

Catalysed thermal decomposition of KClO_3 and carbon gasification

S. Martins · J. B. Fernandes · S. C. Mojumdar

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Abstract The catalytic decomposition of KClO_3 is studied in the presence of MnO_2 , activated carbons and sodium sulphide. This investigation describes the use of thermogravimetry as a convenient technique to investigate catalytic activity of a simple chemical reaction. It is observed that the MnO_2 catalyst decreases the decomposition temperature from 480 to 350 °C while the activated carbons cause its decomposition at 320–325 °C. At the same time the carbons undergo facile gasification. Presence of Na_2S was the most effective as it induced the carbon-catalysed decomposition of KClO_3 at a temperature as low as 220 °C, a temperature at which the carbons were stable and no gasification was observed.

Keywords Activated carbons · KClO_3 decomposition · Carbon gasification · MnO_2 · Na_2S

Introduction

Activated carbons are known to be good catalysts and have been used to catalyse several reactions [1]. They have also been used as supports for other catalysts [2, 3]. The surface

area, pore structure and surface functional groups of the porous carbons determine the variety of catalytic properties.

The catalytic activity can be enhanced by impregnating the carbon with the substance specific catalyst. Heterogeneous catalysis is receiving wide application in removal of pollutants, such as sulphur dioxide and nitrogen dioxide, from coal-based power plants and internal combustion machines having environmental impact [4, 5].

Decomposition of potassium chlorate

Potassium chlorate is used as an oxidising agent and source of oxygen for many chemical reactions [6]. It is an important component in the making of explosives.

It is well known that potassium chlorate decomposes at a higher temperature to give potassium chloride and oxygen. It melts at 355 °C and decomposes at 480 °C (Fig. 1).

To reduce the decomposition temperature, manganese dioxide is the standard catalyst. The search for more efficient and cheap catalyst is on. Carbons as well as impregnated ones are researched upon as viable alternative catalysts.

Catalytic gasification of carbon

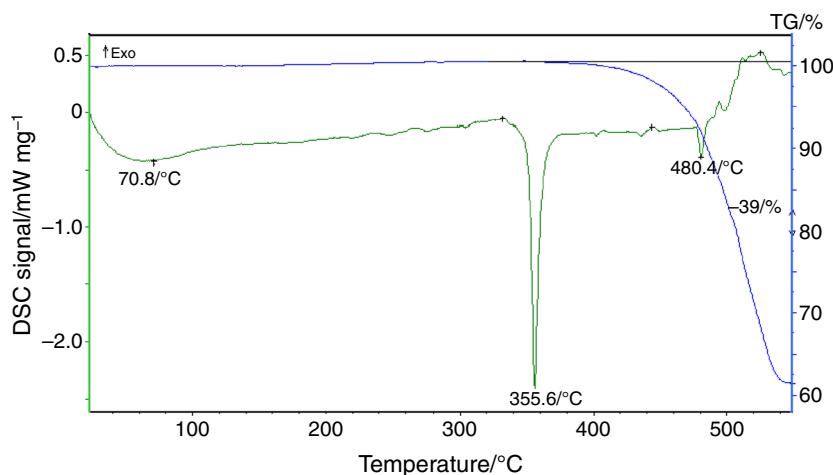
While carbon acts as a catalyst and catalyst support for many reactions, its gasification temperature becomes significant. A recent review by Wood and Sancier [7] provides an excellent survey of the papers published since 1979 on the catalytic gasification of carbon. The carbon oxidation rate is greatly enhanced by catalytic agents, which are often the inorganic impurities that are commonly found in the sample. Rand and Marsh showed the effect of Ni on gasification of polyfuryl alcohol carbon by carbon dioxide [8].

