Journal of the Taiwan Institute of Chemical Engineers 66 (2016) 217–221

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Catalytic oxidation of formaldehyde on iron ore tailing

Yun-long Han*, Zhao Zheng, Chuan-hui Yin, Peng-fei Li, Hao Zhang, Yong-mei Hu

School of Civil Engineering and Architecture, Anhui University of Technology, Ma'anshan 243032, PR China

ARTICLE INFO

Article history:
Received 1 September 2015
Revised 13 April 2016
Accepted 22 June 2016
Available online 22 July 2016

Keywords:
Iron ore tailing
Catalytic oxidation
Formaldehyde
Catalytic activity

ABSTRACT

Raw powder of iron ore tailing, the catalyst prepared by impregnation approach and the modified catalyst loaded Ag^+ were investigated for catalytic oxidation of formaldehyde. Prepared materials were characterized by XRD, XRF and BET surface area. Experiments of catalytic activity were carried out in an electrically heated fixed-bed reactor in which 1.0 g of catalyst mixed fully with 10 g quartz sand was added. 200 ppm of formaldehyde gas was introduced into the reactor at a space velocity of 30,000 ml/g·h. Effects of reaction temperature and calcination temperature were considered. The results show that formaldehyde catalytic efficiencies of all materials increase with the increase of reaction temperature. Furthermore, the catalytic efficiency was enhanced when Ag^+ loaded on the support. Physical properties of raw powder are unsatisfied, but 67% of formaldehyde catalytic efficiency was obtained at the reaction temperature of 100 °C which is far higher than that of other prepared catalysts.

1. Introduction

Formaldehyde (HCHO) is an important chemical material and an additive of the textile for avoiding crimple, increasing handle. However, formaldehyde is one of the close noxious indoor air contaminations with the individual. The furniture, wall paper, wood floor, textiles and the others can release formaldehyde in different levers. Formaldehyde can be absorbed by human's respiratory passage and skin. Sequentially, it may cause the inflammation of respiratory and skin. Seriously, it can irritate to eyes, trigger allergies and induce cancer. With the increase of the living standards the expectation of people's health and longevity is expected higher and higher. Therefore, indoor air contaminations, *e.g.*, formaldehyde, benzene, and other volatile organic gas compounds are concerned deeply.

There are many formaldehyde abatement technologies in indoor environment, *e.g.*, chemical/physical adsorption (activated carbons), catalytic oxidation (catalysts), botanical air cleaning and the others. Catalytic oxidation is one of the most promising abatement formaldehyde technologies for the low formaldehyde concentration in indoor air environment due to its definitive character and save of energy [1]. Catalysts supported noble metals (Pt, Au, Ag, Pd) with the good stability and high activity have been found a good efficiency of abatement formaldehyde at low temperature [2–7]. However, the cost of catalysts supported noble metals is also high. The cheap metals catalysts (Fe, Cu, Mn) also present the good oxidation capacities of formaldehyde [8,9] and can be substituted for noble metals for consumers which expect a low price. Industrial wastes, *e.g.*, metal ore tailings and metal smelting wastes, still contain some using metals (for example, Fe, Cu and Mn, etc.). Therefore, it has great economic and environmental benefit by utilization of waste as a resource and minimizes the land requirement. Especially the recovery of iron value from tailings and recycle of metal tailings are attracting many researchers' attention. Girisun [10] collected the industrial waste from nearby industries and it was subjected to microwave irradiation (900 W, 473 K, 20 min) to recover the valuable metals in the form of metal oxides by thermal method. It was found that the metal oxides derived could be helpful to reduce the burden on the environment, increase the availability of raw materials that are useful for the photonic applications. Lin [11] successfully synthesized Ti-MCM-41 mesoporous molecular sieves by one-step method using sodium silicate extracted from iron ore tailing. The research provided a new method to convert a solid waste to a value-added material. Sakthivel [12] prepared iron oxide–hydroxide support for anchoring nano-gold particles using iron ore tailing, a waste material of iron ore industry. The catalytic conversion of carbon monoxide by Au/FeOOH was around 55%. Zeng [13] studied leaching iron from the electric arc furnace dust by using sulfuric acid to prepare iron oxide sorbent for H_2S removal. The experimental results show that the iron species in the dust were transferred into gamma-Fe_2O_3 center dot H_2O crystal of higher activity for H_2S removal in the sorbent. The desulfurization test revealed that the breakthrough sulfur capacity of the sorbent is similar to that of the commercial active carbon on the same test conditions. In particular, Lebedeva [14] reported that a novel spark erosion technique utilizing

