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Synthesis, characterization and liquefied petroleum gas sensing of cobalt acetylenedicarboxylate and its polymer

Satyendra Singh[a], Archana Singh[a], B.C. Yadav[a,b,*], Poonam Tandon[a], Anuj Shukla[c], Vitaly A. Shershnev[d], Gulzhian I. Dzhardimalieva[d], Nina D. Golubeva[d], Anatolii D. Pomogailo[d]

[a] Department of Physics, University of Lucknow, Lucknow, 226007 UP, India
[b] Department of Applied Physics, School for Physical Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow, 226025 UP, India
[c] Defence Research and Development Organization, Jodhpur, India
[d] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Russia

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ABSTRACT

The synthesis of cobalt acetylenedicarboxylate (fCo2) and polymerized cobalt acetylenedicarboxylate (hCo2) using acetylenedicarboxylic acid (fADC) has been reported. Surface morphologies were analyzed using scanning electron microscope (SEM) and transmission electron microscope (TEM). The UV–vis absorption and infrared spectroscopies were used for optical characterization. Structural properties were studied using X-ray diffractometer with scattering vector analysis. The minimum particle size was found to be 10 nm for polymerized acetylenedicarboxylate and confirmed through the TEM analysis. Thermal properties were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC). Further, the LPG sensing properties of the materials were investigated at room temperature (25 °C). Polymerized acetylenedicarboxylate shows larger variation in resistance in comparison to acetylenedicarboxylate and acetylenedicarboxylic acid both. In addition, the possible sensing mechanism of the interactions of LPG on the surface of the materials has been discussed. The maximum sensor response, small response time and long-term stability demonstrates that the fabricated sensor (hCo2) is challenging for the detection of LPG.

1. Introduction

Liquefied petroleum gas (LPG) is most harmful gas due to its inflammable and explosive nature that causes many hazards to human being as well as environment. So nowadays the LPG sensor has become very interesting in view of the fundamental research as well as industrial applications [1,2]. The development of portable LPG sensors that have sufficient sensitivity in the ambient environment is necessary and demanded in order to prevent the explosion accidents in homes and industries [3–5]. For this reason efforts are made nowadays by scientific research communities in leading laboratories all over the world to focus on the investigation of novel LPG sensitive materials suited for solid-state gas sensors [6,7]. Consequently, their performances have improved dramatically by adopting novel preparation routes and by controlling the deposition processing. Several types of LPG sensors such as chemical sensors, resistive and conductive type sensors using semiconductors and sensors based on metal polymer complexes have been investigated by different research groups [8–10].

In the recent years, considerable efforts have been devoted to the synthesis of nanostructures showing novel morphologies with uniformly distributed meso pores having highly reactive surface [11–13]. As gas sensing being a surface phenomenon, therefore, the nanostructure and the surface morphology play a significant role [11–14]. The response of the sensor increases and response time decreases with the reduction in the particle size; as the high active surface area facilitates rapid adsorption–desorption of oxygen species when the particle size becomes comparable with the Debye length. Hence, structure–property correlation regarding gas sensing is an active area of research in such type of materials [15].

There is an increasing interest in finding new materials in order to develop high performance solid state gas sensor. Many studies on semiconducting materials as gas sensor have been reported in recent years [16,17]. The gas sensing devices based on inorganic materials such as metal oxide semiconductors, work on the principle of the change in conductivity with interaction of gas molecules [18]. These sensors require high operating temperature. Such gas sensors have generally disadvantages of poor selectivity and low

* Corresponding author at: Department of Physics, University of Lucknow, Lucknow, 226007 UP, India. Tel.: +91 9450094590.
E-mail address: balchandra_yadav@rediffmail.com (B.C. Yadav).

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sensitivity to the very low concentration of gases [19,20]. Therefore several different approaches have been explored in order to overcome the above issues. Recently nanostructured polymeric compounds have found place as a gas sensor because of their chief merits such as easy synthesis and room temperature operation [21–28].

Polymer nanocomposites are a class of hybrid materials composed of an organic polymer matrix with dispersed inorganic nanofillers. They show unique properties as they combine the advantages of the inorganic nanofillers (e.g., rigidity and thermal stability) and the organic polymers (e.g., flexibility, dielectric, ductility and processability) [29]. The inorganic nanofillers have large surface area, leading to a dramatic increase in interfacial area [29–31]. These nanofillers can strongly change the macroscopic properties of the polymer, even at very low concentrations [32]. Inorganic nanofillers include nanotubes, metal oxides (e.g., TiO_2, CoO, Fe_2O_3, etc.), metallic nanoparticles (e.g., Au, Cu, Co, Ag, etc.) and semiconductors (e.g., PbS, CdS, ZnS, etc.) [29] have been devoted to polymer/nonporous nanofiller nanocomposites [29–31]. The mesoporous nanofillers have received much attention due to their ordered structure, high surface area and easiness for functionalization of the nanopores. The nanopores are sufficiently porous to accommodate macromolecules which will lead to unusually intimate interactions between the polymer and the inorganic phase [31], and some unusual properties will be observed when compared with nonporous fillers.

