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Fe(III) oxide pillared titanium phosphate (TiP): An effective catalyst for deep oxidation of VOCs

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Abstract

A series of trinuclear acetato complex of Fe(III) intercalated TiP was successfully prepared by ion exchange process by varying the wt% of Fe(III), activated at various temperatures and characterized by various techniques. The PXRD and FTIR analyses reveal that the pillaring has been taken place in the interlayer of the layered materials. All the catalysts were found to be mesoporous in nature. The number of reducing sites was found to be higher than that of oxidizing sites. With increase in the calcination temperature of 5 wt% Fe(III)/TiP, surface area and surface oxygen increase up to 300 °C, thereafter exhibits a slow decrease up to 500 °C. But the oxidizing and reducing properties go on decreasing with activation temperature. Catalytic decomposition of acetone, methanol, diethyl ether and 2-propanol as probe molecules was studied to find out the suitability of the material for VOCs decomposition reactions. Fe(III) pillared TiP (5 wt%) with high iron content, surface area and surface oxygen shows higher catalytic activity towards the complete decomposition of VOCs. Titanium phosphate pillared with 5 wt% Fe(III), calcined at 300 °C showed complete decomposition of VOCs in the range of 180–350 °C. The catalytic activity of these materials is comparable with other reported catalysts.

Keywords: Fe(III) oxide pillared TiP; VOCs; Activation temperature; Surface oxygen

1. Introduction

Volatile organic compounds (VOCs) are an important class of air pollutants, emitted from many industrial processes and transportation activities [1]. Catalytic combustion is one of the most promising technologies for the destruction of VOCs at temperature much lower than those of incineration. Catalytic oxidation of VOCs is a chemical process in which volatile organic compounds are combined with oxygen at specific temperatures to yield CO_2 and water. This process can be considered as an effective way of reducing the emissions of VOCs from stationary sources [1–3]. In this respect, environmental catalysis performs an essential role in minimizing the emission of toxic compounds and the development of energy saving, residue free processes. The design of new catalytic materials is one of our main challenges in achieving the goal [4].

A great deal of work has been done by different researchers for the decomposition of volatile organic compounds taking various supported/neat noble metal oxides. Both noble metals and mixed metal oxides can be used as catalysts [1], the first ones being often preferred for the destruction of non-halogenated VOCs [2]. Noble metals are generally supported on alumina, however other supports particularly zeolites can be also used. Various reports have shown that platinum is more active in total combustion than palladium [5], thus the total oxidation of aromatic VOC (*o*-xylene) was investigated over Pt/zeolite catalysts. Recently Minico et al. [6] have shown that Au/Fe oxide catalysts present a high activity towards the catalytic oxidation of VOCs. In case of transition metal oxides, the Mn and Co is well known as the most active among the single oxides for complete oxidation of VOCs [7–9]. Again, Hosseini et al. [10] reported the promotional effect of gold on palladium supported on a new mesoporous titania towards the oxidation of propene and toluene. In spite of the lower activity of these materials compared with that of noble metals, their relatively low cost has spurred considerable effort in search of suitable combustion catalysts based on transition metal oxides, such as some perovskites and other mixed oxides. A very few articles have been published based on the Fe and Cr oxide towards VOCs decomposition [11,12].

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It is evident from the above literature review; the transition/noble metal oxide supported catalysts are efficient for oxidation of various VOCs. A great deal of work has been done by different research groups on the catalytic activity of modified tetravalent metal phosphates like zirconium phosphate and titanium phosphate towards ketonisation [13], dehydration/cyclohydration [14,15], decomposition of isopropyl alcohol [16], etc. We have extensively studied the catalytic activity of modified zirconium phosphate and titanium phosphate towards the photodegradation of organic and inorganic pollutants [17], bromination of phenol [18] and deep oxidation of VOCs [19]. The present paper deals with the preparation of Fe(III) oxide pillared titanium phosphate (TiP) through ion exchange process, their characterization by various techniques such as PXRD, FTIR, TG-DTA surface oxygen, redox sites, BET-surface area and ultimately testing of their activity towards the deep oxidation of representative VOCs such as acetone, methanol, propan-2-ol and diethyl ether.