---

* Corresponding author. Fax: +86 555 2316522.
E-mail address: yunlhan@hotmail.com (Y.-l. Han).

http://dx.doi.org/10.1016/j.jtice.2016.06.025
1876-1070/

industrial wastes was used to prepare multi-component oxide catalysts. Chromium-iron catalysts produced by the technique were shown to be effective in total oxidation of different VOCs. These studies have demonstrated the feasibility of using industrial wastes for the preparation of catalysts.

However, it is necessary to note the catalytic activity of different metals to VOCs is diverse, especially the multi-component oxide catalyst according to different metal proportion. Salari [15] investigated the catalytic combustions of different naturally oxygenated volatile organic compounds (ethyl acetate, isopropanol, methyl ethyl ketone (MEK), and benzyl alcohol) alone and in binary mixtures over pure γ-Al_2O_3, Mn/γ-Al_2O_3, and Cr/γ-Al_2O_3. The catalysts were prepared by the wet impregnation method. Mn/γ-Al_2O_3 showed higher activity than others in combustion of the O-VOCs, whereas complete conversion of isopropanol (the most reactive O-VOC) occurred at 350 °C and 400 °C on Mn/γ-Al_2O_3 and Cr/γ-Al_2O_3, respectively. Mishra [16] synthesized a series of iron and manganese mixed oxide pillared clay with varying manganese to iron ratio. Surface area and pore volume increases with the increase in the metal uptake irrespective of manganese to iron ratio. Catalyst having high manganese content acts as better catalyst for the acetone decomposition reaction. However, in case of trichloroethylene (TCE) decomposition catalyst with higher iron content shows better activity. Sekine [17] investigated the reactivity between each metal oxide and HCHO at 25 °C. Of these metal oxides, Ag_2O, PdO, CoO, MnO_2, TiO_2, CeO_2 and Mn_3O_4 showed relatively higher removal efficiencies against HCHO over 50%. The production of CO_2 was found in the reaction vessel having MnO_2, Fe_2O_3, CeO_2 and Mn_3O_4, respectively. In this test, MnO_2 showed the highest reactivity to HCHO with 0.03% of produced CO_2.

Domestic iron ore provided for Ma'anshan iron & steel company limited is sourced from the zone of xiangshan. The iron ore is mainly composed of magnetite and calculated iron grade is 68.16% [18]. Besides, the iron ore contains many other metal elements, *e.g.*, Al, Mg, Mn, Co, Cr and so forth. After iron ore processed, iron ore tailing is stored in a tailing reservoir. The metal elements of tailing could contaminate groundwater if poor management. The tailing reservoir is often considered as a dangerous source, too. However, the iron ore tailing still contains a few metals, *e.g.*, Fe, Mn, Cr. As former researchers studied that Fe (III) has the activity towards the oxidation of volatile organic compounds, therefore, catalysts prepared by iron ore tailing may decompose formaldehyde. It can make good use of waste materials and reduce the pollution of the environment. In this paper, the aim is to prepare the catalysts of catalytic oxidation of formaldehyde by physical/chemical modification of iron ore tailing. The properties of the Fe (III) /γ-Al_2O_3 catalysts were characterized by the X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET), and the X-ray fluorescence (XRF), in order to build correlation with the catalytic performance of the catalysts. Also the effects of calcination temperature and reaction temperature were investigated.

