RESEARCH ARTICLE

Study on exposing supported copper compounds to acetylene

Copper acetylide is used to describe copper and acetylene containing compounds. Depending on the valence of copper involved in reaction with acetylene, cuprous acetylide is formed from cuprous ion (Cu^+) while cupric acetylide is formed from cupric ion (Cu^{2+}). This study addresses the use of copper materials for removal of mercury and the potential for accidental accumulation of copper acetylides in the process. Alumina supports with copper oxide, copper carbonate or copper sulfide were exposed to acetylene and a variety of analytical techniques used to evaluate their potential for accumulation of copper acetylides. Copper oxide and copper carbonate exposed to acetylene did not demonstrate accumulation of either cuprous or cupric acetylides. However, resulting accumulated materials were energetic as they decomposed with release of heat during Differential Scanning Calorimeter analysis. The exothermic event was not excessive and it was speculated that the reaction involved copper oxide and carbon at elevated temperature. There was no apparent reaction between copper sulfide and acetylene. The condition for exposure of acetylene to the copper materials in this study was extreme. It concludes that when the copper materials are used for mercury recovery there is no apparent accumulation of copper acetylides.

By Jimmie C. Oxley, James L. Smith, F. Lucus Steinkamp, Jayant Gorawara, Vlado Kanazirev

INTRODUCTION

Mercury removal from hydrocarbon feedstocks can be accomplished in a number of ways. Using a non-regenerable metal sulfide adsorbent has several benefits but one latent drawback. Copper sulfide effectively scavenges mercury; but since acetylene is a possible contaminant under these circumstances, the potential formation of explosive copper acetylide is a cause for concern and is the motivation for this study. Copper acetylide is a general term used somewhat ambiguously for compounds containing copper and acetylene moieties. If the alkyne is acetylene (C_2H_2), both hydrogen atoms can be substituted with a cuprous ion (Cu^+), yielding a molecule with the formula Cu_2C_2. If acetylene reacts with the cupric ion (Cu^{2+}), CuC_2 may be formed. To eliminate ambiguity Cu_2C_2 will be referred to as cuprous acetylide and CuC_2 will be referred to as cupric acetylide for the purposes of this study (Figure 1).

Cuprous acetylide, a primary explosive, has been the subject of research regarding carbon structures composed of linear chains of sp hybridized carbons.[1,2] It is a bright red powder that undergoes Glaser oxidative coupling reactions to form what are called copper polyynides.[1] Identification of cuprous acetylide using infrared spectroscopy (IR) shows three distinct peaks circa 1200 cm^{-1}, 1400 cm^{-1} and 1600 cm^{-1}.[1] Differential Scanning Calorimetric (DSC) traces show broad exothermic peaks ~192 °C. Cupric acetylide, has sometimes been cited as the cause of accidental explosions.[3] Although it has been assigned a CAS number, only qualitative data is available. Cupric acetylide, or copper carbide, is brown to black in color, sometimes forming lustrous plates and is extremely sensitive towards initiation. Its structure is envisioned as a divalent copper ion coordinated to the pi system of acetylene. The lack of physical data makes this assignment speculative, and most reports are only qualitative.[4]

A fundamental understanding of "copper acetylides" is necessary for evaluation of the hazards of using copper materials for mercury removal. Herein we determine whether copper adsorbents on an alumina substrate – copper oxide, copper carbonate, and copper sulfide – form acetylides when exposed to acetylene. Various analytical techniques were employed in an attempt to make that determination.

Jimmie C. Oxley is affiliated with Chemistry Department, University of Rhode Island, Kingston, RI 02881, USA (Tel.: +1 401 874 2103; e-mail: joxley@chm.uri.edu). Currently at Nova Research Inc, Alexandria, VA, USA.

James L. Smith is affiliated with Chemistry Department, University of Rhode Island, Kingston, RI 02881, USA.

F. Lucus Steinkamp is affiliated with Chemistry Department, University of Rhode Island, Kingston, RI 02881, USA.

Jayant Gorawara is affiliated with UOP a Honeywell Company, USA.

Vlado Kanazirev is affiliated with UOP a Honeywell Company, USA.

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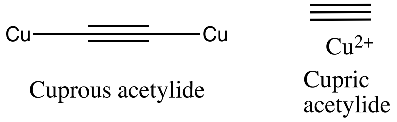

Figure 1. Proposed structure of cuprous (a) and cupric (b) acetylides.

