Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 833-840

ROLE OF THE ACIDIC-BASIC CHARACTERS OF SOME METAL OXIDES IN THE PYROLYSIS OF AMMONIUM PERCHLORATE

S. A. Halawy[*] *and S. S. Al-Shihry*

Department of Chemistry, College of Education, King Faisal University, P.O. Box 1759 Hofuf 31982, Eastern Province, Saudi Arabia

(Received February 10, 1997; in revised form January 8, 1998)

Abstract

Six metal oxide samples were prepared by calcination of the corresponding precursors at 500°C for 5 h in air and were characterized by IR and XRD analyses. Their surface areas were calculated by means of the BET method. The acidities and basicities of these metal oxides were estimated thermogravimetrically by the method of adsorption of pyridine and formic acid as probe molecules. The pyrolyses of pure ammonium perchlorate (AP) and of AP mixed with (10% w/w) metal oxide were studied, in a dynamic atmosphere of N_2, by thermogravimetric analysis (TG) and derivative thermogravimetric analysis. A correlation was found between the catalytic activities of the metal oxides during the pyrolysis of AP, and their acidic-basic characters. The activation energies of the non-catalyzed and catalyzed pyrolysis of AP were calculated from the TG results via the Coats-Redfern equation.

Keywords: acidity, ammonium perchlorate, basicity, characterization, DTG, metal oxides, pyrolysis, TG

Introduction

Perchlorates have been of chemical interest as oxidizers and in different technological applications such as explosives and rocket propellants [1]. Many investigators have studied the pyrolysis of ammonium perchlorate (AP) as a pure compound [2] or the sublimation of AP in the presence of certain inorganic salts, under atmospheric pressure [3] or under vacuum [4], while others have studied the catalyzed thermal decomposition of AP [5, 6]. Different mechanisms have been proposed to illustrate the pyrolysis of AP at low temperatures, based on either a

---

[*] Permanent address: Department of Chemistry, Faculty of Science, South Valley University, Qena 83511, Egypt.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

proton transfer mechanism [7] or an electron transfer mechanism [8]. A novel reaction mechanism was recently published [9], involving the formation of nitryl perchlorate NO_2ClO_4 as a reaction intermediate.

Metal oxides, as individual or mixed catalysts, have been used in different catalytic reactions, such as the oxidation of methanol [10], the Fischer-Tropsch synthesis [11] and the reduction of nitrobenzene [12].

The present work is intended to study the relationship between the catalytic activities of various metal oxides during the non-isothermal pyrolysis of AP in a dynamic atmosphere of nitrogen, and their acidic-basic characters.

Experimental

Materials and techniques

CdO, Cr_2O_3 and Co_3O_4 were obtained by calcination of the corresponding nitrate salts [$Cd(NO_3)_2\cdot 4H_2O$, $Cr(NO_3)_3\cdot 9H_2O$ and $Co(NO_3)_2\cdot 6H_2O$ (BDH, England)]. NiO was prepared by the decomposition of $Ni(OH)_2$, CuO was produced from the calcination of basic copper carbonate, $CuCO_3\cdot Cu(OH)_2$ (Aldrich, USA), while MoO_3 was obtained by calcination of $(NH_4)_6Mo_7O_{24}\cdot 4\,H_2O$ (Fisons, England) at 500°C for 5 h in air. NH_4ClO_4 (BDH, England) was carefully ground with each oxide (10% by weight) in an agate mortar, and the mixtures were then sieved and stored in a desiccator over anhydrous $CaCl_2$.

The produced oxides were identified by X-ray diffraction, using a Philips diffractometer (P.W.2103/00) with Ni-filtered CuK_α radiation (λ=1.542 Å).

IR absorption spectra of the oxide samples were recorded with a Perkin-Elmer 599B IR spectrophotometer, by the KBr disc technique, in the region 1600–200 cm^{-1}.

The surface areas S_{BET} of all the oxides under investigation were determined by the BET method, using N_2 as an adsorbate at –196°C, with the aid of a conventional volumetric gas adsorption apparatus [13].

The activities of the different oxides towards the pyrolysis of AP were measured by a thermogravimetric analysis (TG) technique. TG and derivative thermogravimetric (DTG) analyses of pure AP and AP mixed with 10% (w/w) oxides were carried out with a Shimadzu Stand-Alone Thermal Analyzer Instrument (TGA-50H), supplied with a data acquisition and handling system model Shimadzu Chromatopac C-R4AD, Japan. A heating rate of 5°C min^{-1}, samples of ≅7 mg and a dynamic atmosphere of N_2 (40 ml min^{-1}) were applied.

