Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 374 (2008) 158–167
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Thermal decomposition and kinetic analysis of sodium propoxides

K. Chandran [a], M. Kamruddin [b], P.K. Ajikumar [b], A. Gopalan [c], V. Ganesan [a,*]

[a] *Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India*
[b] *Materials Science Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India*
[c] *Department of Industrial Chemistry, Alagappa University, Karaikudi 630 003, India*

Received 24 April 2007; accepted 6 August 2007

Abstract

Sodium *n*-propoxide and sodium *iso*-propoxides were synthesized and characterized. Thermal decomposition of these compounds was studied using thermogravimetric technique (TGA) coupled with mass spectrometry (MS) under non-isothermal and isothermal conditions. Various analytical techniques namely atomic emission spectroscopy (AES), infrared spectroscopy (IR), powder X-ray diffraction (XRD), elemental and volumetric analyses were employed to characterize these compounds and their decomposition residues. Kinetic parameters, namely, the activation energy and pre-exponential factor were deduced from the dynamic TGA and MS data. The activation energies derived from isothermal runs for the thermal decomposition of sodium *n*-propoxide and sodium *iso*-propoxide were 151.45 ± 2.16 and 128.07 ± 3.44 kJ mol^{-1}, respectively. Decomposition of sodium *n*-propoxide and sodium *iso*-propoxide results in the formation of gaseous products of saturated and unsaturated hydrocarbons leaving behind residue consisting of sodium carbonate, sodium hydroxide and free carbon.

PACS: 81.70.P; 82.30.L; 61.10; 82.80

1. Introduction

Liquid sodium is used as coolant and stainless steels as structural materials in fast reactors systems [1–3]. The physical contact between these two materials at reactor operating temperatures leads to formation of a thin adherent layer of sodium over the surface of the steel components in the coolant circuit due to wetting. Though wetting favours heat exchanging efficiency in the core and intermediate heat exchanger (IHX) regions, it adversely affects the components and maintenance personnel due to high chemical reactivity of sodium with moisture in addition to radiation dose in the case of primary components. During reactor maintenance, some of the stainless steel components are required to be taken out of the reactor for maintenance or replacement. Exposure of sodium wetted components to air could lead to fire and possible explosion as the reaction between sodium and moisture present in air is highly exothermic in nature. In addition to being a fire hazard, the reaction also adversely affects the mechanical properties of the steel components due to the formation of sodium hydroxide resulting in caustic stress corrosion. To overcome these problems, generally, water vapour nitrogen process (WVN) is followed for cleaning sodium from large components such as pumps, IHXs, sub-assemblies, etc. and alcohol process for cleaning small and delicate components like bellow sealed valves, impurity monitoring devices, sampling equipments, gripper tools, etc. [4,5]. Various alcohols namely, methanol [6], ethanol [7,8], Jaysol SS [9], propanol [10,11], butyl cellosolve (butoxy ethanol) [12,13] and ethyl carbitol (diethylene glycol mono ethyl ether or 2,2′ethoxy ethoxy ethanol) [14,15] are used as sodium cleaning agents world wide. Run-away reactions leading to accident reported in the literature when ethyl carbitol was used for sodium cleaning purpose have been postulated to be due to the thermal instability of

* Corresponding author. Tel.: +91 44 27480219; fax: +91 44 27480065.
E-mail address: ganesh@igcar.gov.in (V. Ganesan).

0022-3115/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2007.08.001

the reaction products of sodium and ethyl carbitol [14,15]. The lack of such data, in the literature, on the decomposition of sodium alkoxides, namely, sodium methoxide, sodium ethoxide, sodium *n*-propoxide and sodium *iso*-propoxide, the common reaction products encountered during the sodium cleaning operation employing the widely used ethanol and propanol solvents, enthused the authors to initiate a study on thermal decomposition and kinetic analysis of these alkoxides. The thermal stability data of these alkoxides is highly desirable to arrive at a safe temperature window for the sodium cleaning operation. The present work focuses and reports for the first time, the thermal decomposition studies of sodium *n*-propoxide and sodium *iso*-propoxide and the kinetic parameters, namely, activation energy and pre-exponential factor derived from the decomposition data.

