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Ultra fast formation of CrO_2 by a novel single step self ignition combustion reaction at ambient condition

D. Paul Joseph [a,*,1], P. Dilli babu [a], P. Manimuthu [a], M. Kovendhan [b], C. Venkateswaran [a,*]

[a] Materials Science Centre, Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai 600 025, India
[b] Department of Physics, Presidency College, Chennai 600 005, India

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ABSTRACT

CrO_2 requires non-ambient conditions to stabilize Cr in 4+ state. Usually it is prepared by the hydrothermal method which requires high pressure and super criticality of water. For more than a sesqui century there are no reports on the preparation CrO_2 by a simple single step rapid synthesis method at ambient condition. The self ignition exothermic combustion reaction between CrO_3 and acetone vapor cloud leads to ultra fast formation of CrO_2 particles enroute Cr_2O_3 from CrO_3 at ambient condition. The condition for commencement of self ignition and the reaction mechanism are discussed. The structural, morphological, electrical and magnetic studies of the formed CrO_2 particles are also presented.

1. Introduction

Researchers intensively explore CrO_2 in addition to Diluted Magnetic Semiconductors (DMS) for effective implementation in 'Spintronics' due to its unique half-metallic behavior with one up spin channel and other down spin channel [1–6]. CrO_2 by no means is a new material; it has been researched for nearly a sesqui century, as early from 1859 [7] and practically employed in magnetic recording for quite a long period in audio and video tapes. CrO_2 is also a candidate for magnetic refrigeration applications due to large magneto-resistance behavior, −25% at 1 T [8]. Recently, superconductivity around 10 K has been observed in thin films of CrO_2, thereby CrO_2 gets classified under ferromagnetic superconductors too [9].

It is notoriously difficult to synthesize half-metallic CrO_2 as it requires non-ambient conditions to stabilize CrO_2 with Cr in 4+ state [10]. CrO_2 powders are prepared by different methods, of which some are, thermal decomposition of CrO_3 and mixed chromium oxides, thermal decomposition of $CrO_2.Cl_2$, hydrothermal methods, oxidation of CrO(OH) and $Cr(OH)_3$ [10], etc. Biswas and Ram [11] have prepared shape controlled CrO_2 nanoparticles using CrO_3 and poly vinyl alcohol. It is clear from literature reports that CrO_2 cannot be obtained by any of the methods when carried out at atmospheric pressure or in vacuum [10]. In this juncture, synthesis of CrO_2 by other simple techniques become important. This letter reports the preparation of CrO_2 by a rapid self ignition combustion reaction at ambient condition and its structural, morphological, electrical and magnetic properties.

2. Experimental details

A double walled spray gun (nebulizer) made of glass having a tapered nozzle with the inner tube having an orifice of 0.3 mm and outer tube having two inlets, one for entry of the solution to be sprayed and another for entry of carrier gas has been utilized. Both the nozzle and the outer tubes have tapered end, to increase the rate of the liquid reactant which is continually fed through gravity feed mechanism using polyurethane tube. The spray assembly is fixed inside a fume hood. Compressed and moisture filtered air is fed to the spray gun using a thick double walled gas delivery tube. The fuel, acetone is sprayed/dripped from the inner nozzle such that the cone of flux falls over the flakes of CrO_3 particles placed below the spray gun. Acetone vapor cloud is self ignited with instantaneous blast of flame (Fig. 1) (Also see supporting video online) due to exothermic reaction between CrO_3 and acetone leading to *reduction* of CrO_3 to a mixture of CrO_2 and Cr_2O_3.

Supplementary video related to this article can be found at doi: 10.1016/j.solidstatesciences.2011.01.027

* Corresponding authors. Tel.: +91 44 22202803; fax: +91 44 22352870.
E-mail addresses: palphymail@gmail.com (D. Paul Joseph), cvunom@hotmail.com (C. Venkateswaran).
[1] Present address: Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.

