



## Enhanced performance in catalytic combustion of toluene over mesoporous Beta zeolite-supported platinum catalyst

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### ARTICLE INFO

#### Article history:

Received 29 January 2013

Received in revised form 16 March 2013

Accepted 29 March 2013

Available online 6 April 2013

#### Keywords:

Mesoporous Beta zeolite  
Supported platinum catalyst  
Catalytic combustion  
Volatile organic compounds (VOCs)  
Toluene

### ABSTRACT

Removal of volatile organic compounds (VOCs) has recently been attracted much attention, and catalytic combustion is one of good methods for solving this problem. In this research, we show a successful preparation of mesoporous Beta zeolite-supported Pt catalyst (Pt-R/Beta-H) and its superior performance in the catalytic combustion of toluene. N<sub>2</sub> sorption isotherms show that the mesopore volume of Pt-R/Beta-H reaches 0.18 cm<sup>3</sup>/g, and TEM images exhibit that the Pt particles exist in both micropores and mesopores of the sample. Interestingly, the Pt particles on Pt-R/Beta-H have higher dispersion than the Pt particles on conventional Beta zeolite (Pt-R/Beta). XPS spectra also reveal that Pt-R/Beta-H has higher Pt<sup>0</sup>/Pt<sup>2+</sup> ratio than Pt-R/Beta. Very importantly, Pt-R/Beta-H exhibits much higher catalytic activities and longer catalyst life as well as lower apparent activation energy in the catalytic combustion of toluene than Pt-R/Beta. The extraordinary performance in the catalytic combustion of toluene over Pt-R/Beta-H catalyst is of great importance for obtaining clean environment and enhancing human health.

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## 1. Introduction

Volatile organic compounds (VOCs) are the major components of air pollutants from motor vehicles and industrial processes as well as domestic products. Most of VOCs are precursors of ozone and photochemical smog, which are great threats to the environment and human health because of their toxic, carcinogenic, mutagenic, and teratogenic nature [1–3]. Thus, elimination of VOCs has become one of hot research topics, due to safe concerns together with more stringent legislations [2,4]. Up to now, a series of techniques for removing VOCs have been well developed, such as adsorption, thermal incineration, photocatalytic degradation, plasma catalytic oxidation, and catalytic combustion. Among these techniques, catalytic combustion has been identified as one of the most effective, economically feasible, and promising routes for VOCs abatement, especially for low concentration VOCs at much lower temperature [5–7].

Perovskites [8], transition metal oxides [9], and supported noble metals [10–16] are the most used catalysts for the catalytic combustion of VOCs, due to their excellent activities, high thermal

stabilities, and high resistance to deactivation. Generally, zeolites, alumina, zirconia, titania, and silica have been extensively applied as supports for preparation of supported noble metal catalysts [10–16]. For example, Becker and Förster investigated oxidative decomposition of benzene and its methyl derivatives over NaY, CuY, PdHY, and PdY zeolites [17,18], and they found that PdY was the most active catalyst. Siffert and co-workers compared FAU zeolite, ZrO<sub>2</sub>, and hierarchical macro-mesoporous ZrO<sub>2</sub> impregnated with 0.5% Pd for toluene total oxidation [19,20], and they observed that Pd/FAU zeolite gave better activity than Pd supported on macro-mesoporous ZrO<sub>2</sub> and conventional ZrO<sub>2</sub>. Therefore, zeolite supports have recently been paid much attention in the catalytic combustion of VOCs, due to their large surface area, uniform and intricate channels, high adsorption capacity, acidic property, high thermal and hydrothermal stabilities [21–26]. However, the relatively small and sole micropores in conventional zeolites significantly influence the mass transfer in catalytic reactions, resulting in relatively easy coke formation and deactivation of catalysts [27–29]. For example, Magnoux et al. carefully investigated the coke formation within the pores of zeolite in the catalytic oxidation of *o*-xylene into CO<sub>2</sub> and H<sub>2</sub>O [30–32]. To solve the limitation of the zeolitic micropores, the use of mesoporous zeolites as the catalyst supports is strongly desirable.

Thanks for the great efforts of materials scientists, mesoporous zeolites with good mass transfer have been successfully

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synthesized recently, which combine the advantages of both mesoporous materials and zeolites [33–46]. However, to the best of our knowledge, the applications of mesoporous zeolites in the VOCs catalytic combustion have not been reported yet. Here, we demonstrate that mesoporous Beta (Beta-H) zeolite-supported Pt catalyst has high activities and superior catalyst life as well as low apparent activation energy in the catalytic combustion of low concentration toluene, compared with conventional Beta zeolite-supported Pt catalyst.

## 2. Experimental

### 2.1. Materials

Conventional Beta zeolite was supplied by Sinopec. NaOH (AR) and NaAlO<sub>2</sub> (CP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetraethylammonium hydroxide (TEAOH, 25 wt%) and H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (AR) were purchased from Aladdin. Fumed silica (SiO<sub>2</sub>) was purchased from Shengyang Chemical Co., Ltd. Polydiallyldimethylammonium chloride (PDADMAC, 20 wt%, molecular weight of  $\sim 1.5 \times 10^5$ ) was purchased from Yinhu Chemical Reagent Co., Ltd. NH<sub>4</sub>NO<sub>3</sub> was purchased from Kelong Chemical Reagent Plant. Toluene (AR) was purchased from Hangzhou Chemical Reagent Co., Ltd.

