

THE ROLE OF MoO_3 AND Fe_2O_3 IN THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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The effect of addition of MoO_3 and Fe_2O_3 as well as mixtures of the two oxides (calcined in air at 500 °C) on the thermal decomposition of ammonium perchlorate (AP) was studied using thermogravimetry (TGA) and derivative thermogravimetric analysis (DTG). The catalysts calcined at 500 °C were characterized using TPR, XPS and XRD techniques. The surface area of the catalysts was determined by means of the conventional BET method. The results are discussed in terms of the recently published mechanism in which nityl perchlorate is supposed as an intermediate in the thermal decomposition of pure AP. The correlation between the surface area and activity of the catalysts in the thermal decomposition of AP has been done. The activation energy (ΔE) for non-catalyzed and catalyzed high-temperature thermal decomposition of AP were calculated from the TGA results using the Coats-Redfern equation.

The chemistry of ammonium perchlorate (AP) has been extensively studied because of its use as an oxidizing agent and in many technological applications such as explosives¹ and propellants². Many studies have been published on the sublimation³ and the thermal decomposition of AP at low⁴ and at high temperatures⁵. Many experimental techniques including the microscopic investigation were used to study the stoichiometry of the reaction, to analyze the volatile products^{5,6}. Some of these studies were carried out under vacuum^{5,6} and others in the atmosphere of N_2 to suppress sublimation⁵. The effect of various additives on the decomposition of AP was studied⁶⁻⁸, too.

Two different mechanisms based on the transfer of either a proton⁹ or an electron¹⁰ have been early proposed to explain the low-temperature thermal decomposition of AP. A novel reaction mechanism published recently¹¹ is based on the formation of nityl perchlorate (NP) NO_2ClO_4 as the reaction intermediate. Transition-metal oxides such as pure or mixed MoO_3 and Fe_2O_3 are known to be good catalysts for oxidation of propylene and methanol^{12,13} and for hydrogenation of benzene¹⁴. Different techniques have been used to characterize MoO_3 (ref.¹⁵), Fe_2O_3 (ref.¹⁶), and multicomponent catalysts^{12,17} containing MoO_3 and Fe_2O_3 .

The present work is intended to study the catalyzed thermal decomposition of AP in the presence of MoO_3 , Fe_2O_3 and mixtures of these two oxides.

EXPERIMENTAL

Materials and Techniques

Preparation of the catalysts. Analytical grade ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$ (Fisons) and ferric nitrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Hopkin and Williams), were calcined for 5 h in air at 500 °C to prepare MoO_3 and Fe_2O_3 . MoO_3 mixed with 0.5 and 50 mole % Fe_2O_3 were prepared using the calculated amounts of ferric nitrate (dissolved in 50 ml deionized water) and ammonium molybdate, which was suspended in the solution. The suspension was dried first by evaporation under continuous stirring at 120 °C for 12 h and finally calcined in air at 500 °C for 5 h. Ammonium perchlorate (AP) was gently ground with the catalyst (10% w/w) in an agate mortar and sieved. The mixture was stored in a desiccator.

Characterization of the Catalysts

The temperature-programmed reduction (TPR) of the calcinated catalysts was done in apparatus described elsewhere¹⁸. TPR profiles of samples were recorded on ca 10 mg samples and H_2 consumption was monitored while the sample was heated from ambient temperature to 1100 °C in a stream of 6% H_2/N_2 (40 ml/min) at a heating rate of 5 °C/min.

X-Ray powder diffraction analysis (XRD) of the calcined catalysts was carried out using a Philips diffractometer (P.W.2103/00) with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$).

X-Ray photoelectron spectroscopy was carried out using a Kratos ES 300 spectrometer. The aluminium $\text{K}\alpha$ line (1486.6 eV) was used for excitation. The X-ray power supply was run at 14 kV and 15 mA with a response time of 1 s and a range of 10^{14} CPS.

Surface area (S_{BET}) of both pure and mixed oxides were determined on a Carlo-Erba single point SORPTY 1750 unit by the BET method using N_2 at -196 °C as an adsorbate.