S. Martins · J. B. Fernandes
Department of Chemistry, Goa University, Goa 403206, India

S. C. Mojumdar (✉)
Department of Chemistry, University of Guelph, 50 Stone Rd. E,
Guelph, ON N1G 2W1, Canada
e-mail: scmojumdar@yahoo.com

S. C. Mojumdar
Department of Chemical Technologies and Environment,
Faculty of Industrial Technologies, Trenčín University of A.
Dubček, 020 32 Púchov, Slovakia

Fig. 1 TG–DSC curves of potassium chlorate



The gasification of carbons in the presence of catalytic agents is loosely referred to as “catalytic gasification”. The implications of catalytic gasification have practical importance in the conversion of coal by reaction with H₂O (steam) or CO₂ to gaseous fuels or chemical feedstocks.

Catalysts are used in pyrolysis to increase the gas production and decrease the liquids evolved [9].

The catalytic effect of Carbon and MnO₂/C in the decomposition reaction of potassium chlorate is the subject of investigation as well as the catalytic effect of KClO₃ and Na₂S on carbon gasification.

Thermal properties are very important for material characterizations. Therefore, many authors have studied various thermoanalytical properties of various materials [10–37].

Experimental

The thermal analysis was carried out on NETZCH-STA 409 PC instrument (Germany) at a heating rate of 10 °C min⁻¹ in the temperature range of 30–700 °C by using 10 mg samples in dry alumina crucibles. Argon was used as purge gas.

- (1) (a) C1—is activated carbon obtained from SD Fine Chemicals (India).
(b) CMC—activated carbon synthesized from CMC by the decomposition of CMC salt at 400 °C in inert atmosphere and subjecting it to the boiling water treatment. The details of synthesis and characterization of the activated carbon samples are given in the previous communication [38, 39].
- (2) (a) MnO₂—synthesized by calcining manganese nitrate in nitrogen for 2 h at 200 °C.
(b) MnO₂/C1—manganese dioxide supported on C1 was synthesized by making a paste of manganese

nitrate and C1 in propanol, evaporated to dryness, and then calcined in nitrogen environment for 2 h at 200 °C to get 20 % loading of MnO₂ on C.

- (3) (a) K is KClO₃—obtained from Loba Chemicals (India)
(b) MK—prepared by mixing KClO₃ and MnO₂
(c) C1K—prepared by mixing C1 and KClO₃
(d) CMC-K—prepared by mixing CMC and KClO₃ and
(e) MC1K—prepared by mixing MnO₂/C1 and KClO₃
- (4) (a) NS—fused sodium sulphide obtained from Loba chemicals
(b) C1NS—prepared by mixing C1 and fused sodium sulphide
(c) C1 KNS—prepared by mixing C1, KClO₃, Na₂S, CMCKNS prepared by mixing CMC, KClO₃, Na₂S

The ratio of mixing was 1:1 by mass, for two component mixtures used and 1:1:1 for sample mixtures where three components were used.

Results and discussion

Decomposition of potassium chlorate in the presence of MnO₂

KClO₃ is a well-known oxidising agent due to its oxygen releasing ability. It is a source of oxygen for many chemical reactions [5]. It is also an important component in the making of explosives.

It decomposes at 480 °C as per the reaction $2\text{KClO}_3 \rightarrow 2\text{KCl} + 3\text{O}_2$ with the expected mass loss of ~39 %. Figure 1 gives the TG–DSC curves of KClO₃. Thus KClO₃ melts at ~355.6 °C and decomposes at 480 °C.

