

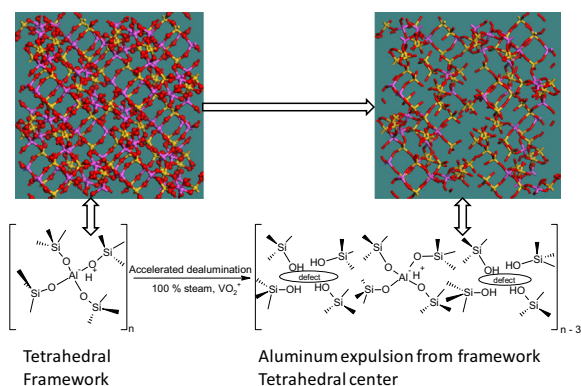
# Effect of vanadium contamination on the framework and micropore structure of ultra stable Y-zeolite



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## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 23 June 2015

Revised 3 October 2015

Accepted 20 October 2015

Available online 23 October 2015

### Keywords:

Zeolite  
Pore structure  
Framework  
Dealumination  
Passivation

## ABSTRACT

Y-zeolites are the main component of fluid catalytic cracking (FCC) catalyst for conversion of crude petroleum to products of high demand including transportation fuel. We investigated effects of vanadium which is present as one of the impurities in FCC feedstock on the framework and micropore structure of ultra-stable (US) Y-zeolite. The zeolite samples were prepared and characterized using standard techniques including: (1) X-ray diffraction, (2) N<sub>2</sub> adsorption employing non local density functional theory method, NLDFT, (3) Transmittance and Pyridine FTIR, (4) Transmittance electron microscopy (TEM), and (5) <sup>27</sup>Al and <sup>29</sup>Si MAS-NMR. Results revealed that in the presence of steam, vanadium caused excessive evolution of non inter-crystalline mesopores and structural damage. The evolved mesopore size averaged about 25.0 nm at 0.5 wt.% vanadium loading, far larger than mesopore size in zeolitic materials with improved hydrothermal stability and performance for FCC catalyst. A mechanism of mesopore formation based on accelerated dealumination has been proposed and discussed. Vanadium immobilization experiments conducted to mitigate vanadium migration into the framework clearly showed vanadium is mobile at reaction conditions. From the results, interaction of vanadium with the passivator limits and decreases mobility and activity of vanadium into inner cavities of the zeolite capable of causing huge structure breakdown and acid sites destruction. This study therefore deepens insight into the causes of alteration in activity and selectivity of vanadium contaminated catalyst and hints on a possible mechanism of passivation in vanadium passivated FCC catalyst.

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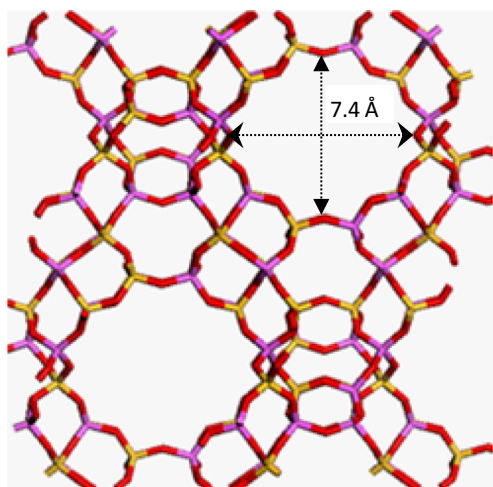
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## 1. Introduction

Zeolites are an important class of microporous, crystalline aluminosilicates with three-dimensional pore structure widely used in various applications including catalysts [1–14]. Their use as catalysts for different conversion processes has unarguably underpinned the major application in petroleum refining, petrochemical and allied industries. In the case of petroleum refining, zeolite is quite indispensable. The discovery of zeolite catalyst in the 1960s has remained a major turnaround in the petroleum industry that has resulted in improved production and increased profitability [15]. Zeolite is exclusively responsible for cracking catalyst's activity and Y-zeolite, having faujasite structure (Fig. 1), with well-defined pore network ( $7.4 \times 7.4 \text{ \AA}$ ) in its pure crystalline form, is the active component of fluid catalytic cracking (FCC) catalyst and it is used in acidic and rare earth forms to increase the yield of gasoline and diesel fuel from feedstock by cracking heavy paraffins into liquid fuels.

During FCC process zeolite catalysts are exposed to certain conditions that can modify important physiochemical properties such as aluminum content and acids strength. Such changes in zeolite composition and properties have significant impacts on catalytic activity, selectivity and stability. It has been established that the harsh FCC unit conditions, together with impurities present in the feedstock are directly linked with properties alterations [16,17]. Amongst the impurities are metals including sodium [18], iron and calcium [19] and nickel and vanadium [20,21]. However, nickel and vanadium are grievously detrimental to FCC catalyst's performance [22–24].

