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Reaction hazards of triethylaluminum under closed conditions

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ABSTRACT

We evaluate the reaction hazards of triethylaluminum (TEA) under closed conditions for safe treatment of aluminum alkyls. The explosive reactions of TEA are difficult to be estimated using thermal analysis because the estimate reactions are too slow under these conditions. The results of our closed vessel tests and chemical equilibrium calculations show that the TEA and water system mixture in closed conditions decomposes into lower-molecular-weight compounds than the products by using well-known hydrolysis of TEA. The present work also demonstrates that large temperature and pressure increases could occur because of the existence of TEA and aluminum hydroxide. Since aluminum hydroxide contains water as alumina hydrates, aluminum hydroxide could have been the source of water at high temperatures and could have contributed to the mixed reaction between TEA and water.

1. Introduction

Aluminum alkyls are one of the most important catalyst compounds for the polymerization of ethylene and propylene. For example, in Ziegler–Natta polymerization, a tetrachlorotitanium and hydrocarbon solution containing triethylaluminum (TEA) polymerizes ethylene under atmospheric pressure (Cotton & Wilkinson, 1972; Streitwieser & Heathcock, 1989). Synthetic rubber is produced by copolymerization of styrene, butadiene, and other components (dichloropentadiene or 1,4-hexadiene) by using the Ziegler–Natta polymerization (Cotton & Wilkinson, 1972). Moreover, aluminum alkyls are widely used as alkylating agents of transition metal complexes and reducing reagents (Anderson, 1963). In addition, aluminum alkyls have been considered for use in igniter systems in ramjets and afterburner sustainers for jet engines (Anderson, 1963; Heck & Johnson, 1962).

However, aluminum alkyls are very reactive. Compounds with alkyl groups of C_4 and below ignite immediately on exposure to air unless they are diluted with a hydrocarbon solvent to concentrations of 10–20% (Mirviss, Rutkowski, Seelback, & Oakley, 1961; Urben, 2007a). Even these solutions may ignite on prolonged exposure to air because of exothermic autoxidation, which becomes rapid if the solutions are spilled (Heck & Johnson, 1962; Urben, 2007a). Alkylaluminum derivatives up to C_4 react explosively with methanol or ethanol, and TEA with 2-propanol (Mirviss et al., 1961; Urben, 2007a). Mixing aluminum alkyls with chlorinated hydrocarbons is a hazardous procedure because the mixture could undergo uncontrolled decomposition. Thomas (1982) conducted a series of experiments on mixtures of seven alkylaluminums with seven chlorocarbons individually. He determined that chloroform and carbon tetrachloride may react violently with alkylaluminum derivatives. Interaction of alkylaluminum derivatives with chain lengths up to C_9 and liquid water is explosive (Mirviss et al., 1961; Urben, 2007a).

Even though it is understood that aluminum alkyls must be treated carefully, some accidents have occurred (Urben, 2007b) because the procedures for handling these are difficult. The causes of accidents are generally the exothermic autoxidation of aluminum alkyls and the contact between aluminum alkyls and chlorocarbons. However, some accidents due to unknown causes have also occurred. As a recent example, in 2007, an explosion occurred in a plant producing aluminum alkyls in Japan (Japan Society for Safety Engineering, 2009). The accident occurred during resumption of production following a periodic shutdown and inspection. One of the causes of the accident was thought to be the reaction of aluminum alkyls. A tee joint of steel piping burst, leading to a fire. In addition, an expanding deformation of the steel piping was observed. An estimated pressure rise of more than 70 MPa was necessary to cause this burst and the deformation. However, a large amount of nucleophilic reagents such as water

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and chlorocarbons did not exist in the laid pipes. Thus, the cause of the explosive reactions of the aluminum alkyls is still unknown, implying that unknown explosive reactions of aluminum alkyls occurred. It is very important to investigate the possible explosive reactions of aluminum alkyls to promote safe treatment of aluminum alkyls.

In this study, we conducted various tests to evaluate reaction hazards of aluminum alkyls under closed conditions. Because TEA is used in great quantities as a catalyst for the polymerization of olefin, it was chosen as the research topic. We analyzed TEA by using differential scanning calorimetry (DSC) and a RADEX calorimeter to measure its behavior and learn about the associated explosion hazards. Temperature and pressure were measured when TEA and water were mixed in a closed vessel to evaluate the incompatibility hazards concerning TEA and water. Aluminum hydroxide scale from an aluminum alkyls production plant was mixed with TEA and water to investigate the influences of reactions of TEA and water. Gaseous products after mixing were analyzed, and chemical equilibrium calculations were conducted to estimate the reaction mechanism of TEA and water.