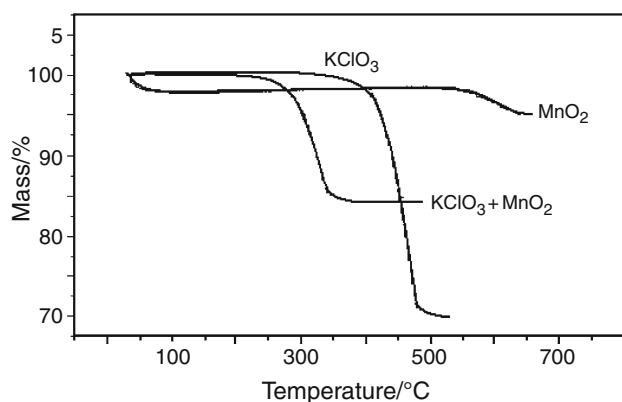


Fig. 2 TG curves for the decomposition of KClO_3 in the presence of MnO_2

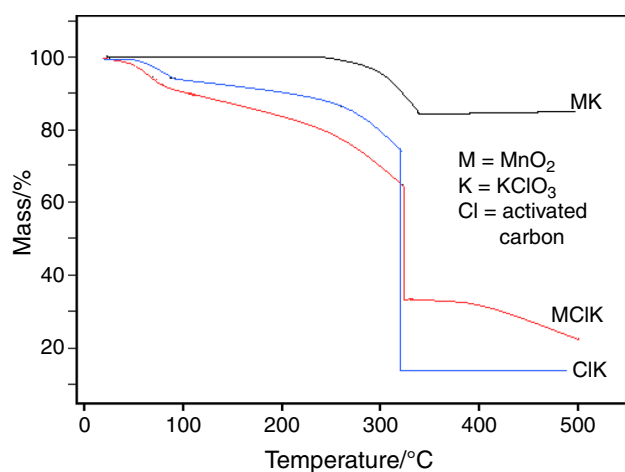


Fig. 3 TG curves of KClO_3 in the presence of activated C, MnO_2 and both activated C and MnO_2 together

The observed mass loss is in agreement with the above reaction stoichiometry. To reduce the decomposition temperature, manganese dioxide was used as a catalyst.

Figure 2 gives the TG curves for the decomposition of KClO_3 in the presence of MnO_2 catalyst. The experiment was carried out with approximately a (1:1) mixture of MnO_2 and KClO_3 .

It can be seen that the temperature of decomposition of KClO_3 is brought down from 480 to 350 °C in the presence of the MnO_2 catalyst. At this temperature MnO_2 is unaffected as it would decompose only beyond 520 °C as evident from the MnO_2 only profile in the above figure.

Decomposition of potassium chlorate in the presence of carbons and gasification of carbons

TG curves of KClO_3 in the presence of activated C, MnO_2 and both activated C and MnO_2 together are given in Fig. 3.

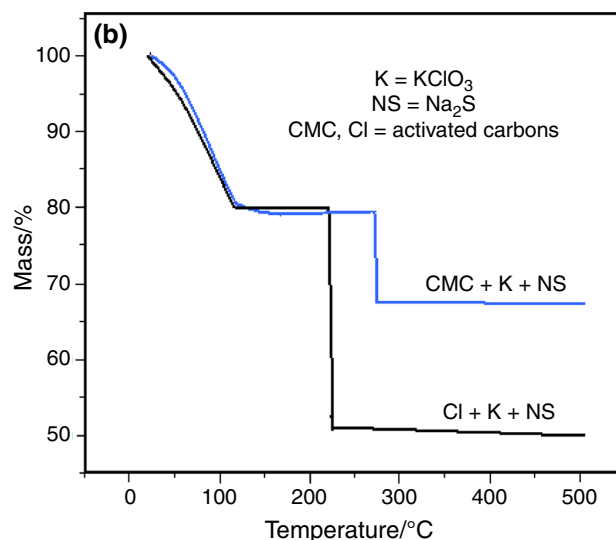
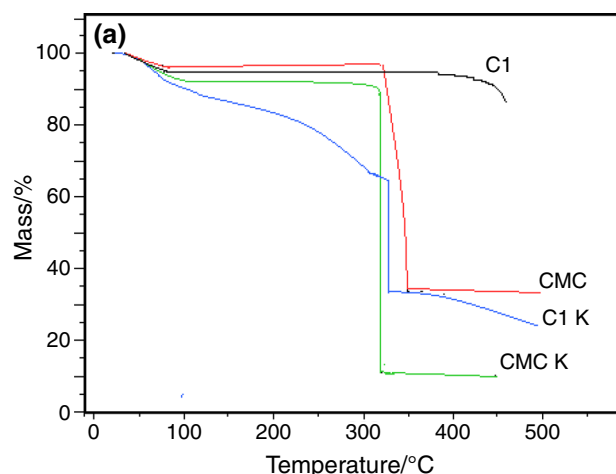