Reactivity Measurements

The activity of different catalysts towards the thermal decomposition of AP was measured on 100 mg samples using a gasometric¹⁹ technique at a heating rate of 5 °C/min. Thermogravimetric analysis (TGA) measurements of pure AP and AP mixtures with 10% (by weight) catalysts were carried out using Shimadzu Stand-Alone Thermal Analyzer Instrument (TGA-50H) supplied with a data acquisition and handling system model Shimadzu Chromatopac C-R4AD. Heating rate of 5 °C/min, 10 mg samples and a dynamic atmosphere of N_2 (40 ml/min) were applied.

Data Analysis

The activation energies (ΔE) of the high-temperature thermal decomposition of pure AP and AP mixed with 10% of each catalyst were calculated using the Coats-Redfern equations as follows²⁰:

$$\log \left[\frac{1 - (1 - \alpha)^{(1-n)}}{T^2 (1-n)} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad \text{for } n < 1 \quad \text{or} \quad (1)$$

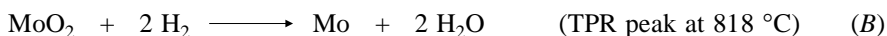
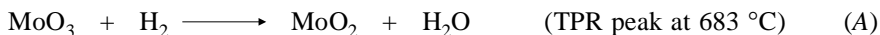
$$\log \left[-\log \frac{(1-\alpha)}{T^2} \right] = \log \frac{AR}{aE} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad \text{for } n = 1 \quad , \quad (2)$$

where α is the fractional weight loss (calculated from TGA results), n is the reaction order, A is the frequency factor, a is the heating rate, R is gas constant and T is the absolute temperature (K). Using values of n equal to 0.25, 0.5, 0.75 and 1.0 for a given set of experimental values of α and T plots of $\log [1 - (1 - \alpha)^{1 - n/T^2} (1 - n)]$ or $\log [-\log (1 - \alpha)/T^2]$ against $1/T$ were constructed. The value of n that has given the best fit was chosen as a reaction order and from the slope of that line (ΔE) was calculated.

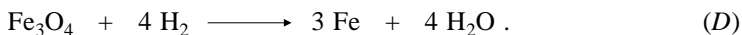
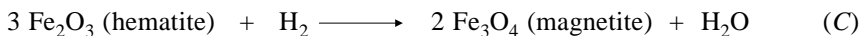
RESULTS AND DISCUSSION

Temperature-Programmed Reduction (TPR)

The TPR profiles of $\text{MoO}_3\text{-Fe}_2\text{O}_3$ catalysts calcined in air at 500 °C for 5 h are shown in Fig. 1. The TPR profile of MoO_3 (Fig. 1, curve 1) has two reduction peaks with T_{\max} at 683 and 818 °C which are ascribed to the following two reduction steps²¹.



The calculated H_2 uptake was equal to $2.14 \cdot 10^{-2}$ mol/g (which is close to the theoretical value of $2.08 \cdot 10^{-2}$ mol/g). The TPR pattern of Fe_2O_3 (Fig. 1, curve 4) consists of a small peak at 353 °C and a strong peak at 537 °C which might be attributed²² to the stepwise reduction of Fe^{3+} to Fe metal as follows:



This is in agreement with the reduction mechanism, previously reported²³⁻²⁵ where FeO (Wüstite) could not be obtained below 575 °C. This is also consistent with the calculated area under the two peaks. The theoretical amount of hydrogen required for the complete reduction of Fe_2O_3 (ref.²⁶) is $1.87 \cdot 10^{-2}$ mol/g which is in close agreement with the found H_2 uptake (i.e. $1.95 \cdot 10^{-2}$ mol/g). The addition of 0.5 mole % Fe_2O_3 to MoO_3 had little effect on the reduction process. The TPR profile of Mo-Fe-I (Fig. 1, curve 2) showed the same peaks as those for MoO_3 with T_{\max} shifted to lower values (ca 653 and 814 °C) and, in addition, a shoulder at 567 °C which may be due to the reduction of Fe_2O_3 . An increase in the initial amount of Fe_2O_3 up to 50 mole % (Mo-Fe-II, Fig. 1, curve 3) resulted in the TPR profile with a shoulder at 432 °C (attributed to the

reduction of Fe_2O_3) followed by two peaks at 524 and 773 °C corresponding to the catalyzed reduction of MoO_3 . The reduction of MoO_3 is known^{27,28} to be strongly catalyzed by traces of foreign transition metals. The sharpness of the TPR peaks observed in Fig. 1 suggests that the nucleation and/or autocatalysis is the rate-determining step in reduction process²¹.