2. Experimental

2.1. Material preparation

Trinuclear acetato complex Fe(III) was prepared by following the reported method [20] and used as such. Various wt% of Fe(III) intercalated TiP was prepared by cation exchange method taking required amount of Fe(III) acetato complex and sodium-exchanged TiP in distilled water. This mixture was stirred for 3 h at room temperature. Then it was filtered and washed. The residue was activated in the temperature range 110–500 °C for further use.

2.2. Physico-chemical characterization

2.2.1. Chemical analysis

During filtration, the filtrate was collected in a volumetric flask to analyze the amount of Fe(III) left out in the solution after the intercalation process. The amount of Fe(III) in the filtrate was analyzed by standard titrimetric method [21].

2.2.2. Textural properties

The PXRD patterns were taken on a Philips PW 3710 diffractometer with automatic control. The patterns were run with monochromatic Cu Kα radiation with nickel filter from $2\theta = 5^\circ$ to 70° with a scan rate of $2^\circ\,\mathrm{min}^{-1}$. Basal spacing was calculated from the d_{001} reflection. The FTIR spectra was taken using a Nicolet Instruments Corporation instrument (Model: Magna 550) in a KBr matrix in the range of 400–4000 cm^{-1}. BET-surface area was determined by N_2 adsorption–desorption method at liquid nitrogen temperature (−196 °C) using Sorptomatic 1990 series instrument. Prior to adsorption–desorption measurements all the samples were degassed at 110 °C at 10^{-3} Torr for 5 h. TG-DTA analyses of samples dried at 110 °C were carried out using a Thermal Analyzer (Perkin-Elmer (TG/DTA), Model: Diamond). The thermogravimetry (TG) and differential thermal analysis (DTA) experiments were performed in N_2 using 4–5 mg samples at a heating rate of 10 °C/min.

2.2.3. Surface properties

One-electron donor and acceptor properties were determined on the basis of irreversible adsorption of *m*-dinitrobenzene (EA = −1.26 eV) and phenothiazine (IP = −7.13 eV), respectively, by spectrophotometric method [22]. Surface oxygen was determined according to the method of Uchijima et al. [23]. In this method, a known amount of catalyst, 15 ml of buffer solution of pH 7.6 and about 2 g of KI were placed in a 100 ml stoppered conical flask, shaken vigorously for 7 h with the help of a thermostatic shaker (Remi Equipments). The reaction mixture was filtered, acidified with 1 M HCl and the liberated iodine was titrated against 0.01N sodium thiosulphate using starch as indicator.

2.3. Catalytic activity

In the present study, acetone, methanol, diethyl ether and 2-propanol were chosen as representative VOCs. The catalytic oxidation of acetone (3000–3300 ppm), methanol (2400–2700 ppm), diethyl ether (1200–1500 ppm) and 2-propanol (1500–1800 ppm) was carried out in a specially designed fixed bed catalytic reactor (10 mm i.d.) with space velocity of 3600 ml/h. The reactor containing 0.05 g of the catalyst was kept in a programmable tubular furnace (Stanton Redcroft, UK) to maintain the reactor temperature. The VOCs were quantitatively (0.1–1.0 ml/h) injected into the reactor from the micro-feeder (Orion, USA) through a vaporiser using air as carrier (20–60 ml/min). The gaseous products were analyzed with an on-line Gas Chromatography (Shimadzu GC-17A) in FID mode using a capillary column. Amount of CO_2 was estimated in TCD mode through a capillary column.

3. Results and discussion

3.1. Intercalation

The uptake of Fe(III) complex by sodium exchanged TiP was presented in Fig. 1. It was observed that the uptake of Fe(III) increases with increase in the Fe(III) concentration in the solution up to 5 wt% and thereafter remains almost constant. It seems intercalation is less favored in higher concentration of Fe(III), as a result of which up to 5 wt% of Fe(III) loading in TiP helps in increasing the surface area and basal spacing. With further increase in the Fe(III) concentration, the surface area and basal spacing decrease because of the blockage of the pores with excess of Fe(III) complex. Similar observations were reported earlier in case of Cr (III) acetato complex intercalated montmorillonite [24].

3.2. Textural properties

The shifting of the d_{001} reflection towards lower 2θ indicates successful pillaring of the complex (Fig. 2A). The basal spacing increases with the increase in the wt% of complex in the solution up to 5 wt% and thereafter remains almost constant. With increase in the activation temperature, it was observed that at 300 °C the complex is completely decomposed to Fe(III) oxide