Specifically, behaviors of zeolites in the presence of steam and metal contaminants; sodium, vanadium and nickel have been studied. For instance, Pine [25] studied vanadium catalyzed destruction of USY zeolite and results showed steam has ability to destroy the zeolite system; however, his study was on siliceous zeolite. Vanadium and nickel interaction in REY had been reported. The authors discovered that during steam treatment in the presence of vanadium, dealumination of framework alumina and partial collapse of REY structure occur; vanadium also promotes coke formation of the zeolite. However, crystallinity of the zeolite structure was preserved in the presence of nickel under similar conditions, but coke formation rate was generally on the increase [20,21]. Tsiatouras and Evmiridis [24], in their study reported a complete structure breakdown of steam treated chromium-exchanged USY zeolite incorporated with vanadium. They authors added structure collapse was nearly proportional to dealumina-



**Fig. 1.** Structure of Y-zeolite showing average micropore width in the supercage formed by 12-membered ring.

tion, and impregnated vanadium selectively removed framework Al atoms. In a study to understand the influence of vanadium on the physiochemical and catalytic properties of USHY zeolite, Torrealba et al. [26] reported that vanadium decreased the stability of the zeolite through decrease in crystallinity and increase of dealumination rate during the hydrothermal treatment, and consequently the activity of the zeolite; but however, this decrease in activity was thought to be due partly to other phenomena, particularly to the exchange of the protonic sites by cationic vanadium species. Generally, vanadium deposited on the surface of the catalyst migrates into the zeolite structure in the presence of steam; however, matters concerning these facts are still debating and no comprehensive report is available in the literature on the action of vanadium on the pore-structure of USY zeolite. In view of the latter, a study of USY zeolite targeting the pore structure in the presence of a contaminating substance such as vanadium becomes necessary to fully comprehend causes of alteration in performance of vanadium contaminated Y-zeolite based catalyst. Results could find application in fabrication of better catalysts and improvement in general FCC catalyst technologies. In this report, we present the effects of vanadium contamination on the framework and micropore structure of USY zeolite using  $N_2$  adsorption by non-local density functional theory (NLDFT) method, powder XRD, MAS-NMR, FTIR and TEM. We have also demonstrated, using physiochemical properties, mitigation of vanadium poisoning of zeolite with a novel synthesized material.

## 2. Experimental methods

### 2.1. Samples preparation

Zeolite sample of this research, with unit cell size of  $24.53 \text{ \AA}$ , Si/Al ratio 2.8 and sodium content ( $Na_2O$ ) of 0.42 wt.% was supplied by a catalyst manufacturing Company in Qingdao, China. Working sample was exchanged twice with  $1.0 \text{ M } NH_4NO_3$  at  $80 \text{ }^\circ\text{C}$  to remove sodium residue and calcined in air at  $500 \text{ }^\circ\text{C}$  for 4 h. Vanadium USY ( $xV$ -USY), where “x” is weight percentage (wt.%) of vanadium in a given sample, were prepared by wet impregnation of vanadyl naphthenate dissolved in n-hexane. Excess organic solvent was evaporated freely in air and oven dried at  $120 \text{ }^\circ\text{C}$  overnight. Oven dried samples were calcined in air at  $550 \text{ }^\circ\text{C}$  for 5 h to obtain the test samples. Unless otherwise stated, all samples were steamed treated for 5 h at a temperature of  $760 \text{ }^\circ\text{C}$ . Passivator as a separate particle was added to oven dried samples by physically admixing desirable amount before subjected to hydrothermal treatment.

### 2.2. Preparation of vanadium immobilizer

We used yttrium-magnesium oxide (Y/MgO) as our immobilizer here in referred to as “passivator”. Five (5.0) g MgO was dispersed in 40 ml distilled water and stirred for 20 min. Yttrium nitrate ( $Y(NO_3)_3 \cdot 6H_2O$ ) (4.75 g) dissolved in 10 ml distilled water was added and the mixture allowed stirring for another 30 min. After this time the white suspension formed was transferred to a water bath at  $101 \text{ }^\circ\text{C}$  and allowed to stir until evaporation to dryness. The white solid obtained was oven dried overnight at  $110 \text{ }^\circ\text{C}$  and calcined in air at  $600 \text{ }^\circ\text{C}$  for 5 h.

### 2.3. Characterizations

Internal structure examination and patterns generation were carried out by powder X-ray diffraction (XRD) of the zeolite samples on a PAN analytical X'pert PRO (Germany), X-ray diffractometer using  $Cu \text{ K}\alpha$  radiation generated at 40 kV and 40 mA. A

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