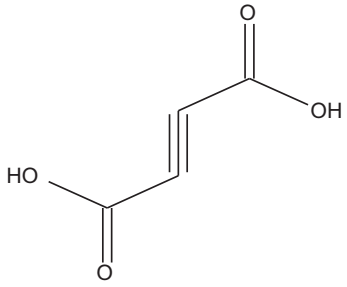
Interest in the carboxylates with unsaturated ligands of acetylene type depends on their solid state polymerization capacity determined by the short distances between reaction centers and occurrence of short acetylene-acetylene contacts. In addition, dicarboxylic acids complexes with bidentate carboxylic bridges between paramagnetic centers are efficient magneto concentrated systems [33]. Here in the present communication, different ligands of acetylene type were considered, depending on their functional groups and number of C-atoms between multiple bonds, in order to obtain metal-containing monomers, polymers and nanocomposites on their base. There is a great variety of structures including monomeric salts, linear and three-dimensional coordinating polymers depending on metal type. Initially acetylenedicarboxylic acid was taken, as it is simplest among acetylene type di-carboxylic acids, moreover it is interesting because of probable conjugation of C═C and C═O bonds in polymeric compounds. In the sensing field, the conjugated polymers have found applications in medical and environmental fields due to their electrical conductivity and sensitivity to specific photon energies or chemical species. Several researchers have shown interest in synthesis and structure of different acetylene di-carboxylic acid salts. There is information about cobalt, nickel [34], calcium, magnesium, lead [35] and other acetylene di-carboxylic acid salts. Also there are few studies on the solid state polymerization of acetylenedicarboxylic acid [36], its cadmium [37] and potassium salts. In addition, acetylene carboxylic acid salts can be used for nanocomposite materials preparation [38]. Having such conjugated systems at the stage of polymerization acetylene dicarboxylates-based nanocomposites could reveal interesting magnetic properties.

Present approach is useful for developing nanocrystalline materials, which can also provide an effective way to examine an influence of the surface morphology on the LPG sensing characteristics. Acetylenedicarboxylic acid salt (fADC) was used as a precursor for further polymerization and thermal degradation to obtain nanocomposites. Monomers and composite structures were investigated using different techniques including IR spectroscopy, thermal analysis and electron microscopy. The LPG sensing characteristics of the nanostructured polymerized cobalt acetylenedicarboxylate (hCo2) was found better than or comparable to other LPG sensors [39–45].

2. Experimental

2.1. Synthesis of materials

For the synthesis of cobalt (II) acetylenedicarboxylate and polymerized cobalt (II) acetylenedicarboxylate, acetylenedicarboxylic acid (fADC) was procured from Aldrich and its structure is given by:



Cobalt (II) acetylenedicarboxylate (cobalt salt of acetylenedicarboxylic acid, fCo2) i.e., $Co(C_4O_4)(H_2O)_4{\cdot}2H_2O$ – monomer was synthesized by grinding cobalt acetate tetrahydrate (5.1 g, 20.5 mmol) and acetylenedicarboxylic acid (2.3 g, 20.5 mmol) in an agate mortar in air.

Polymerized fCo2 was prepared by heating of quartz vessel with fCo2 in a pipe furnace. The process was carried out in vacuum at 200 °C and heated for 1 h (temperature was increased gradually; it took about an hour and half to reach 200 °C). During that, liquid and gas evolving was observed (it's known from DSC and mass spectra that water and carbon dioxide evolve at about 190 °C).

2.2. Characterization techniques

The synthesized materials were characterized for their structural investigations by X-ray diffractometer (X'Pert PRO PANalytical). The XRD data of synthesized material was recorded using Cu K_α radiation having wavelength $\lambda = 1.5406$ Å. The crystallite size of the samples was calculated by Debye–Scherrer's equation. The surface morphologies of the sensing materials were analyzed using a scanning electron microscope (SEM, LEO Cambridge) and transmission electron microscope (TEM, JEOL 2000 FX 11). Optical characterization was done using UV–vis absorption spectrophotometer (Varian, Carry-50 Bio) in UV and visible ranges. The infrared absorption spectra of the samples were recorded using a Specord M80/85 instrument from 200 to 4000 cm^{-1}.

2.3. LPG sensing measurements

To study the LPG sensing characteristics, sensing pellets were put within the Ag-pellet-Ag electrode configuration respectively. This electrode was inserted in a specially designed gas chamber having a gas inlet knob for entering of LPG and an outlet knob for gas purging. Now the chamber was exposed with LPG through an inlet knob associated with concentration measuring system and the variations in resistance of the sensing material with the time for different volume% of LPG were recorded using a Keithley electrometer (model: 6514A). The sensitivity of the sensing material is defined as given below [46]:

$$S = \frac{\Delta R}{\Delta t}$$

where ΔR is the change in resistance in time interval Δt.

Percentage sensor response for the sensing pellet is defined as [43]:

$$\%S.R. = \frac{|R_a - R_g|}{R_a} \times 100$$