

# 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. © 2007 Elsevier B.V. All rights reserved.

**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<sub>2</sub> 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 var-

ious supported/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 K $\alpha$  radiation with nickel filter from  $2\theta = 5^\circ$  to  $70^\circ$  with a scan rate of  $2^\circ \text{ min}^{-1}$ . 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  $\text{cm}^{-1}$ . BET-surface area was determined by  $\text{N}_2$  adsorption–desorption method at liquid nitrogen temperature ( $-196^\circ\text{C}$ ) using Sorptomatic 1990 series instrument. Prior to adsorption–desorption measurements all the samples were degassed at  $110^\circ\text{C}$  at  $10^{-3}$  Torr for 5 h. TG-DTA analyses of samples dried at  $110^\circ\text{C}$  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  $\text{N}_2$  using 4–5 mg samples at a heating rate of  $10^\circ\text{C}/\text{min}$ .

### 2.2.3. Surface properties

One-electron donor and acceptor properties were determined on the basis of irreversible adsorption of *m*-dinitrobenzene (EA =  $-1.26 \text{ eV}$ ) and phenothiazine (IP =  $-7.13 \text{ eV}$ ), 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  $\text{CO}_2$  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  $2\theta$  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  $300^\circ\text{C}$  the complex is completely decomposed to Fe(III) oxide

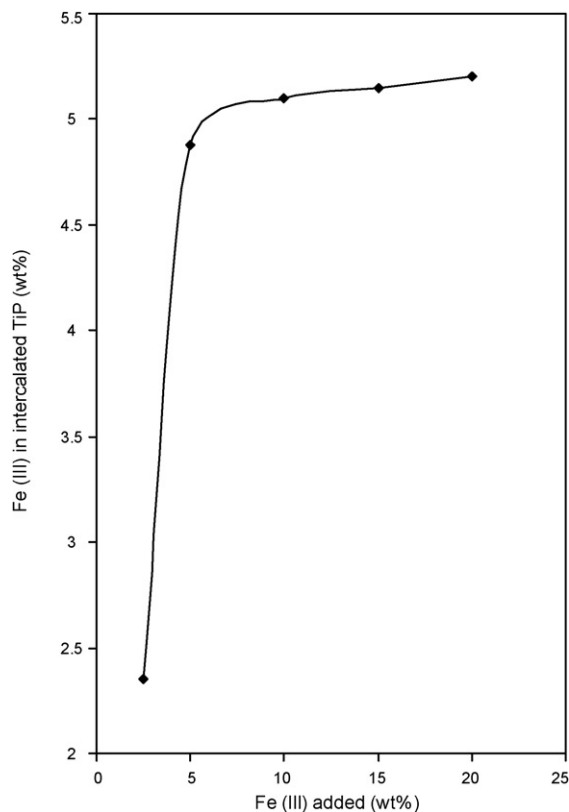


Fig. 1. Uptake of Fe(III) by sodium exchanged TiP.

inside the layers of titanium phosphate. Again the basal spacing was found to increase with increase in the activation temperature up to 300 °C (9.5 Å) and thereafter it decreases to 7.65 Å at 500 °C (see Table 1). This may probably be due to formation of metal oxide pillars at 300 °C. But due to the gradual collapsing of the layered structure, basal spacing decreases with further increase in the activation temperature up to 500 °C.

Fig. 2B and C show the FTIR spectra of 110 °C dried different wt% of Fe(III) intercalated TiP and 5 wt% Fe(III) oxide pillared TiP activated at various temperatures. The characteristic bands at 1550 and 1446 cm<sup>-1</sup> corresponding to COO<sup>-</sup> asymmetrical ( $\nu_{as}$ ) and symmetrical ( $\nu_s$ ) stretching vibrations, respectively, were observed. In addition to these bands, a band at 659 cm<sup>-1</sup> was observed, the intensity of which is increased