2. Experimental

2.1. Catalyst preparation

Fe(III)/γ-Al_2O_3 catalysts were prepared by an impregnation approach. The samples were mixed well which were collected from six different points in the tailing reservoir of Heshangqiao iron mine. Then, samples of iron ore tailing were crushed, ground and sifted. 10 g of iron ore powder dried was slowly added into a beaker contained 50 ml of HNO_3 (70%) solution. Then the beaker was set on a stirrer and vigorously stirred for 2 h at 100 °C. The beaker was cooled fully and the mixture was filtered. 0.5 g $AgNO_3$ was injected into the leached solution if the catalyst loaded Ag+ will be prepared. An appropriate amount of dilute ammonia solution was added slowly into a beaker in which leached solution was added as far as neutral solution measured by a pH instrument. The γ-Al_2O_3 (analytical reagent) was washed by deionized water, and dried at 105 °C for 2 h. Then the solution in the beaker mixed with 10 g of γ-Al_2O_3, vigorously stirred for 3 h to disperse completely. In this instance alumina to ferric oxide was controlled at a ratio of about 6:1. The mud pie filtered by filter paper from the impregnation solution was dried at 105 °C for 3 h. The dried materiel was divided averagely as 3 pieces, and calcined at 350 °C, 450 °C and 550 °C, respectively for 3 h in a muffle furnace. Then, the raw powder was marked as C1. The catalyst was marked as C2, C3 and C4, respectively according to the calcination temperature of 350 °C, 450 °C and 550 °C. The catalyst loaded Ag+ was marked as C5 calcined at 450 °C.

2.2. Catalyst characterization

X-ray diffraction studies were performed with a Bruker D8 advance diffractometer. Cu Ka radiation and a fixed power source (40 kV, 40 mA) were used. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. X-ray Fluorescence measurements were performed with an ARL Advant'X Intellipower 3600. The voltage and current for the measurements are 60 kV and 120 mA, respectively. Surface area measurements were carried out using the BET nitrogen adsorption method with a V-Sorb 2800S (Gold APP Instrument Corporation China).

2.3. Catalytic activity measurement

The activity of the catalysts for catalytic oxidation of formaldehyde was tested in a quartz glass fixed-bed reactor with an external diameter of 35 mm as shown in Fig. 1. For each test, 1.0 g of catalyst mixed fully with 10 g quartz sand was loaded. The gaseous reactant mixture was fed into the reactor by an air flow through an air compressor, which passes through a container filled with formalin (an aqueous solution of 37% formaldehyde). The flow rate passing through the reactor in all the experiments was controlled at 500 ml/ min by a mass-flow controller. This flow rate is equivalent to 200 ppm of formaldehyde. The space velocity of the catalytic oxidative test is 30,000 ml/g·h. The catalytic activity was tested in the temperature range from 100 to 300 °C. Firstly, the blank experiment on quartz sand only loaded into the reactor was carried out in order that it can show no catalytic activity of silicon dioxide to formaldehyde. The relative humidity of effluent gases is about 76% and the effluent gases were analyzed by the acetylacetone spectrophotometric method.

The acetylacetone spectrophotometric method is a state standard of the People's Republic of China (GB/T 15,516–1995) for determination of formaldehyde. The formaldehyde gas sample is absorbed into deionized water, in a pH = 6 acetic acid-ammonium acetate buffer solution, reacts with acetylacetone and generates quickly steady yellow compound under the condition of boiling water bath. Then, the solution containing the yellow compound is sampled in a 1 cm *absorption cell*. Formaldehyde determinates at wavelength 413 nm in an *ultraviolet spectrophotometer.* Then the concentration of formaldehyde was determined and the catalytic efficiency of formaldehyde can be calculated.

3. Results and discussion

3.1. Characterization measurement

The catalysts supported metals and silver were set into a muffle furnace and calcined at 350 °C, 450 °C and 550 °C for 3 h, respectively. The BET data were shown in Table 1. It was found from