Preparation and Investigation of Pd/Ti-SBA-15 Catalysts for Catalytic Oxidation of Benzene

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Published online 24 March 2010 in Wiley Online Library (wileyonlinelibrary.com). DOI 10.1002/ep.10427

The feasibility of Pd/Ti-SBA-15 catalysts in the elimination of benzene was explored comprehensively. The effects of the titanium incorporation on catalyst physicochemical property and activity were investigated by X-ray diffraction, N₂ adsorption/desorption, Fourier transform infrared spectroscopy, DRUV-vis, NH₃-TPD, scanning electron microscope, and transmission electron microscope techniques. Only a certain quantity of titanium can be incorporated into the support, and titanium has a positive influence on active phase dispersion. Titanium-modified catalysts possess larger pore diameter than the pure Pd/SBA-15 and titanium can introduce the acid sites to the support. The evaluation result shows that the titanium incorporation can noticeably improve the catalytic activity, and all evaluated catalysts possess excellent stability, without obviously activity loss during 60 h test. © 2010 American Institute of Chemical Engineers Environ Prog, 29: 435–442, 2010

Keywords: titanium-modified, SBA-15, mesoporous molecular sieves, VOC

INTRODUCTION

The emission of volatile organic compounds (VOCs) into atmosphere has a great negative impact on the environment and public health because of their toxic, mutagenic, and carcinogenic nature. Moreover, the VOCs can act indirectly as the ozone and smog precursors. As a consequence, proper control of VOCs emission is required. Many techniques have been developed to eliminate VOCs including

the non-destructive and destructive approaches. The non-destructive methods retain VOCs composition. In contrast, the destructive approaches (such as thermal incineration and catalytic oxidation) transform VOCs into inert or less dangerous compounds. However, thermal incineration consumes a large amount of energy and leads to lots of toxic byproducts although it is an effective approach to convert VOCs into CO₂ and H₂O [1]. In comparison with the thermal incineration, the catalytic oxidation is an energy-saving and high-efficiency technique. Furthermore, the selectivity of catalytic reaction could be controlled.

More attention has been paid to develop effective catalytic materials and improve their catalytic performances, such as noble metals and metal oxides catalysts [2, 3]. Microporous zeolites with uniform pores have been widely used as industrial catalysts for removing of VOCs [4]. However, these catalysts cannot effectively catalyze large VOCs molecules because of their relatively small pore size. Fortunately, the discovery of mesoporous silica materials with uniform pore diameter in the range of 2.0–10.0 nm (such as MCM-41) offers a good opportunity for silicate as versatile catalysts or supports for oxidation of large VOC molecules. However, the weak stability of these materials limits their extensive applications [5]. More recently, SBA-15 with uniform and large pore channels (more suitable for deal with bulky VOCs molecules), thick pore wall and high hydrothermal stability has been successfully synthesized [6]. Pure SBA-15 is inert in oxidation of VOCs, and many hetero-atoms have been successfully incorporated into SBA-15 in the past decades [7–10]. Yang *et al.* [11] synthesized the CuO/SBA-15 catalyst for catalytic oxidation of benzene. Mu *et al.* [3] have investigated the Co/Ce-SBA-15 materials and their catalytic activity

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Figure 1. A: Small-angle XRD patterns of (a) Pd/SBA-15, (b) Pd/Ti-SBA-15(80), (c) Pd/Ti-SBA-15(40), (d) Pd/Ti-SBA-15(20), and (e) Pd/Ti-SBA-15(10); B: Wide-angle XRD patterns of (b) Pd/Ti-SBA-15(80), (c) Pd/Ti-SBA-15(40), (d) Pd/Ti-SBA-15(20), and (e) Pd/Ti-SBA-15(10).

in elimination of benzene. The catalytic oxidation of benzene on two types of mesoporous Co/SBA-15 catalysts was reported by Li *et al.* [12]. It is well known that TiO_2 is good support for VOCs catalytic oxidation, which was extensively investigated in recent decades [13–15]. Zepeda *et al.* [16] revealed that the presence of Ti^{4+} ions could strengthen the metal-support interaction, and titanium atoms could provide better dispersion for active phases over the support [17, 18]. However, the Ti-modified SBA-15 mesoporous materials have been seldom reported in catalytic oxidation of benzene-like VOCs.