up to 5 wt%, thereafter decreases. The bands at 1617 and 659 cm<sup>-1</sup> (due to –OH bonding and Fe(III) hydrolysed species, respectively) are disappearing slowly with activation temperature (Fig. 2C). Fe(III)/TiP, calcined at 300 °C shows a band at around 450–600 cm<sup>-1</sup> which is possibly be due to Fe<sub>2</sub>O<sub>3</sub> [25]. This may probably be the indication that iron oxide pillars are formed at 300 °C inside the phosphate layers. The observations of PXRD and FTIR were supported by TG-DTA (Fig. 2D). From the TG plot (Fig. 2D), a weight loss of 8.31% accounts for the loss of physisorbed water and acetate group. From DTA pattern, an endothermic in the range of 200–210 °C was observed due to loss of physisorbed water. A broad exothermic peak starting from 220 to 600 °C was observed which could probably be due to the combined effect of loss of acetyl group of the complex and partial phase transition of TiP.

Table 1 summarizes the textural and surface properties of the series of catalysts. The surface area is maximum in case of 5 wt% Fe(III)/TiP (185 m<sup>2</sup>/g). With further increase in the Fe(III) concentration, the surface area goes on decreasing from 185 to 151 m<sup>2</sup>/g due to blockage of the pores. Also with increase in the calcination temperature up to 300 °C, the surface area increases to 240 m<sup>2</sup>/g due to formation of metal oxide pillaring in the inter-layer. Again from Table 1, it was observed that surface oxygen shows almost similar trend as that of the surface area. From the analysis of redox sites, it was found that the reducing properties are higher than that of oxidizing properties. With increase in the Fe(III) concentration and activation temperature, the oxidizing property decreases. But the reducing properties go on increasing with increase in the concentration of Fe(III) up to 5 wt%, thereafter it remains almost constant (Table 1). With increase in the activation temperature from 110 to 500 °C, the reducing property of 5 wt% Fe(III)/TiP, goes on decreasing.

### 3.3. Catalytic activity

The catalytic oxidation of acetone, methanol, and diethyl ether was presented in Fig. 3 for 5 wt% Fe(III) oxide intercalated TiP activated at different temperatures as a function of reaction temperature. In case of acetone, the reaction starts at 120 °C and no toxic intermediate product like acetaldehyde was formed during the reaction. But very negligible quantities of CO (which ultimately oxidized to CO<sub>2</sub>) could possibly be formed for

Table 1  
Textural properties Fe(III) pillared TiP

Catalyst	Basal spacing (Å)	Surface area (m <sup>2</sup> /g)	Surface oxygen (meq/g)	Redox sites (μmol/g)	
				DNB	PNTZ
Fe(III)/TiP 2.5 wt% (110 °C) <sup>a</sup>	7.7	150	0.65	32	62
Fe(III)/TiP 5 wt% (110 °C)	7.9	185	0.85	30	93
Fe(III)/TiP 10 wt% (110 °C)	8.0	179	0.92	22	94
Fe(III)/TiP 15 wt% (110 °C)	8.01	162	0.95	17	96
Fe(III)/TiP 20 wt% (110 °C)	8.01	151	0.93	15	98
Fe(III)/TiP 5 wt% (200 °C)	8.2	200	1.02	12	92
Fe(III)/TiP 5 wt% (300 °C)	9.5	240	1.2	9	85
Fe(III)/TiP 5 wt% (400 °C)	7.82	225	1.15	5	80
Fe(III)/TiP 5 wt% (500 °C)	7.65	215	1.0	3	72

<sup>a</sup> Fe(III)/TiP 2.5 wt% (110 °C) stands for 110 °C activated 2.5 wt% Fe(III) promoted TiP.