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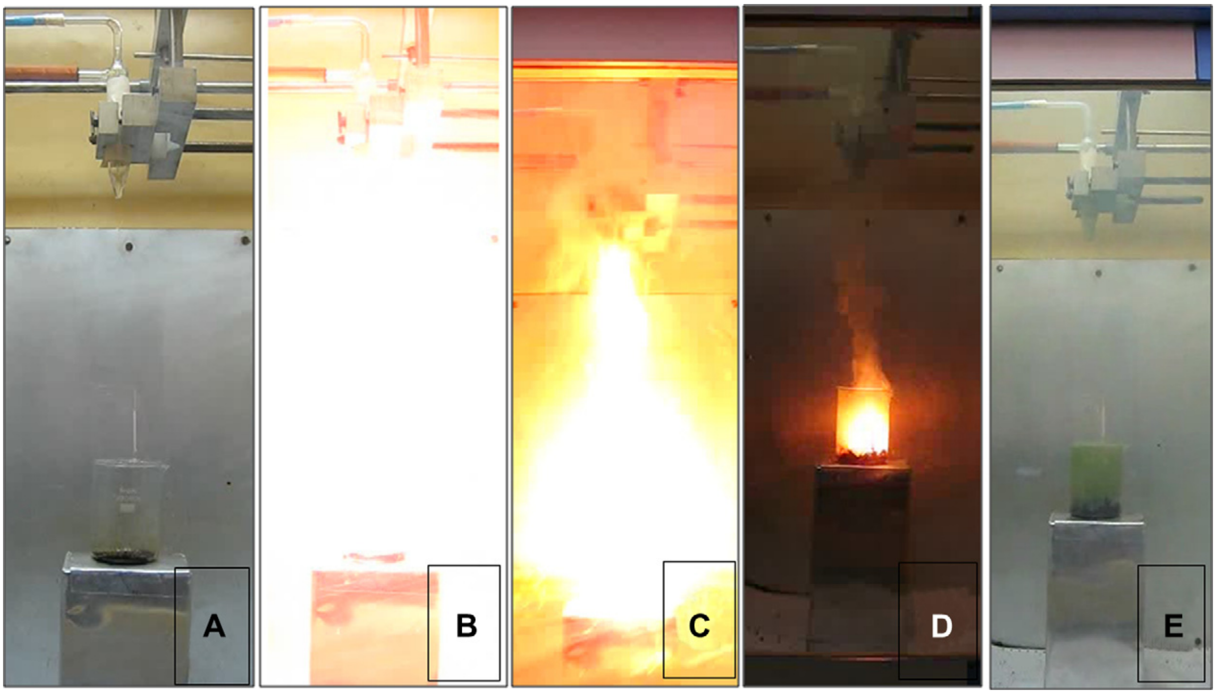

Fig. 1. Photographs of formation of CrO_2–Cr_2O_3 mixture by self ignition combustion reaction. A) Acetone added to CrO_3, B) Spontaneous self ignition, C) Reaction in progress, D) Reaction being completed, and E) Beaker containing particulates of Cr_2O_3 and CrO_2.

Acetone, having a high enthalpy of combustion of −1789.9 kJ/mol to −1820.7 kJ/mol from liquid to gaseous form [12] reacts vigorously with CrO_3 and creates a localized internal pressure and high temperature for a fraction of a second to rapidly form CrO_2 particles. Cooling effect of acetone and thermal inertia of the thermocouple lowers the flame temperature. The value of adiabatic flame temperature due to the reaction of acetone with CrO_3, measured by repeated trials, ranged from 350 °C to 475 °C. The measured instantaneous flame temperatures may be typically lower than the actual value due to loss by radiation, incomplete combustion, inertia of the thermocouple and cooling by the surrounding air, etc.

Cr_2O_3 is inevitably formed over the surface of CrO_2 (Similar to a core-shell like structure with CrO_2 at the core and Cr_2O_3 at the periphery) due to the uncontrollable nature and short duration of the reaction. Owing to the fact that CrO_2 is ferromagnetic and Cr_2O_3 is antiferromagnetic, one can easily purify by separating out the CrO_2 particles by ultrasonic de-agglomeration and subsequent magnetic decantation.

3. Reaction mechanism

This combustion reaction is slightly different from the conventional combustion synthesis procedures. Here, 'Fuel Rich' condition leads to 'No combustion' state and 'Fuel lean' condition leads to commencement of the combustion reaction. If excess of acetone is added, CrO_3 particles are completely immersed or dissolved forming a solution which inhibits self ignition. If acetone is added in small quantity such that it forms a wet semi-solid mass, exothermic reaction takes place and ignites in the presence of air with the support of surrounding acetone vapors. The condition for commencement of the reaction is schematically shown in Fig. 2. The reaction can be represented by the following equation,

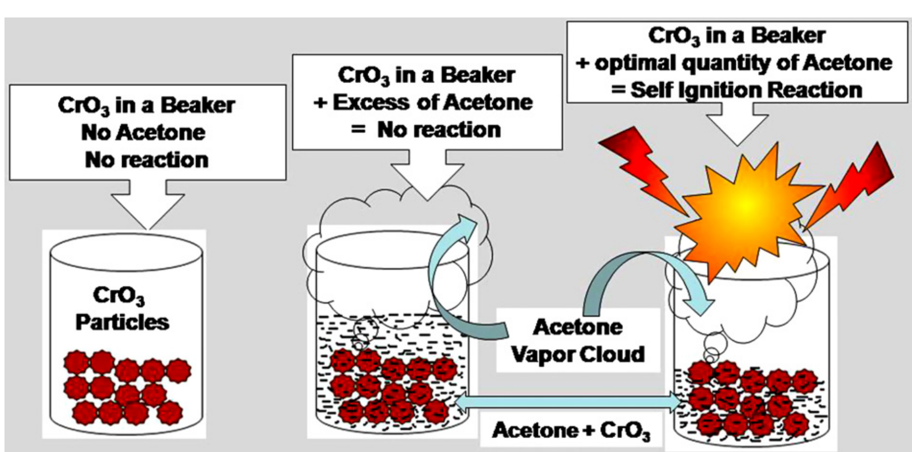

Fig. 2. Condition for the commencement of self ignition reaction of acetone and CrO_3.