X-Ray Powder Diffraction Analysis

Figures 2a, 2b show the diffractograms of MoO_3 and Mo-Fe-I calcined at 500 °C in air. The patterns match the ASTM card No. 5-0508 of MoO_3 , where the most intense peaks appeared at $d = 6.86, 3.82, 3.47, 3.27, 2.65, 2.31$ and 1.85 \AA , in both patterns of MoO_3 and Mo-Fe-I. This supports the TPR results where no change has been observed upon the addition of a small amount of Fe_2O_3 to MoO_3 .

Figure 2c shows the diffraction lines of Mo-Fe-II which matches well the $\text{Fe}_2(\text{MoO}_4)_3$ pattern (ASTM card No. 20-526) especially those lines at $d = 4.44, 4.12, 3.97, 3.52, 3.29, 3.19$ and 2.88 \AA .

The XRD pattern of Fe_2O_3 calcined in air at 500 °C (Fig. 2d) matches well the hematite Fe_2O_3 lines (ASTM card No. 24-72A) at $d = 3.73, 2.70, 2.51, 2.21$ and 1.69 \AA .

XPS Results

The values of the binding energies of Mo 3d and Fe 2p levels for MoO_3 - Fe_2O_3 catalysts under investigation are listed in Table I. All binding energies were referenced to the contaminated carbon (C 1s = 384.6 eV). The binding energy of Mo $3d_{5/2}$ level was 233.4 eV, in case of MoO_3 , corresponding²⁹ to Mo(VI). The addition of 0.5 and 50 mole % Fe_2O_3

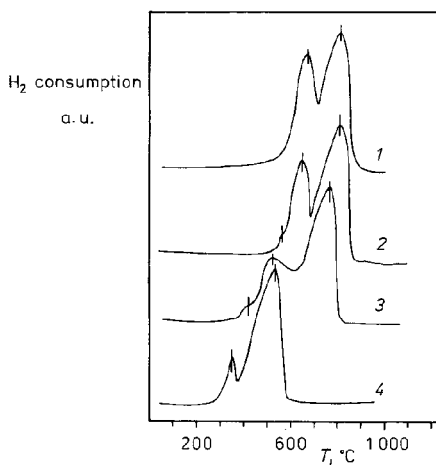


FIG. 1
TPR profiles of catalysts calcined in air at 500 °C for 5 h: 1 MoO_3 ; 2 Mo-Fe-I; 3 Mo-Fe-II; 4 Fe_2O_3 carried out at 5 °C/min in 6% H_2/N_2 (40 ml/min)

(Mo-Fe-I and Mo-Fe-II), respectively, had no effect on the binding energy of Mo $3d_{5/2}$. The value of the binding energy of Mo $3d_{5/2}$ was still in the range 233.1 – 233.3 eV.

In the case of Fe_2O_3 , the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ levels were calculated as 713.6 and 727.2 eV, respectively. These are nearly the same as those reported by Armour et al.³⁰. The binding energy of Fe $2p_{3/2}$ level (ca 713.6 eV) corresponds to Fe(III) (ref.³¹). The same value was calculated for Fe $2p_{3/2}$ level in case of the mixtures. This supports our previous results of XRD, where the formation of $Fe_2(MoO_4)_3$ was identified from the X-ray analysis.

Reactivity Measurements

TG curves of pure AP and AP mixed with 10% w/w of the catalysts are shown in Fig. 3. After the slow initial stage, the low-temperature decomposition (LTD) of pure AP appears at 345 °C and is completed at ≈ 385 °C. The second step (i.e. the high-temperature thermal decomposition, HTD) takes place in the temperature range 440 – 510 °C. The DTG curve of the thermal decomposition of AP, as shown in Fig. 4, curve 1, displays two peaks with T_{max} at 350 and 505 °C corresponding to two decomposition steps of AP.