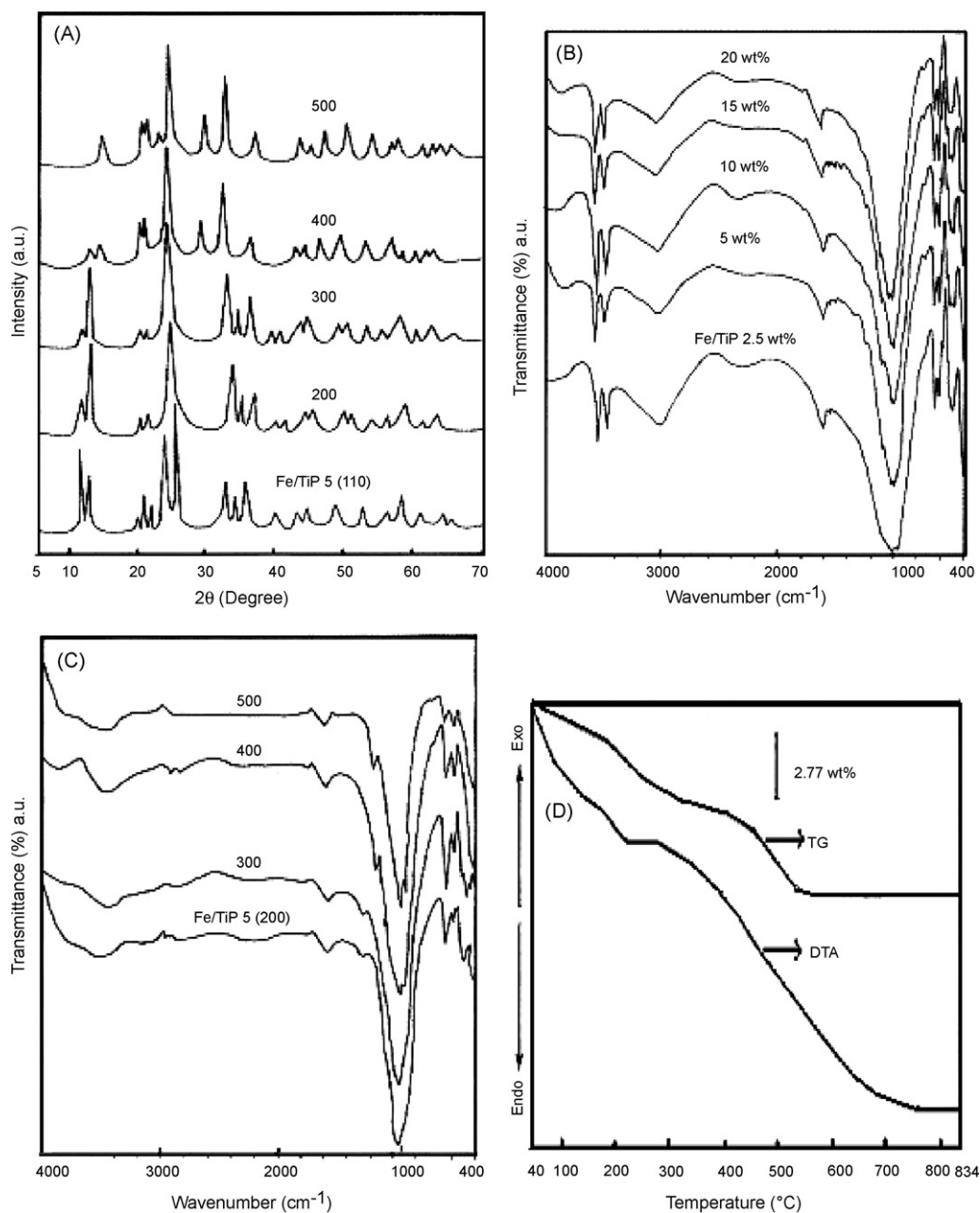


Fig. 2. (A) XRD pattern, (B) FTIR spectra of different wt% of Fe(III) loaded TiP, (C) FTIR spectra of 5 wt% Fe(III) loaded TiP activated at various temperatures and (D) TG-DTA pattern of 5 wt% Fe(III) loaded TiP.