In this work, we attempt to direct synthesis the Ti-SBA-15 mesoporous support with high Ti content (the Si/Ti molar ratio = 10), and the feasibility of as-prepared materials in the elimination of benzene (a typical VOCs and widely used in a great number of chemical processes) was further investigated.

EXPERIMENTAL

Catalyst Preparation

Ti-SBA-15 samples with different Si/Ti molar ratios were synthesized using the P123 (Sigma-Aldrich) as the structure-directing agent, and using the tetrabutyl titanate (TBOT) and tetraethyl orthosilicate (TEOS) as titanium and silica sources, respectively. The typical synthesis procedure was as follows: 1 g of P123 was dissolved in 35 mL of HCl aqueous solution at pH 2.0 at room temperature, followed by addition of 2.3 mL of TEOS and mixed at 35°C. Then, a given amount of TBOT was added to the acidic solution under vigorous stirring at 35°C for 24 h. Then, the mixture was transferred into an autoclave and aged at 100°C for 48 h. The solid product was filtered and thoroughly washed with deionized water, and dried at 100°C overnight. Then the material was calcined in a muffle furnace at 500°C for 4 h with a heating rate of 5°C/min, and the mesoporous Ti-SBA-15 samples were finally obtained.

Pd/Ti-SBA-15 catalysts with a Pd loading of 0.3 wt % were prepared by impregnating these supports with a PdCl_2 aqueous solution and drying at 100°C

Figure 2. N_2 adsorption/desorption isotherms (A) and pore size distribution (B) of (a) Pd/Ti-SBA-15(10), (b) Pd/Ti-SBA-15(20), (c) Pd/Ti-SBA-15(40), (d) Pd/Ti-SBA-15(80).

overnight, and then being calcined at 500°C for 4 h and being reduced in a pure hydrogen stream (30 mL/min) at 480°C for 2 h. The solid products are denoted Pd/Ti-SBA-15(x), where x stands for the Si/Ti molar ratio. For comparison purposes, the Pd/ TiO_2 , Pd/SBA-15, Pd/Ti-SBA-15(y) (y stands for the calcinations time (1–8 h)), and Pd/Ti-SBA-15(z) (z stands for the calcinations temperature (400–800°C)) samples were also prepared. The pure TiO_2 was prepared according to the procedure reported by Wang [19], and the pure SBA-15 was synthesized following the same procedure as described above without adding the titanium source.

Catalyst Characterizations

Small-angle X-ray diffraction (XRD) patterns were recorded on a Rigaku TTR2 powder diffraction system using Cu $\text{K}\alpha$ radiation ($\lambda = 0.15418$) in the 2θ range of 0.7–7° with a scanning rate of 0.5°/min. The wide-angle XRD patterns were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu $\text{K}\alpha$ radiation in the 2θ range of 20–80° with a scanning rate of 4°/min. The exact Pd wt % in all calcined samples was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an OPTIMA 2000. The N_2 adsorption/desorption isotherms were measured at 77 K on a NOVA1200 gas sorption analyzer. All samples were degassed under vacuum at 300°C for 3 h before measurement. The infrared spectra were recorded on a Bruker Tensor 27 using DRIFT technique, scanned from 2000 to 600 cm^{-1} . All samples were ground with KBr and pressed into a thin wafer. Diffuse reflectance UV–vis spectra were collected on a Hitachi UV3000 spectrophotometer scanning from 190 to 600 nm. NH_3 -TPD was performed on a Micromeritics 2720. Typically, 0.1 g of sample was pre-treated in a helium stream (50 mL/min) at 300°C for 1 h and then cooled down to room temperature prior to adsorption of NH_3 (NH_3/He of 1:49 (v/v)) for 1 h. After saturated with NH_3 , the catalyst was flushed with He (50 mL/min) for 1 h at room temperature to remove the physisorbed NH_3 . After that, the desorption pattern was recorded from 150°C to 550°C at a heating rate of

Table 1. Physicochemical property of catalysts.