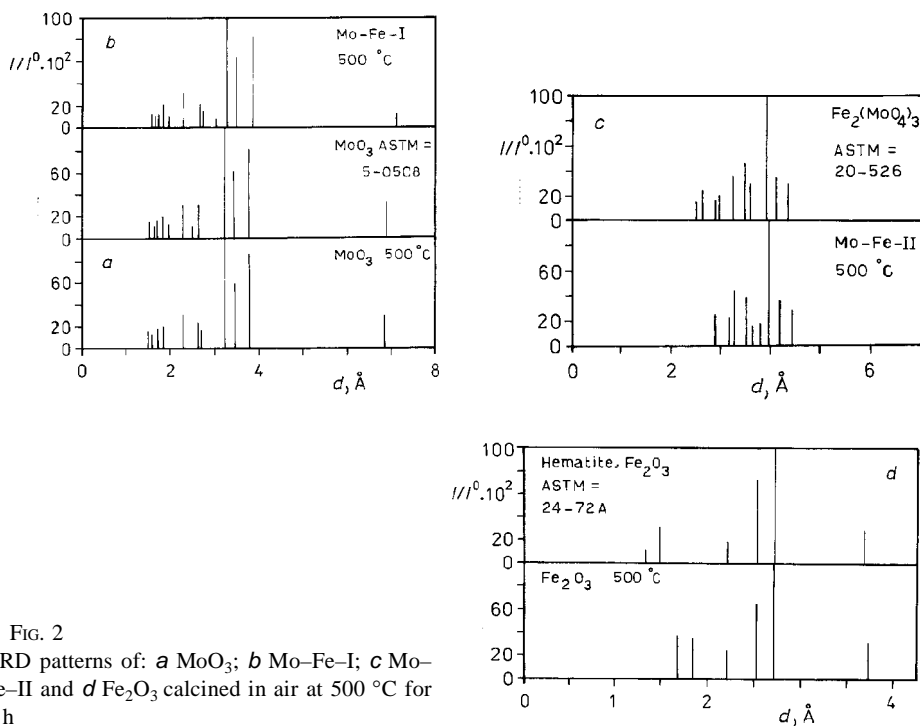


FIG. 2

XRD patterns of: *a* MoO_3 ; *b* Mo-Fe-I; *c* Mo-Fe-II and *d* Fe_2O_3 calcined in air at 500 °C for 5 h

Preliminary experiments were carried out on the thermal decomposition of AP with different concentrations of MoO_3 , calcined in air at 500°C , (namely 10, 20 and 30% oxide, w/w). The decomposition processes of AP were enhanced as the concentration of the oxide increases. This is concluded from the observed shifts of T_{max} of both LTD ($295, 281$ and 265°C) and of HTD ($395, 388$ and 380°C), towards lower temperatures as a content of oxide increases.

We can conclude that the addition of 10% MoO_3 or Fe_2O_3 , to the pure AP, has enhanced the two decomposition steps of AP. A comparison of the relative catalytic effect of these two oxides showed that Fe_2O_3 has a much greater activity than MoO_3 in the decomposition of AP. This is evident from Figs 3, 4 and Table II where T_{max} values (for the LTD and HTD) appeared at 270 and 320°C for AP + Fe_2O_3 instead of 295 and 395°C in case of AP + MoO_3 . The fact that an increase in the content of Fe_2O_3 in the mixed catalyst enhances the decomposition of AP (compare T_{max} values for Mo-Fe-I and Mo-Fe-II catalysts in Table II and Fig. 4) confirms the above conclusion.

TABLE I

Binding energies (± 0.5 eV) relative to $\text{C } 1s = 284.6$ eV of Mo $3d$ and Fe $2p$ levels for MoO_3 - Fe_2O_3 catalysts, calcined in air at 500°C for 5h

Sample	Mo		Fe	
	$3d_{5/2}$	$3d_{3/2}$	$2p_{3/2}$	$2p_{1/2}$
MoO_3	233.4	236.5	—	—
Mo-Fe-I	233.3	237.3	712.4	726.0
Mo-Fe-II	233.1	236.1	712.6	727.6
Fe_2O_3	—	—	713.6	727.2

