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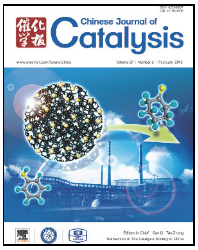

Article

Complete oxidation of 1,4-dioxane over zeolite-13X-supported Fe catalysts in the presence of air

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Zeolite-13X-supported Fe (Fe/zeolite-13X) catalysts with various Fe contents were prepared by the wet impregnation method. The catalysts were characterized by N_2 adsorption-desorption isotherms to estimate the Brunauer–Emmett–Teller surface areas and Barrett–Joyner–Hanlenda pore size distributions. X-ray diffraction, scanning electron microscopy, temperature-programmed reduction, and temperature-programmed desorption of NH_3 were used to investigate the textural properties of the Fe/zeolite-13X catalysts. Their catalytic activities were determined for the complete oxidation of 1,4-dioxane using air as the oxidant in a fixed-bed flow reactor in the temperature range 100–400 °C. The influences of various process parameters, such as reaction temperature, metal loading, and gas hourly space velocity (GHSV), on the dioxane removal efficiency by catalytic oxidation were investigated. The stability of the catalyst was tested at 400 °C by performing time-on-stream analysis for 50 h. The Fe/zeolite-13X catalyst with 6 wt% Fe exhibited the best catalytic activity among the Fe/zeolite-13X catalysts at 400 °C and a GHSV of 24000 h^{-1}, with 97% dioxane conversion and 95% selectivity for the formation of carbon oxides (CO and CO_2). Trace amounts (< 3%) of acetaldehyde, ethylene glycol monoformate, ethylene glycol diformate, 1,4-dioxane-2-ol, 1,4-dioxane-2-one, and 2-methoxy-1,3-dioxalane were also formed as degradation products. A plausible degradation mechanism is proposed based on the products identified by GC-MS analysis.

1. Introduction

Catalytic removal of organic pollutants has attracted considerable interest owing to the high toxicity and low detection limits of these compounds. However, highly toxic pollutants that have adverse effects on the environment are regulated by stringent environmental policies [1,2]. However, some non-biodegradable substances are still a threat to ecosystems and human health. 1,4-Dioxane is an example of such a pollutant. 1,4-Dioxane is frequently used as an industrial solvent and as a solvent stabilizer [3] in many industrial processes, such as of the production of pulp, textiles, and electronics. In addition, it is an undesired byproduct in the production of surfactants and polyethylene terephthalate processes [4], and is widely used in consumer products like cosmetics and personal care products [5,6]. Its widespread use in many industrial processes and high solubility in water leads to contamination of surface groundwater [7]. According to the United States Environmental Protection Agency (US EPA) 2003 report, around 1146641 pounds of dioxane is released into the atmosphere every year,

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of which 105484 pounds is released into the atmosphere and the rest is released into surface water, land, and off-site. 1,4-Dioxane is suspected to damage the central nervous system and cause liver and kidney failure. Furthermore, it is a potential carcinogen to animals and also a probable carcinogen to human beings [8]. 1,4-Dioxane is classified as a Group 2B carcinogen by the International Agency for Research on Cancer and it falls under the regulations of the US EPA, which has set a limit of 30 μg/L for drinking water at a 10^{-5} risk level. Therefore, dioxane is a hazardous waste and a priority pollutant for human health and ecosystems.

Conventional water treatment techniques have limited effectiveness for the treatment of dioxane-contaminated water because of its high solubility in water and low vapor pressure. Its high resistance to biotransformation [9,10] also limits the effective application of biological processes. However, the use of enriched microbial cultures shows some level of dioxane biodegradation [11]. Furthermore, carbon adsorption and air stripping are not cost effective for the removal of dioxane from contaminated water. Therefore, development of new technologies for the treatment of dioxane in industrial wastewater and the atmosphere is required.

Advanced oxidation processes using ozone have been investigated for treating dioxane. Adams and co-workers [12] used the O_3/H_2O_2 process to enhance the biodegradability of 1,4-dioxane. Kwon et al. [13] developed double and triple systems (O_3, O_3/ultraviolet (UV), and $O_3/UV/H_2O_2$) for effective treatment of dioxane-contaminated water. Beckett et al. [14] reported improved biodegradation of dioxane using ultrasound sonication. More recent studies have focused on photocatalysis using titania nanoparticles for the degradation of dioxane in aqueous media [15–19].