Catalysts	Si/Ti molar ratio	Pd* (wt %)	C _t ** (°C)	S _{BET} [†] (m ² /g)	D _v ^{††} (cm ³ /g)	D _p [‡] (nm)
Pd/TiO ₂	—	0.29	500	4.35	0.121	3.7
Pd/SBA-15	—	0.28	500	784.6	1.041	5.2
Pd/Ti-SBA-15	10	0.28	500	688.2	0.612	5.1
	20	0.29	500	736.4	0.832	5.8
	40	0.27	500	740.7	0.846	5.5
	80	0.28	500	761.2	0.898	5.2
	20	0.29	400	702.1	0.718	5.3
	20	0.29	600	729.6	0.793	5.7
	20	0.29	700	595.8	0.554	5.4
	20	0.29	800	565.4	0.513	5.3

*Actual Pd contents obtained by the ICP-OES analysis.

**Calcination temperature.

[†]BET specific surface area, which was calculated by the linear part of the BET equation ($P/P_0 = 0.05-0.25$).

^{††}Total pore volume obtained at $P/P_0 = 0.99$.

[‡]BJH pore diameter calculated from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

10°C/min. The SEM was performed on a Hitachi S-3000N instrument operating at 20 kV. TEM images were collected on a Hitachi H-7500 microscope operating at an accelerating voltage of 80 kV.

Catalytic Oxidation Activities

All evaluation experiments were performed in a continuous-flow fixed-bed reactor under atmospheric pressure. It consists of a 6 mm i.d. stainless steel tube that was placed in a tubular electrical furnace. The temperature of catalyst bed and tubular electric furnace were monitored automatically with E-type thermocouples, respectively. One air stream was passed through a saturator to make a mixed gas containing high concentration of benzene and then further diluted with another air stream before reaching the reaction bed. The total flow rate was set to be 300 mL/min with the benzene concentration of 1500 ppm by adjusting the two flow rates above.

In each test, 300 mg of catalyst (40–60 μ) was placed at the center of the reactor and the gas hourly space velocity (GHSV) for all tests was kept at 26,000 h⁻¹. Before each test, the catalytic bed temperature was risen to 130°C with the feed stream passing (no oxidation was detected) and stabilized for 30 min, and then the catalyst bed temperature was risen with a heating rate of 5°C/min to the next point and stabilized for 20 min prior to online analysis of the effluent gas composition in an Agilent gas chromatograph equipped with an FID and a TCD. The VOC concentrations in the feed and effluent streams were determined with the FID after being separated in an AB-GASPRO capillary column, and CO/CO₂ in the effluent stream were separated in a TDX-01 column and their concentrations were determined with the TCD.

Long-term stability tests (60 h) of Pd-SBA-15 and Pd/Ti-SBA-15(20) were carried out with the benzene feed concentration of 1500 ppm. The GHSV was fixed at 26,000 h⁻¹, and the operation temperature was kept at 200 and 240°C, respectively.

RESULTS AND DISCUSSION

XRD

Figure 1A shows that all Pd/Ti-SBA-15(x) samples display three well-resolved diffraction peaks, which can be indexed as the (100), (110), and (200) diffractions of the two-dimensional hexagonal mesostructure that match well with the pure SBA-15 [20], indicating that titanium did not destroy the original structure of the support. However, the structural order of support decreased with the increasing of Ti/Si ratio (Figure 1A) [21]. Moreover, the (100) peak moved from 0.98 to 0.84° when the Si/Ti molar ratio decreases (Figure 1A), indicating that the presence of Ti⁴⁺ in SBA-15 framework as the Ti—O bond distance is larger than the Si—O bond. Besides, both the calcination temperature and calcination time have negligible influences on the ordered mesoporous structure of SBA-15 (Supplementary material: Figure S1). The wide-angle XRD patterns (Figure 1B) reveal that the anatase TiO₂ begins to form in Pd/Ti-SBA-15(10), as the appearance of the diffraction peaks at $2\theta = 37.8, 48.4, 54.7, \text{ and } 63.5^\circ$ [22]. This result suggests that a limited amount of titanium can be incorporated into SBA-15 framework. Moreover, the diffraction peaks of Pd are visible in neither of curves.