2. Experimental

2.1. Chemicals

Nuclear grade sodium (purity 99.5%) from Alkali Metals, India, was further purified by vacuum distillation. AR grade *n*-propanol (purity >99.5%) from S.D. Fine Chemicals, India, and high pressure liquid chromatography (HPLC) grade *iso*-propanol (purity 99.7%) from Ranbaxy Laboratories, India, were further purified by distillation [16]. These chemicals were used for the preparation of sodium *n*-propoxide and sodium *iso*-propoxide.

2.2. Preparation of compound

The formation and subsequent separation of pure sodium alkoxides can be represented by the following reactions:

$$\mathrm{Na} + \mathrm{ROH}_{\mathrm{excess}} \rightarrow [\mathrm{RONa}]_{\mathrm{ROH}} + 1/2\mathrm{H}_2; \quad \text{where R} = n \text{ and } \textit{iso}\text{-propyl}, \tag{1}$$

$$[\mathrm{RONa}]_{\mathrm{ROH}} \xrightarrow{\text{Vacuum distillation}} \mathrm{RONa}. \tag{2}$$

The detailed methods of preparation and characterization of these alkoxides were reported elsewhere [17].

2.3. TGA-MS measurements

Thermogravimetric analyzer model SETSYS 16/18 of Setaram, France, was used in the present work for simultaneous TGA-MS studies. The detailed descriptions of the system and the experimental procedure are reported elsewhere [18].

2.4. Characterisation of residue

2.4.1. X-ray diffraction analysis

X-ray diffractometer of STOE, Germany, was employed to characterize these sodium alkoxides, their decomposition residues and the insoluble black particles. XRD pattern was recorded at room temperature using Cu Kα (λ:1.5406 Å) radiation. The samples were loaded in Lindemann glass capillaries and sealed with paraffin wax in argon atmosphere glove box to protect them from moisture. The XRD patterns were recorded in the angular range of 5–65° with a step size of 0.05° and scan rate of 10 s per step.

2.4.2. Infrared analysis

Fourier transform infrared spectrometer model MB100 of BOMEM, USA, was employed for recording IR spectra of these compounds, their decomposition residues and insoluble content of black particles. Sodium *n*-propoxide was mixed with spectroscopic grade KBr powder and pelletised by uniaxial pressing. The pellet was sandwiched between two ZnSe windows fitted in a leak tight sample holder to protect the sample from moisture. All these operations were carried out inside an argon atmosphere glove box. The IR spectrum of the sample thus prepared was recorded in the range of 4000–400 cm^{-1} at 4 cm^{-1} resolution. Similar procedure was followed for recording IR spectra of sodium *iso*-propoxide, decomposition residue of these compounds and the insoluble portions of decomposition residues. To compare the spectral features of the residue, IR spectrum of GR grade sodium carbonate was also recorded.

2.4.3. Estimation of sodium carbonate and sodium hydroxide

Standard lime water test was performed to confirm the presence of carbonate radical in the decomposition residue of sodium *n*-propoxide and sodium *iso*-propoxide. Sodium carbonate and sodium hydroxide contents were estimated by volumetric titration method. For this purpose, about 100 mg each of residue was dissolved in distilled water, filtered and the filtrate was titrated against the standard hydrochloric acid using methyl orange or phenolphthalein as indicator to find the total alkalinity and sodium hydroxide alkalinity, respectively. The estimated quantities of sodium carbonate and sodium hydroxide are given in Table 1. The values are the mean of six measurements and the

Table 1
Sodium content estimated from the sodium carbonate and sodium hydroxide (volumetric analysis) of the residues along with the insoluble content

Decomposition residue	Soluble content (wt%)			Insoluble content (wt%)		Sodium content (wt%)		
	Na_2CO_3	NaOH	Total	Calculated	Observed	From Na_2CO_3	From NaOH	Total
Sodium *n*-propoxide	45.45	35.42	80.87	19.13	18.84	19.72	20.37	40.09
Sodium *iso*-propoxide	43.07	32.62	75.69	24.31	19.78	18.69	18.77	37.46