EXPERIMENTAL

Cuprous Acetylide Synthesis

The synthesis of cuprous acetylide followed the synthesis described by Cataldo.[2] Generally, a flask equipped with a stir bar was charged with ammonium hydroxide, hydroxyl amine and cuprous iodide. Acetylene was bubbled through the solution and a bright red precipitate formed immediately. The newly formed precipitate was filtered, washed with water and then with ethanol to dry. Cupric acetylides were synthesized using methods described by Brameld et al.[4] *Safety note: Copper acetylides are primary explosives that are very sensitive to external stimuli such as friction and heat. The syntheses were governed by a standard operating procedure scrutinized by a peer-reviewed process. Handling minimal amounts of the dry material should proceed behind an approved blast shield with great caution to avoid accidental initiation of the material. Never grind the material in a mortar and pestel or expose to flame. Analysis of cupric acetylides by Raman spectroscopy was unsuccessful resulting in ignition while irradiated by a 1064 nm laser even at low power.*

Acetylene Exposure

A 3-neck, 500 mL round-bottom flask was placed in a heating mantle connected to a variable AC controller. A thermocouple was pushed through a rubber septum and inserted into the middle neck of the flask. Stopcock flow controllers were placed in the two remaining necks. A bubbler filled with mineral oil was attached to the outlet so that a visual confirmation of flow could be monitored. A tank containing acetylene dissolved in acetone was regulated into a vacuum trap filled with water when moisture was desired. When moisture was not required acetylene flowed directly into the flask. The vacuum trap filled with water was wrapped with a heating sleeve controlled by a second variable AC controller.

Standard procedure involved placing 10.00 g of the ground adsorbent into the apparatus, sealing everything and insulating it with glass wool and aluminum foil. The flask was evacuated and backfilled with acetylene. When moisture was desired the water temperature was maintained at 37 °C to prevent any possible condensation while operating at 40 °C. Once flow of acetylene started the temperature controller for the flask was activated and monitored until the flask achieved the desired temperature. After the temperature stabilized the flow of acetylene was maintained for one week. The entire apparatus was situated behind a blast shield for safety. Flow of acetylene was stopped at the end of the one-week interval, temperature controllers were turned off and flask was lifted from the heating mantle. The flask and contents were evacuated to remove residual acetylene and backfilled with dry nitrogen. *Safety note: As with the synthesis of neat acetylides the process of exposing copper-containing materials to acetylene could result in the formation of acetylides so the resulting products were treated in a similar manner. The process was also governed by a standard operating procedure that went through a peer-review process. The process was conducted behind an approved blast shield. The entire reaction was completed inside a fume hood with the sash closed for extra protection. A sign indicating what was occurring was present during the entire duration of the experiment.*

Phenylacetylene Experiments

A 5:1 molar ratio of phenylacetylene to copper material mixture was stirred at room temperature for 16 h followed by extraction into methylene chloride and analysis by GC/MS.

Elemental Analysis/Isotopic Ratio Mass Spectrometry

A Thermo Flash 2000 organic elemental analyzer coupled to a Thermo Delta V Advantage isotopic ratio mass spectrometer was used to determine carbon content of samples before and after exposure to acetylene. Urea was used as an external standard for carbon quantification.

Thermal Analysis

A TA Instruments Q100 Differential Scanning Calorimeter (DSC) was used to monitor heat flow at a programmed temperature rate. Approximately 2.00 mg of samples were placed into hermetically sealed aluminum DSC pans. The samples were heated at a rate of 20 °C/min from 30 °C to 450 °C. Flowing nitrogen (50 mL/min) purged the DSC cell during the experiments.

A TA Instruments Q5000 thermogravimetric analyzer (TGA) was used. In a high temperature platinum pan the sample was heated under an inert nitrogen atmosphere (25 mL/min) from room temperature to 900 °C at a rate of 20 °C/min.

Infrared Spectroscopy

A Thermo Nicolet 6700 Fourier transform infrared spectrometer (FTIR) was use to collect 64 scans at a resolution of 4 cm^{-1} from 375 to 4000 cm^{-1}. Approximately 2 wt% of sample was mixed for 2 min with KBr in a wiggle bug followed by pressing under 15,000 psi for approximately 10 min into a pellet.

Raman Spectroscopy

A Bruker Senterra Raman microscope was used to collect Raman data. The laser source was 785 nm set at 100 mW. With a resolution of 9–15 cm^{-1} spectra were collected from 148 to 3818 cm^{-1} using an integration time of 3 s and 2 coadditions.

Gas Chromatography/Mass Spectrometry

An Agilent GC6980 gas chromatograph coupled to an Agilent 5973 mass selective detector was used for analysis of the phenylacetylene experiments. The inlet was operated at 225 °C in split mode with a 2:1 split. Helium

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