The acidities (Ψ) and basicities (Φ) of the oxide samples were determined thermogravimetrically, as described previously [14], by the adsorption of pyridine and formic acid as probe molecules, respectively. The mass loss was estimated as the acidity or basicity of the catalyst. Values of Ψ and Φ were calculated as mol sites$\times 10^{18}$ m_{cat}^{-2} [15, 16].

Results and discussion

Characterization of the oxides

The prepared oxide specimens were identified by XRD analysis. The diffraction lines of the XRD patterns of these oxides matched the corresponding ASTM card data as follows: CdO at *d*=2.71, 2.35 and 1.66 Å (ASTM card no. 5-0640), Cr_2O_3 at *d*=2.71, 2.52, 2.20, 1.69 and 1.47 Å (ASTM card no. 6-0504), Co_3O_4 at *d*=3.99, 3.09, 2.85, 2.45, 1.56 and 1.43 Å (ASTM card no. 9-418), CuO at *d*=2.75, 2.52, 2.33, 1.91 and 1.50 Å (ASTM card no. 5-0661), NiO at *d*=2.05, 1.55 and 1.09 Å (ASTM card no. 4-0835) and MoO_3 at *d*=6.86, 3.82, 3.47, 3.27, 2.65 and 2.31 Å (ASTM card no. 5-0508).

All the oxides prepared by calcination of the corresponding precursors at 500°C for 5 h in air were also characterized by IR spectroscopy. The locations of the absorption bands observed in the spectra of all the oxides are listed in Table 1 with their references.

Table 1 IR absorption frequencies of metal oxides prepared by calcination of the corresponding salts at 500°C for 5 h in air

Metal oxide	Observed absorption frequency/cm^{-1}	Reference
CdO	725, 575, 490, 275	[17]
Cr_2O_3	625, 560, 440, 405	[18]
Co_3O_4	660, 575, 390, 350	[18]
CuO	610, 505, 415	[18]
NiO	510, 440	[17]
MoO_3	990, 870, 660, 375	[19]

From the results of the XRD and IR analyses, it is concluded that all the prepared oxides were obtained in a pure state.

Reactivity measurements

TG curves of pure AP and AP mixed with 10% (w/w) of each oxide are shown in Fig. 1. After the slow initial stage, the low-temperature pyrolysis (LTP) of pure AP (curve a) started at 295°C and was completed at ≅330°C, the second step (i.e. the high-temperature pyrolysis, HTP) taking place in the temperature range 335–365°C. The DTG curve of the pyrolysis of AP (Fig. 2a) revealed two peaks, with T_{max} at 307 and 349°C, corresponding to the two stages of pyrolysis of pure AP. The addition of 10% (w/w) of MoO_3, CuO, Co_3O_4 or Cr_2O_3 to AP reduced the two pyrolysis stages (LTP and HTP) to one step. It started at 260–285°C and was completely finished at 370°C in the case of MoO_3, and at ≅340°C in the cases of CuO and Co_3O_4. The pyrolysis of AP was notably enhanced by the addition of Cr_2O_3, where it was completed at 330°C.

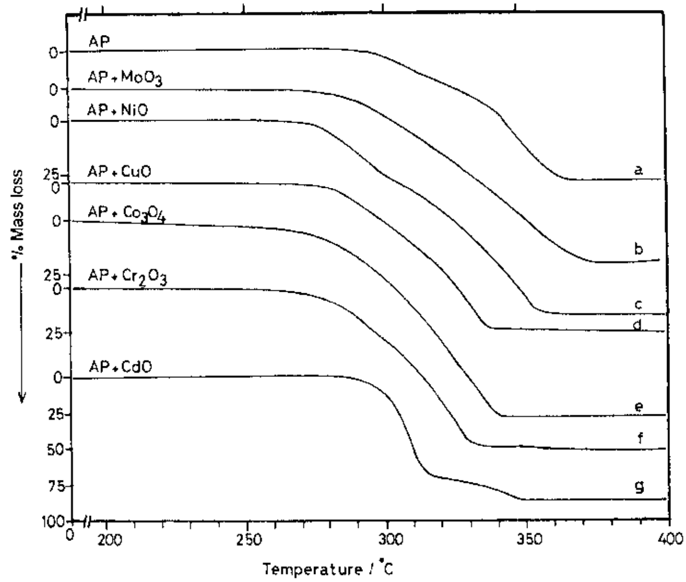

Fig. 1 TG curves of the pyrolysis of NH_4ClO_4 (AP) and AP mixed with 10% (w/w) of different oxides, carried out at 5°C min^{-1} in a dynamic atmosphere of N_2 (40 ml min^{-1})