### 2.2. Catalyst preparation

Mesoporous Beta zeolite (Beta-H) was synthesized according to the literature [33]. In a typical synthesis of Beta-H: NaOH (0.16 g) and NaAlO<sub>2</sub> (0.30 g) were mixed with TEAOH (32 mL), followed by addition of fumed silica (4.8 g). After stirring for 1 h at room temperature, PDADMAC (1.6 g) was added into the mixture. After stirring for 10–24 h at room temperature, the mixture was transferred into an autoclave at 140 °C for 120–240 h for crystallization. The product was collected by filtration, dried in air, and calcined at 550 °C for 5 h to remove the organic templates.

The H-form of Beta zeolite samples were ion-exchanged twice with a NH<sub>4</sub>NO<sub>3</sub> solution (1 M) at 80 °C for 3 h, followed by calcination at 550 °C for 5 h.

Zeolite-supported Pt (1 wt%) catalysts were prepared by incipient wetness impregnation method using an appropriate amounts of aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O. The samples were then calcined at 550 °C for 5 h under dry air flow. These calcined Beta-H and Beta supported Pt catalysts were denoted as Pt-O/Beta-H and Pt-O/Beta. After reduction of Pt-O/Beta-H and Pt-O/Beta under 5% H<sub>2</sub>/Ar flow (100 mL/min) at 500 °C for 2 h, the catalysts were denoted as Pt-R/Beta-H and Pt-R/Beta.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained with a RIGAKU Ultimate IV diffractometer using Cu K $\alpha$  radiation. Nitrogen sorption isotherms at  $-196$  °C were measured using a Micromeritics ASAP 2020M system. The surface area was calculated by using the Brunauer–Emmett–Teller (BET) method. The Si/Al ratios of the samples were determined by inductively coupled plasma (ICP) with a Perkin–Elmer plasma 40 emission spectrometer. The acidity of the samples was determined using the stepwise temperature-programmed desorption of ammonia automated chemisorption analysis unit (NH<sub>3</sub>-TPD) with a thermal conductivity detector (TCD) under nitrogen flow. X-ray photoelectron spectra (XPS) of the samples were recorded using a Thermo ESCALAB 250 with Al K $\alpha$  X-ray radiation for the X-ray source. The binding energies (BEs) were calibrated against Si2p (103.5 eV), Al2p (73.9 eV), and C1s (285.0 eV) peaks. Thermal gravimetric analysis (TGA) experiments were performed on a SDT Q600 V8.2 Build100 thermogravimetric

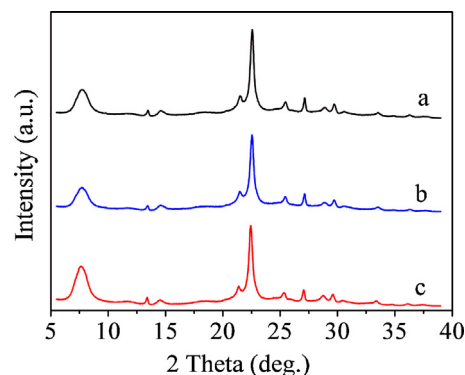


Fig. 1. XRD patterns of (a) Beta-H, (b) Pt-O/Beta-H, and (c) Pt-R/Beta-H samples.

analyzer. The scanning electron microscopy (SEM) images of the samples were recorded on a Hitachi SU 1510 apparatus. Transmission electron microscopy (TEM) experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 110 kV.

### 2.4. Catalytic evaluation

The catalytic combustion of toluene experiments were performed in a continuous flow fixed-bed microreactor at the atmospheric pressure and temperatures between 100 and 240 °C, consisting of a quartz tube (6 mm i.d.) that was filled with the catalyst. A typical experiment was performed using a catalytic bed of 100 mg of catalyst (0.45–0.90 mm size) and with total flow rate of feed stream at 100 mL/min, giving a space velocity (SV) at 60,000 mL/(g h). The feed gas containing 1000 ppm toluene was generated by bubbling standard air (79% N<sub>2</sub> + 21% O<sub>2</sub>) through a bottle containing pure toluene chilled in an ice-water isothermal bath, and then further diluted with another standard air stream before reaching the reaction bed. The concentrations of the toluene and oxidative products in the tail gas were analyzed by a gas chromatography (Kexiao, GC1690) equipped with a flame ionization detector (FID) using a 19091N-113 INNOWAX capillary column (Agilent, 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m) for toluene, and a gas chromatography (Kexiao, GC1690) equipped with a thermal conductivity detector (TCD) using a Carboxen packed column (JieDao, 2 m  $\times$  2 mm) for CO<sub>2</sub> and CO.

The conversion of toluene was obtained based on toluene consumption, calculated by the inlet and outlet concentration of toluene. The selectivity to CO<sub>2</sub> was calculated by toluene consumption and outlet concentration of CO<sub>2</sub>. The selectivity to side products was calculated by subtracting the selectivity to CO<sub>2</sub> from one. The catalytic activities were evaluated by the values of  $T_5$ ,  $T_{50}$ , and  $T_{98}$ , which were defined as the temperatures at 5%, 50%, and 98% of toluene conversion, respectively.

## 3. Results and discussion

### 3.1. Catalyst characterization

Fig. 1 shows the XRD patterns of Beta-H, Pt-O/Beta-H, and Pt-R/Beta-H samples, exhibiting well-resolved characteristic peaks associated with Beta zeolite structure. These results suggest that these samples are basically stable during the impregnation, calcination, and reduction. Fig. 2 shows the nitrogen sorption isotherms of Beta-H, Pt-O/Beta-H, and Pt-R/Beta-H samples, giving a step at a relative pressure ( $P/P_0$ ) of 0.4–0.95, which indicates the presence of mesoporosity in the samples. Correspondingly, these samples show BET surface areas and pore volumes at 432–483 m<sup>2</sup>/g and

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