2. Experiments and calculations

2.1. Materials

TEA from Tosoh Finechem Corporation was used without further purification. We also used deionized water. Explosives were used to mix TEA with water remotely. We first used black powder as the explosive substance. Since the sulfur in the black powder might have had an effect on the reactions of TEA as results of the mixing experiments, we used the handmade explosive instead. This explosive was a mixture of potassium perchlorate (70 wt%, Japan Carlit) and aluminum flake (30 wt%, Nakatsuka), and it is referred to as report composition hereafter. The scale of aluminum hydroxide formed at the TEA production plant in which the explosion accident occurred, hereafter referred to as the $Al(OH)_3$ scale, was used. The $Al(OH)_3$ scale adhered to the steel piping in the TEA production plants. For this study, we crushed and ground the $Al(OH)_3$ scale in an agate mortar. The $Al(OH)_3$ scale was analyzed using thermogravimetric-differential thermal analyzer-mass spectrometry (TG-DTA-MS) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). A Thermo Mass system (RIGAKU, Japan) equipped with a Thermo Plus TG1820 TG, a DTA (RIGAKU, Japan), and an M-200QA quadrupole MS (ANELVA, Japan) was used for the TG-DTA-MS measurements. This apparatus can analyze the mass of gases evolved from heated samples. We placed the $Al(OH)_3$ scale into an aluminum cell with an open pinhole cap and heated it from room temperature to 500 °C at a heating rate of 10 K min^{-1} under a 200 mL min^{-1} helium flow. An OPTIMA3300DV (PerkinElmer, USA) was used for the ICP-OES analysis. Metal compositions of the $Al(OH)_3$ scale were quantitatively analyzed using ICP-OES. The chemical composition of the $Al(OH)_3$ scale was estimated by the measured metal content.

2.2. Thermal analysis by using DSC and a RADEX calorimeter

During the DSC analysis, we analyzed the TEA with an HP-DSC 2920 (TA Instruments, USA.) A sample of 0.71 mg was placed in a nickel–chromium alloy (Hastelloy-C) sealed crucible (NETSZCH, Germany,), which was sealed in a glove box under nitrogen atmosphere. The sample was heated from room temperature to 500 °C at a rate of 5 K min^{-1}; the initial pressure was 0.1 MPa (nitrogen atmosphere).

During thermal analysis, a RADEX calorimeter (SYSTAG, Switzerland) (Center for Chemical Process Safety, 1995; Hub, 1985) was used to analyze the TEA. A 0.1 mL sample was poured into a glass-lined stainless sealed vessel, and the vessel was sealed in a glove box under a nitrogen atmosphere. The sample was heated from room temperature to 370 °C at a rate of 1 K min^{-1}. The thermogram (temperature difference between the sample and the furnace of the calorimeter) and the pressure in the vessel were monitored as the sample was heated.

2.3. Closed vessel tests

Fig. 1 shows the exterior view of the closed vessel, and Fig. 2 shows a block diagram of the closed vessel tests. A closed nickel–chromium alloy (Inconel 625) vessel with a volume of 100 mL was used. The design temperature was 650 °C. The design pressure was 20 MPa. We measured the temperature in the closed vessel with a K-type sheath thermocouple inserted in the closed vessel by using CONAX (USA) sealing grand. Pressure in the closed vessel was measured using a pressure transducer. We recorded signals from the thermocouple and the pressure transducer by using a data logger. A strain amplifier amplified signals from the pressure transducer.

Dosing of chemicals using injection equipment such as syringes is generally used when samples are mixed in a closed vessel. However, it is difficult to seal the closed vessel and to pour the sample into the vessel because the reaction of TEA and water generates a large volume of gaseous products and the pressure in the closed vessel is high. Therefore, we designed a remote mixing technique in a closed vessel using explosives. Fig. 3 shows an exterior view of the arrangement of samples in the closed vessel tests. We packed 5 mL TEA in a 10 mL glass bottle in a glove box under a nitrogen atmosphere. A prescribed amount of water and/or the $Al(OH)_3$ scale was packed in a plastic bag, and the plastic bag was sealed with a sealer. A prescribed amount of explosive was packed with a fuse head (NIPPON KAYAKU, Japan) in a sheet of plastic wrap. We fixed these prepared samples with a roll of plastic tape. The electrical lead from the fuse head was clipped to the

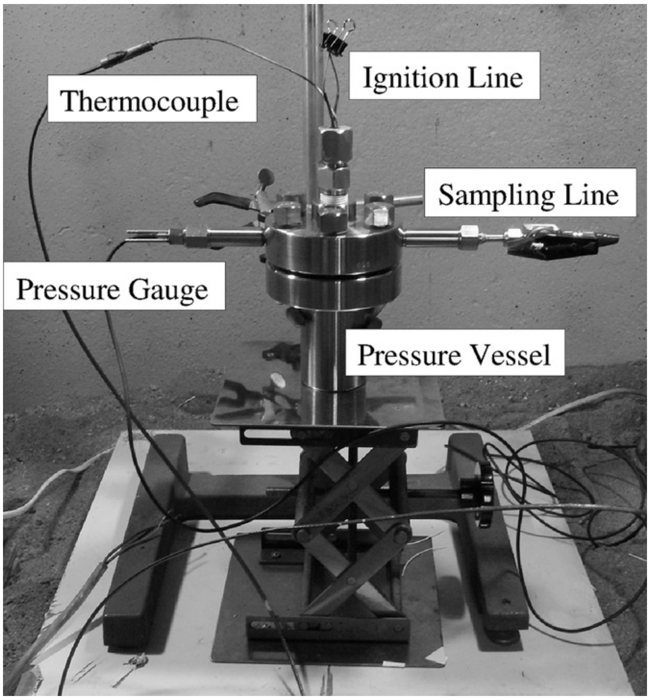

Fig. 1. Exterior view of the closed vessel.