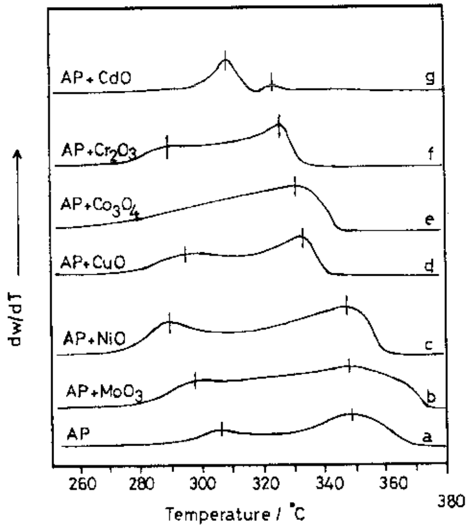

Fig. 2 DTG curves of the pyrolysis of NH_4ClO_4 (AP) and AP mixed with 10% (w/w) of different oxides, carried out at 5°C min^{-1} in a dynamic atmosphere of N_2 (40 ml min^{-1})

The DTG curves of the catalyzed pyrolyses of AP mixed with the above-mentioned oxides are shown in Fig. 2. They have different shapes, depending on the enhancing effects of the oxides. The values of T_{max} of the DTG curves are given in Table 3. Two other oxides, NiO and CdO, accelerated the pyrolysis of AP through two consecutive steps (Fig. 1, curves c, g). CdO proved to be the most active of the used oxides. The first step (LTP) of AP in the presence of CdO was in the temperature range 290–315°C, with a 69% mass loss, while the second step (HTP) occurred between 315 and 350°C, with a 21% mass loss. The DTG curve of the pyrolysis of AP+10% CdO displayed a large peak at 308°C, where most of the AP decomposed (69%), followed by a weak broad peak at 322°C.

AP is stable at room temperature, but decomposes with measurable rates at temperatures above 150°C. At temperatures below 300°C, AP undergoes an autocatalytic reaction [20]. This is called the low-temperature reaction. The autocatalytic pyrolysis of AP [20] can be represented as follows:

$$2NH_4ClO_4 \rightarrow NO_2ClO_4+NH_3+HCl+2H_2O$$

The intermediate NO_2ClO_4 is formed during the LTP of AP.

In a recently published mechanism [21], the intermediate NO_2ClO_4 undergoes rupture of the covalent bonds, with further decomposition, in the HTP stage, according to the following scheme [21]:

$$NO_2ClO_4^- \rightarrow O_2N^+ + OClO_3^- \rightarrow [O_2N\text{–}O\text{–}ClO_3] \rightarrow [N^+O_3]+ClO_3^- \rightarrow$$

$$\rightarrow NO^+ + ClO_3^- + 2O \text{ (or } O_2)$$

Table 2 Values of S_{BET}, acidity and basicity of the metal oxides prepared by calcination of the corresponding precursors at 500°C for 5 h in air

Metal oxide	S_{BET}/m^2 g^{-1}	Acidity(Ψ)*	Basicity(Φ)*
CdO	2.0	15.2	0.9
Cr_2O_3	21.0	1.8	357.1
Co_3O_4	6.0	0.6	17.4
CuO	20.0	6.2	69.8
NiO	12.0	25.4	116.3
MoO_3	0.8	16.6	–

* ψ or $\Phi\times10^{18}$ mol sites/m$^2_{cat}$

We therefore consider that there will be a competition between ClO_3^- and NO^+ over the acidic and basic sites of the metal oxide to give the final decomposition products. From the calculated values of acidity and basicity (Table 2), the metal oxides under investigation can be classified into three main groups, depending on their catalytic activities, as follows:

(i) Fairly acidic oxides, such as MoO_3 [22]. This type of oxide retards the pyrolysis of AP at sites where no basic sites are available on the oxide surface for decomposition of the acidic anion ClO_3^-.

(ii) Basic oxides possessing a higher concentration of basic sites (Φ) than of acidic sites (Ψ), e.g. Cr_2O_3, Co_3O_4, CuO and NiO [23], which accelerate the pyrolysis of AP according to the ratio Φ/Ψ. The higher the ratio Φ/Ψ, the more active the oxide is during the pyrolysis of AP. From the data in Table 2 and Figs 1 and 2, it is worth noting that Cr_2O_3 was the most active oxide with a ratio Φ/Ψ of 198.4 and a T_{max} of the HTP of AP catalyzed by Cr_2O_3=326°C. In contrast, NiO was the least active oxide in this group, with a ratio Φ/Ψ of 4.6 and a T_{max} of the HTP of AP in the presence of NiO at 347°C. Therefore, the higher the ratio Φ/Ψ and the lower the T_{max} of HTP of a certain metal oxide, the easier is the pyrolysis of AP. On the basis of their ratio Φ/Ψ and the T_{max} of the HTP of AP this group of metal oxides can be arranged in the sequence Cr_2O_3>Co_3O_4>CuO>NiO.