which the combined selectivity of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was not found to be 100%. Some authors also reported acetaldehyde and CO as intermediate product using basic metal oxide catalysts [26]. One can clearly notice from Fig. 3A that complete decomposition occurs at 230 °C for 5 wt% Fe(III)/TiP, calcined at 300 °C. With further increase in the activation temperature, the decomposition temperature increases. We see the methanol decomposition starts at 120 °C (Fig. 3B) and complete decomposition occurs at 270 °C to produce only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as major byproducts. Our observation agrees with Scire et al. [27]. The absence of intermediate compounds can be explained considering that formic aldehyde (which should be the intermediate oxidation product) is a very reactive species which evolves easily  $\text{CO}_2$  [28]. The

formation of water vapor was observed at higher reaction temperature. If we compare the selectivity of the catalysts activated at various temperatures, the selectivity ratio between  $\text{CO}_2$  and water vapor for 300 °C calcined catalyst was found to be less in all reaction temperatures. This could possibly be due to partial collapsing of the layered structure of TiP above 300 °C. This shows more water vapors are produced over the above said catalyst rather than a toxic product  $\text{CO}_2$ . Hence this catalyst is more suitable for VOC decomposition in environment point of view. This was also evidenced from the basal spacing results (Table 1). Fig. 3C represents the catalytic decomposition of diethyl ether. The decomposition starts at 160 °C and the reaction was found to be completed at 280 °C. It was observed that only  $\text{CO}_2$  and

