the catalyst.

Comparison of the rate of catalytic re-action calculated for the burning zone conditions with that measured in conventional chemical reactors suggests that under burning conditions the weight part of oxidizer–fuel mixture reacting on the catalyst is very small. This is consistent with the heterogeneous–homogeneous mechanism of catalysis in flames.

Dependence of the burning rate on catalyst content also agrees with such a mechanism. It was observed that small additives of Aerosil promoted the burning of a rich AP-fuel mixture, but inhibited the burning of AP and lean AP-fuel mixture. This observation provides further evidence in favor of the proposed mechanism.

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