(iii) Oxides which possess more acidic sites than basic sites, such as CdO. The presence of a minute concentration of the basic sites, necessary for the decomposition of ClO_3^-, accelerates the whole process of AP pyrolysis. ClO_3^- is known to promote the decomposition of AP, as is the presence of a higher concentration of acidic sites, required for the decomposition of NO^+. CdO therefore exhibited the highest activity as concerns the pyrolysis of AP. The values of T_{max} in the DTG curve of AP+CdO (Fig. 2g) were 308 and 322°C.

The activation energies (E_a) for the LTP and HTP of pure AP and AP catalyzed by 10% (w/w) metal oxide were calculated by using the Coats-Redfern equation [24] as follows [25]:

$$\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)] = \log_{10}(AR/aE_a)[1-(2RT/E_a)] - E_a/2.3RT \quad \text{(for } n<1\text{); or}$$

$$\log_{10}[-\log_{10}(1-\alpha)/T^2] = \log_{10}(AR/aE_a)[1-(2RT/E_a)] - E_a/2.3RT \quad \text{(for } n=1\text{)}$$

where α=the fractional mass loss (calculated from the TG results), n=the reaction order, A=the frequency factor, and a=the heating rate, R=the gas constant and T=the absolute temperature (K). Different values of n (≤ 1) were used for a set of experimental values of (α) and (T), and plots of $\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ or $\log_{10}[-\log_{10}(1-\alpha)/T^2]$ *vs.* ($1/T$) were constructed. The value of n that gave the best fit was chosen as reaction order and from the slope of that line E_a was calculated. The values of E_a and n, with the corresponding temperature range, are listed in Table 3. From the calculated values of E_a for the catalyzed pyrolysis of AP, it may be observed that E_a for both the LTP and the HTP is less than the corresponding value calculated for the pyrolysis of pure AP, except in the case of AP+CuO. The high values of E_a in the presence of CuO are consistent with previously published findings [26]. CuO seems to catalyze the pyrolysis of AP, as shown from the T_{max} value of the LTP and HTP stages, but a chemical reaction may occur between AP and CuO during the pyrolysis of AP. The lower values of E_a in the case of MoO_3 could be attributed to the presence of Mo^{6+} in MoO_3, as concluded from the catalyzed pyrolysis of $NaClO_2$ in the presence of fourth-pe-

Table 3 Summary of DTG results and kinetic results of the pyrolysis of NH_4ClO_4 (AP) and AP mixed with 10% (w/w) metal oxides

Sample	DTG T_{max}/°C		E_a/kJ mol^{-1} LTP	n	E_a/kJ mol^{-1} HTP	n
	(1)	(2)				
Pure AP	307	349	170.5 (300–335)*	1	145.1 (335–360)*	0.5
AP+CdO	308	322	135.4 (300–315)*	0.5	28.2 (315–340)*	0.5
AP+Cr_2O_3	289	326	127.9 (290–310)*	0.5	141.3 (310–330)*	0.5
AP+Co_3O_4	–	330	127.9 (285–310)*	0.5	115.1 (310–335)*	0.5
AP+CuO	294	332	205.4 (285–315)*	0.5	160.0 (330–355)*	0.5
AP+NiO	289	347	163.5 (280–330)*	0.5	107.1 (330–355)*	0.5
AP+MoO_3	297	348	109.4 (300–330)*	0.5	90.4 (335–365)*	0.5

* Temperature range °C, n=order of reaction

riod metal oxides [27]. The values of E_a (Table 3) are in good agreement with those to be found in the literature [5, 28].