Industrial treatment before dioxane is released into water, land, and the atmosphere is the best way to prevent its hazardous effects. Thermal oxidation, catalytic oxidation, adsorption, and incineration are frequently used to treat volatile organic pollutants in many industrial processes. Among these methods, catalytic oxidation is a promising effluent treatment method to control the emission of toxic/hazardous substances. Many methods have been reported for catalytic oxidation using transition metals and metal oxide catalysts for gas-phase catalytic oxidation of hydrocarbons, methanol, acetone, and chlorobenzene with air as the oxidant [20–22]. Recently, supported metal oxide catalysts/nanocatalysts have gained considerable attention because of their better catalytic performance compared with the bulk metal oxide materials owing to their larger surface area, smaller particle size, and densely populated unsaturated surface coordination sites [23,24].

Industrial air emission treatment is the best choice for continuous elimination/reduction of the release of toxic/hazardous matter into the atmosphere. In the present study, we aimed to decompose 1,4-dioxane to carbon oxides using catalytic oxidation with air as the oxidant in a fixed-bed flow reactor to test the continuous removal efficiency. We chose zeolite-13X-supported iron oxide catalysts for dioxane treatment because of their low cost and ready availability. Furthermore, zeolite-13X materials are mesoporous with high specific surface area, and iron is a proven catalyst for many industrial processes, such as catalytic removal of ethyl benzene, cyclohexane, and hexadecane [25–31].

Battin et al. [32] also investigated gas-phase oxidation of equimolecular mixtures of 1,4-dioxane and O_2 in a conventional static apparatus in the temperature range 200–400 °C at low pressure (10–300 Torr). They reported formation of CO, CO_2, HCHO, H_2, C_2H_4, and H_2O as the main thermal oxidation products, small amounts of acetaldehyde and acrolein, and trace amounts of CHO–CHO, $CH_3O–CH_2–CHO$, and $CH_3–CH_2O–CH_2–CHO$ as the gas-phase oxidation products. However, their process was not catalytic and also suffers from many disadvantages, such as poor selectivity and autoinhibition of the reaction at longer residence times.

In the present study, we investigated the influence of various process parameters on the catalytic removal of dioxane using air as an oxidant, such as reaction temperature, metal loading, and gas hourly space velocity (GHSV). We focused on the long-term stability and effectiveness of the catalytic process for complete oxidation of dioxane, and propose a probable degradation pathway for the products identified by gas chromatography–mass spectroscopy (GC-MS) analysis.

2. Experimental

2.1. Materials

$Fe(NO_3)_3·9H_2O$ (purity 99%) and 1,4-dioxane (purity 99%) were purchased from Sigma-Aldrich India Pvt. Ltd. Zeolite 13X was purchased from Sorbead India Ltd. Nitrogen (purity 99.99%) and air (purity 99.99%, ~22% O_2 by volume) gas cylinders were supplied by Baruka Gases India Ltd. Mass flow controllers (MFCs, precision ±1%) were procured from Sierra, Switzerland. CO (range 1–2000 ppm, ±1 ppm) and CO_2 (range 10–20000 ppm, ±10 ppm) analyzers (Technovation Analytical Instruments Ltd. India) were used to measure the concentrations of carbon oxides. The temperature controller was purchased from West Control Solutions (West 6400, UK) and the infusion pump was purchased from KD Scientific 2000 India Ltd..

2.2. Preparation of the catalyst

Zeolite-13X-supported iron (Fe/13X) catalysts of different compositions were prepared by the wet impregnation method. Impregnation was achieved by soaking the crushed zeolite-13X (sieved to BSS 18/25 mesh) support in 60 mL of an aqueous solution containing the requisite amount of $Fe(NO_3)_3·9H_2O$ for 3 h and subsequent water evaporation in a microwave oven. The catalyst material was then dried in a vacuum oven at 120 °C for 10 h. The resulting catalyst was activated by calcination in air for 4 h at 400 °C. Fe/13X catalysts with 2, 4, 6, and 8 wt% Fe were prepared and activated.

2.3. Physicochemical characterization of the catalysts

N_2 adsorption-desorption isotherms of Fe/13X calcined cat-