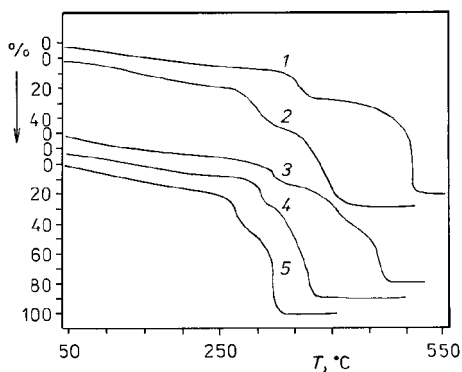


FIG. 3
TG curves of the thermal decomposition carried out at $5^\circ\text{C}/\text{min}$ of: 1 AP and its mixtures with 10% w/w of the respective catalyst calcined at 500°C ; 2 AP + MoO_3 ; 3 AP + Mo-Fe-I; 4 AP + Mo-Fe-II; 5 AP + Fe_2O_3

The activation energies for the non-isothermal, high-temperature decomposition of pure AP and AP mixed with 10% (w/w) of catalysts under investigation, were calculated from the TG results using the Coats–Redfern equation²⁰ (see Experimental). The value of $n = 1$ has given the best fit for all the catalysts used. This indicates that the HTD of AP is a first order reaction³². The values of the activation energies are cited in Table II.

The catalytic effect of the additive in the thermal decomposition of AP manifests itself when there is no direct contact between the additive and the perchlorate particles. The efficiency of an additive functioning in that way is necessary proportional to the

TABLE II

Summary of the DTG results of the thermal decomposition of NH_4ClO_4 (AP) and AP mixed with (10% w/w) $\text{MoO}_3\text{-Fe}_2\text{O}_3$ catalysts calcined at 500 °C in air for 5 h. S_{BET} is the surface area of the catalysts, E_A is the activation energy

Sample	$T_{\text{max}1}$, °C	$T_{\text{max}2}$, °C	S_{BET} , m ² /g	E_A , kJ/mol
Pure AP	350	505	–	160 ± 10
AP + MoO_3	295	395	0.8	136 ± 8
AP + Mo–Fe–I	317	465	0.6	128 ± 4
AP + Mo–Fe–II	305	365	10.6	122 ± 3
AP + Fe_2O_3	270	320	21.8	106 ± 4

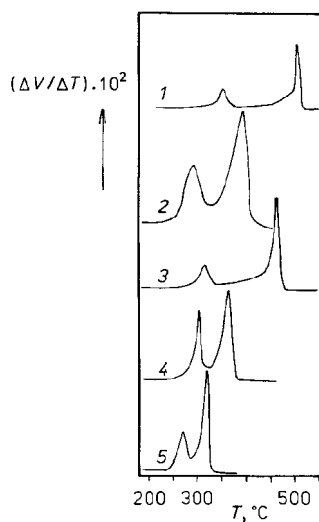


FIG. 4

DTG curves of the thermal decomposition carried out at 5 °C/min of: 1 AP and its mixtures with 10% w/w of the respective catalyst calcined at 500 °C; 2 AP + MoO_3 ; 3 AP + Mo–Fe–I; 4 AP + Mo–Fe–II; 5 AP + Fe_2O_3

area of its entire surface rather than to the area between the additive and the perchlorate crystals³³.

The catalytic effect of the samples under investigation on the thermal decomposition of AP is clearly dependent on their surface area (see Table II). The most active sample, Fe₂O₃ calcined at 500 °C, has the greatest surface area, 21.8 m²/g, while the least active catalyst, Mo-Fe-I at 500 °C, has the smallest S_{BET} surface (ca 0.6 m²/g).

According to the mechanism of Galwey and Mohamed¹¹, the nitryl perchlorate is formed as a reaction intermediate during the thermal decomposition of AP. When the surface area of the catalyst increases, the dissociation rate of the intermediate increases³³ as well and, consequently, the rate of decomposition of AP will raise (see Table II). Also, the calculated values of E_A for the high-temperature decomposition of AP supports the above assumption. In case of pure AP, the activation energy was ascertained to 160 ± 10 kJ/mol, and for AP mixed with 10% Fe₂O₃ to 106 ± 4 kJ/mol. These values are in close agreement with those calculated by Solymosi et al.⁸. The activation energy of HTD of AP mixed with 10% MoO₃, 136 ± 8 kJ/mol, is in good agreement with that found by Glasner et al.⁷ (129.7 kJ/mol).

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