Conclusions

Many factors affect the catalyzed pyrolysis of AP, including the conditions under which the pyrolysis process was carried out. In static air, with use of a gasometric technique, the surface area of the applied catalysts was an important factor, as concluded in a recent study [5] and as proposed earlier [29]. In the present work, the catalytic pyrolysis of AP in a dynamic atmosphere of N_2 was studied to illustrate the catalytic effect of metal oxides in the absence of atmospheric oxygen. The pyrolysis of AP in this case depends mainly on the dual acidic-basic characters of the metal oxides used. The oxides that have a higher concentration of acidic than basic sites were shown to be the most active catalysts, e.g. CdO. These were followed by the metal oxides with a higher ratio Φ/Ψ, e.g. Cr_2O_3, Co_3O_4, CuO and NiO. The fairly acidic oxides were the least active as regards the pyrolysis of AP. The values of T_{max} of the HTP stage furnish the following sequence for the metal oxides used in this study for the catalyzed pyrolysis of AP:

$$CdO>Cr_2O_3>Co_3O_4>CuO>NiO>MoO_3$$

If CdO is excluded, the above sequence matches the basicity sequence of these oxides. If CdO and MoO_3 are excluded, the sequence of the ratio Φ/Ψ for these oxides is as follows:

$$Cr_2O_3 \gg Co_3O_4 > CuO > NiO$$

Finally, it is difficult to correlate the E_a values of the two stages for the catalyzed pyrolysis of AP with T_{max} or the acidic-basic characters of the metal oxides. This is due to the different valency states of the metal atoms present in the metal oxides used in this study.

References

1 R. B. Beyer and N. Fishman, Progress in astronautics and aeronautics, Vol. I, Solid propellant rocket research, Academic Press, New York 1960, p. 673.
2 A. K. Galwey, P. J. Herley and M. A. Mohamed, Reactivity of Solids, 6 (1988) 205.
3 V. R. Pai Verneker, K. Kishor and M. P. Kannan, J. Appl. Chem. Biotechnol., 27 (1977) 309.
4 A. K. Galwey, P. J. Herley and M. A. Mohamed, Thermochim. Acta, 132 (1988) 205.
5 S. A. Halawy and M. A. Mohamed, Collect. Czech. Chem. Commun., 59 (1994) 2253.
6 R. P. Rastogi, G. Singh, B. L. Dubey and C. S. Shukla, J. Catal., 65 (1980) 25.
7 V. V. Boldyrev, V. V. Alexandrov and A. V. Boldyreva, Combust. Flame, 15 (1970) 71.
8 G. P. Owen, J. M. Thomas and J. O. Williams, J. Chem. Soc., Faraday Trans., I, 70 (1974) 1934.
9 A. K. Galwey and M. A. Mohamed, Proc. Roy. Soc. (London), A396 (1984) 425.
10 K. Ivanov, P. Litcheva and D. Klissurski, Collect. Czech. Chem. Commun., 57 (1992) 2539.
11 H. Jung and W. J. Thomson, J. Catal., 139 (1993) 375.
12 A. Maltha, S. C. van Wermeskerken, B. Brunet and V. Ponec, J. Mol. Catal., 93 (1994) 305.
13 A. S. Joy, Vacuum, 3 (1953) 254.
14 S. A. Halawy and M. A. Mohamed, J. Mol. Catal. A: Chemical., 98 (1995) 63.
15 M. A. Makarova, E. A. Paukshtis, J. M. Thomas, C. Williams and K. I. Zamaraev, J. Catal., 149 (1994) 36.
16 C. T. Fishel and R. J. Davis, Catal. Lett., 25 (1994) 87.
17 J. R. Ferraro, Low-frequency vibration of inorganic and coordination compounds, Plenum Press, New York 1971.
18 N. T. McDevitt and W. L. Baun, Spectrochim. Acta, 20 (1964) 799.
19 F. Trifiro, S. Notarbartolo and I. Pasquon, J. Catal., 22 (1971) 324.
20 L. L. Bircumshaw and B. H. Newman, Proc. Roy. Soc. (London), A227 (1954) 115.
21 A. K. Galwey and M. A. Mohamed, Nature (London), 311 (1984) 642.
22 G. C. Bond, S. A. Halawy, K. M. Abd El-Salaam, E. A. Hassan and H. M. Ragih, J. Chem. Tech. Biotechnol., 59 (1994) 181.
23 C. P. Bezouhanova and M. A. Al-Zihari, Catal. Lett., 11 (1991) 245.
24 J. W. Coast and J. P. Redfern, Nature (London), 201 (1964) 58, 101.
25 W. W. Wendlandt, Thermal Methods of Analysis, 2nd edn., John Wiley & Sons, New York 1974, p. 48.
26 G. Singh and R. R. Singh, Indian J. Chem., 16A (1978) 406.
27 S. A. Halawy, J. Anal. Appl. Pyrolysis, 38 (1996) 89.
28 A. G. Keenan and R. F. Siegmund, Quarterly Reviews, Chem. Soc. London, 23 (1969) 430.
29 V. V. Boldyrev, M. Bulens and B. Delmon, The control of the reactivity of solids, Elsevier, Amsterdam 1979, p. 160.