Fig. 4 a TG curves of activated carbons C1 and CMC independently and in combination with KClO_3 . b TG curves of activated carbons with KClO_3 and Na_2S

While MnO_2 decreased the decomposition temperature of KClO_3 from 480 to 350 °C, it is observed that in the presence of activated carbon **C1** in a (1:1) mechanical mixture of (**C1** + KClO_3), the temperature of its decomposition decreased further to 325 °C. This was accompanied by gradual evolution of O_2 from chlorate up to ~300 °C. The evolved O_2 further oxidised carbon to CO_2 . This combined evolution of O_2 & CO_2 resulted in large mass loss leaving a residue of KCl alone (TG profile of C1 K).

Thus both **C1** and MnO_2 catalysed the decomposition of KClO_3 . The profile **MC1K** is the TG curve of KClO_3 decomposition during simultaneous presence of both MnO_2 and the activated carbon **C1**. However, it did not alter its decomposition temperature. The sharp decrease in mass loss beyond 300 °C is due to rapid oxidation of carbon to form CO_2 .

Thus this investigation suggests that while activated carbon facilitates decomposition of KClO_3 and conversely KClO_3 facilitates gasification of carbons as in the absence of KClO_3 , C1 oxidises at 425 °C as shown from TG profile of C1 given in Fig. 4a.

Decomposition of potassium chlorate in the presence of carbons and sodium sulphide

It can be seen from Fig. 4a that the activated carbons C1 and CMC are oxidised in O_2 at 425 and 340 °C, respectively. The CMC carbon has a significantly oxygenated surface [38, 39] which could be the reason for its ease of oxidation or combustion.

C1-K and CMC-K are TG profiles in argon atmosphere of 1:1 mechanical mixtures of the said carbons with KClO_3 . It is clear that KClO_3 decomposition is enhanced and occurs easily at ~ 320 °C in both the cases with the onset of decomposition with CMC-K being slightly earlier.

Figure 4b describes the effect of additional presence of Na_2S (1:1:1 mechanical mixture of carbon + KClO_3 + Na_2S). The decomposition of KClO_3 occurs at much lower temperatures.

In fact the TG curves show two distinct decomposition steps. Region A \rightarrow B which extends up to 120 °C and a sharp region C \rightarrow D at 220 °C. The mass loss up to B (~ 120 °C) of ~ 19 % is ascribed to the loss of water molecule from $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$. The region C \rightarrow D corresponds to the decomposition of KClO_3 . Thus with the CMC carbon, KClO_3 decomposes at 275 °C and surprisingly the decomposition with C1 carbon, KClO_3 decomposed at a temperature as low as 220 °C. At this relatively low temperature, the carbons would not get oxidised to cause any gasification.

Conclusions

Thermal decomposition of KClO_3 is investigated in the presence of MnO_2 , activated carbons and sodium sulphide. MnO_2 was prepared by thermal decomposition of $\text{Mn}(\text{NO}_3)_2$ at 180 °C. Two activated carbons were used. C1 was a commercial carbon of surface area $873 \text{ m}^2 \text{ g}^{-1}$, and CMC was another activated carbon obtained by low temperature physical activation of carboxymethylcellulose [38, 39]. This carbon had an oxygenated surface such as the presence of hydroxyl groups. It had a surface area of $1025 \text{ m}^2 \text{ g}^{-1}$.

1. KClO_3 upon heating melts at 355 °C and decomposes at 480 °C. The decomposition temperature decreases to 350 °C in the presence of MnO_2 catalyst.

2. In the presence of activated carbons, the KClO_3 decomposes at even lower temperatures ~ 320 °C and slightly depended on the nature of carbon. However, this also induces burning off of carbon causing its gasification.
3. Sodium sulphides greatly enhanced the decomposition of KClO_3 causing its decomposition at 220 °C.

Thus KClO_3 greatly facilitate gasification of carbon while Na_2S greatly enhances decomposition of KClO_3 .

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