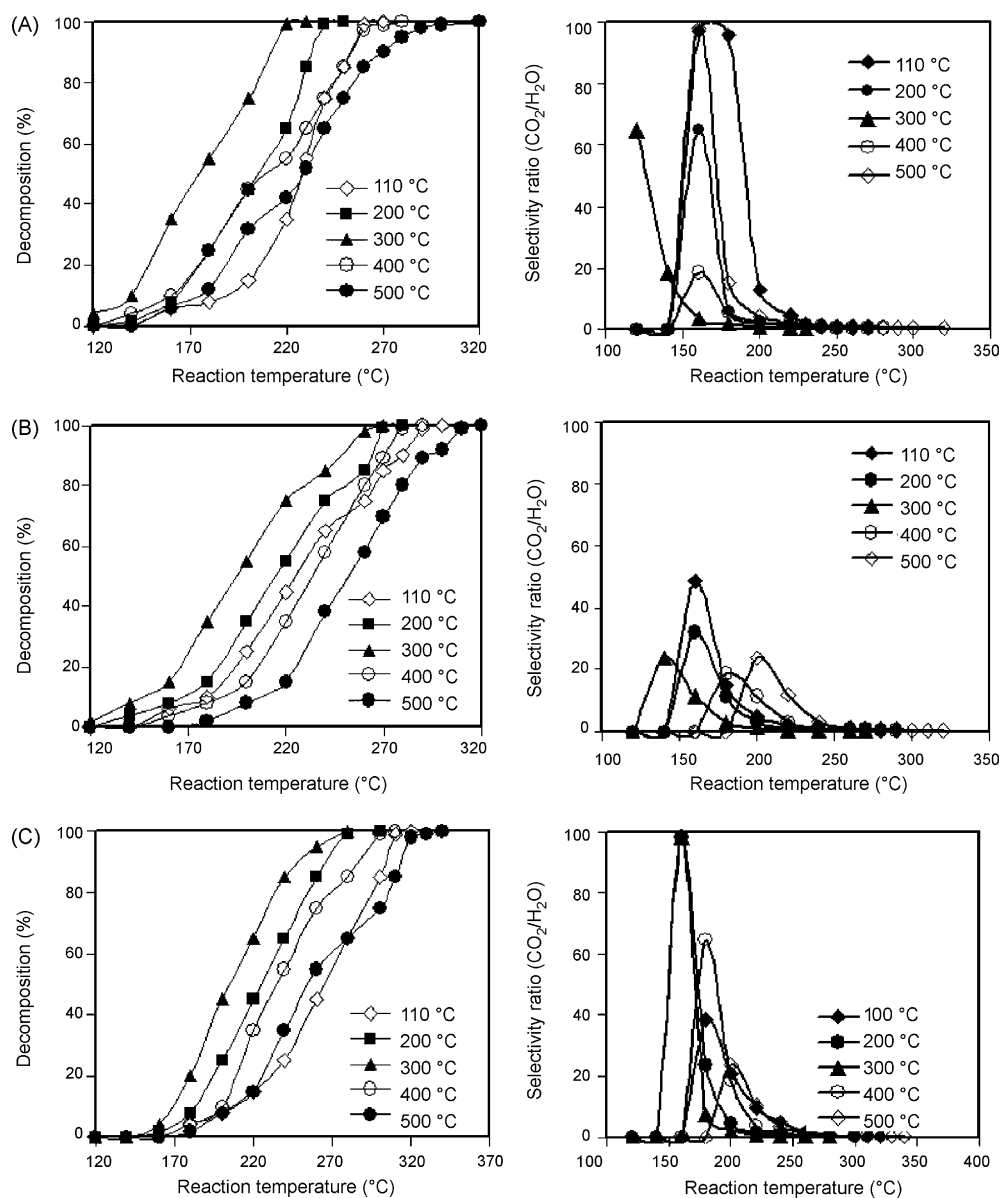


Fig. 3. Catalytic oxidation and selectivity (CO<sub>2</sub>/H<sub>2</sub>O) profile of (A) acetone, (B) methanol and (C) diethyl ether over 5 wt% Fe(III) oxide pillared TiP activated at various temperatures as a function of reaction temperature.

H<sub>2</sub>O were formed as final major product and CO was produced in very minor quantity for which the combined selectivity of CO<sub>2</sub> and H<sub>2</sub>O formed was not found to be 100%. Table 2 summarizes the 2-propanol decomposition over 5 wt% Fe(III) pillared TiP, at various activation temperatures ranging from 110 to 500 °C. From Table 2, it was clear that with increase in the activation temperature up to 300 °C, the conversion increases to 100% at reaction temperature 230 °C, thereafter decreases. This could possibly be due to increase in the surface oxygen up to 300 °C and thereafter it decreases with activation temperature. In almost all the samples, acetone and diisopropyl ether were produced with negligible quantity of propene at 230 °C. The mechanism of 2-propanol oxidation seems to begin with the adsorption of gaseous 2-propanol as 2-propoxide surface species [29]. With increase in the activation temperature, selectivity towards diisopropyl ether decreases with more acetone

Table 2

Summary of the results from catalysis tests on decomposition of isopropanol<sup>a</sup> at 230 °C over 5 wt% Fe(III) promoted TiP

Catalysts	Conversion (%)	Selectivity (%) <sup>b</sup>		
		Acetone	Isopropylether	Propene
Fe(III)/TiP 15 (110 °C)	78	20	72	8
Fe(III)/TiP 15 (200 °C)	87	56	38	6
Fe(III)/TiP 15 (300 °C)	100	88	8	4
Fe(III)/TiP 15 (400 °C)	90	90	7	3
Fe(III)/TiP 15 (500 °C)	83	93	7	0

<sup>a</sup> Reactant flow = 1 ml/h, air flow = 60 ml/min and catalyst amount = 0.05 g.

<sup>b</sup> Analyzed and quantified by GC 17A through capillary column.

Table 3  
Comparison of supported/unsupported noble metal and transition metal oxide catalysts with that of Mn(III) pillared TiP

Entry	Catalysts	Type of VOCs	Space velocity (ml/h)	Temperature (°C) and conversion (%)	Reference
1.	Best noble metal catalyst	Methanol (250–300 ppm)	–	260 (90)	[31]
2.	Pd, Ag, Rh, Cu, Cr, Pt on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Methanol (0.2%)	52,000–87,000	20–427	[32]
3.	LaMnO <sub>3</sub> , LaCoO <sub>3</sub>	Acetone 2-propanol Benzene	14,100	150–260 (95–100) 150–260 (89–100) 240–350 (75–90)	[33]
4.	Pd/Al <sub>2</sub> O <sub>3</sub> , Mn <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> , Mn <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	Acetone (600 ppm) Toluene (225 ppm)	–	20–400	[34]
5.	Manganese nodules	Acetone (500–550 ppm) Metanol (400–450 ppm) 2-propanol (250–300 ppm)	2,400	180–260 (99) 170–220 (100) 180–280 (99)	[35]
6.	Mn/TiO <sub>2</sub> -SiO <sub>2</sub>	Acetone (500–550 ppm) Metanol (400–450 ppm) 2-propanol (250–300 ppm)	2,400	100–200 (100) 120–220 (100) 150–250 (100)	[36]
7.	Mn(III)/TiP	Acetone (3000–3300 ppm) Methanol (2400–2700 ppm) 2-propanol (1500–1800 ppm) Diethyl ether (1200–1500 ppm)	3,600	180 (100) 230 (100) 200 (100) 290 (100)	[19]
8.	Fe(III)/TiP	Acetone (3000–3300 ppm) Methanol (2400–2700 ppm) 2-propanol (1500–1800 ppm) Diethyl ether (1200–1500 ppm)	3,600	230 (100) 270 (100) 250 (100) 280 (100)	[This work]

formation, i.e. selectivity ratio between CO<sub>2</sub> and water increases with activation temperature (Fig. 4). Although this reaction condition is enough to decompose the byproducts to CO<sub>2</sub> and H<sub>2</sub>O, the complete decomposition occurs at 250 °C. This is mainly due to the fact that not only minimum temperature is required for the decomposition of 2-propanol, but also the decomposition

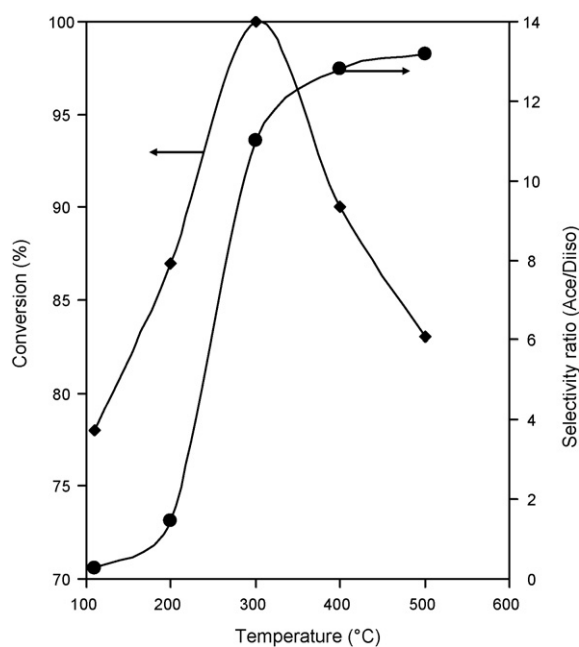


Fig. 4. Conversion of 2-propanol and its selectivity ratio over Fe(III)/TiP 5 wt% at different activation temperature (selectivity ratio (Ace/Diiso) = selectivity ratio of acetone and diisopropyl ether).

depends on the reactor diameter, reaction conditions, particularly residence time, oxygen to 2-propanol ratio, flow rate, etc. [26]. Residence time is required more which may not be attained here for the complete decomposition of the primary compound, 2-propanol to CO<sub>2</sub> and H<sub>2</sub>O. Our observation agrees with Lopez et al. [30]. It was also found that the activity of 5 wt% Fe(III) pillared TiP remained almost same during TOS run for 10 h.

Table 3 gives a comparative study of Fe(III) oxide pillared titanium phosphate with that of noble and other transition metal oxide supported catalysts towards complete oxidation of VOCs. One can clearly notice, Fe(III) oxide pillared titanium phosphate is comparable with that of supported/unsupported noble metal oxides and perovskite type of oxidation catalysts. So they can be effectively used as a substitute over the precious metal supported catalysts for low temperature oxidation of VOCs.

#### 4. Conclusions

Present paper reports the preparation of thermally stable iron oxide pillared TiP. Different weight percentage of trinuclear Fe(III) acetato complex was successfully intercalated into the layers of titanium phosphate by ion exchange process. From the chemical analyses of the filtrate, it was found that intercalation is maximum at 5 wt% of Fe(III) which was also supported by PXRD, surface area, surface oxygen and reducing properties. By varying the activation temperature, it was observed that the material activated at 300 °C showed highest surface area, basal spacing and surface oxygen. Complete decomposition of VOCs such as methanol, acetone, diethyl ether and 2-propanol is feasible in the temperature range 180–350 °C over 5 wt% Fe(III)

pillared TiP, activated at 300 °C. This catalyst showed consistent activity in the time on stream experiment and hence can be utilized for the decomposition of VOCs.

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