N₂ Adsorption/Desorption

The results of N₂ adsorption/desorption are shown in Figure 2 and Table 1. As it can be observed in Figure 2A, all catalysts exhibit type IV adsorption/desorption isotherms with H1-type hysteresis loop, which are typical characteristic of mesoporous materials according to the IUPAC classification [23]. Figure 2A shows that the sharpness of the steep rises as the Si/Ti molar ratio increases from 10 to 80, indicating that the titanium atoms makes a broader mesopore size distribution as the sharpness of the adsorption branch suggests the uniformity of the mesopore size distribution [24]. This result can be verified by the

Figure 3. FT-IR spectra in the 600–2000 cm^{-1} range of (a) Pd/Ti-SBA-15(10), (b) Pd/Ti-SBA-15(20), (c) Pd/Ti-SBA-15(40), (d) Pd/Ti-SBA-15(80), and (e) Pd/SBA-15.

Figure 5. The NH_3 -TPD profiles of (a) Pd/Ti-SBA-15(10), (b) Pd/Ti-SBA-15(20), (c) Pd/Ti-SBA-15(40), (d) Pd/Ti-SBA-15(80), and (e) Pd/SBA-15.

Figure 4. DRUV-vis spectra of Pd/Ti-SBA-15(x) catalysts (A) and its differentiated curve (B): (a) Pd/Ti-SBA-15(10), (b) Pd/Ti-SBA-15(20), (c) Pd/Ti-SBA-15(40), and (d) Pd/Ti-SBA-15(80).

pore size distribution curves (Figure 2B). The experimental result shows that the specific surface area and total pore volume of Pd/Ti-SBA-15(x) decreased with the rising of the Ti/Si ratio. However, the Pd/Ti-SBA-15(20) possesses the largest average pore diameter (5.8 nm), and the average pore diameter decreased to 5.1 nm when there is a further decrease in the Si/Ti ratio, which may be because of the formation of TiO_2 crystal in pore channels (Figure 1B).

FT-IR, DRUV-vis, and NH_3 -TPD

Fourier transform infrared spectroscopy (FT-IR) and DRUV-vis were carried out as former reports illuminated that the Ti^{4+} ions could strengthen the

metal-support interaction, which can provide better dispersion for active phases [16–18]. Figure 3 shows that the peak at 1630 cm^{-1} is associated to the bending of $\text{H}-\text{O}-\text{H}$ from adsorbed water, and the broad peak at 1185 cm^{-1} refers to the asymmetrical stretching of $\text{Si}-\text{O}-\text{Si}$ within the mesoporous structure [25]. The peak at 820 cm^{-1} accounts for the asymmetrical stretching of SiO_4 groups. The peak at 970 cm^{-1} , with the intensity increasing with the Ti/Si ratio increase, may be attributed to the stretching mode of SiO_4 unit bonded to the Ti^{4+} ion [26]. This indicates that titanium is positioned in the SBA-15 framework (see Figure 3). The DRUV-vis patterns reveal that Pd/Ti-SBA-15(x) samples possess an adsorption peak at 216 nm, and its intensity decreased with the rising of Si/Ti ratio, which is directly connected with the framework Ti^{4+} with tetrahedral coordination [25]. An absorption peak with the maximum at 266 nm is also found for all curves, while the Pd/Ti-SBA-15(10) possesses a broader peak than the other samples. This adsorption peak is ascribed to the presence of a low-energy charge-transfer transition between tetrahedral oxygen ligands and central Ti^{4+} ions [27]. Figure 4B shows that the Pd/Ti-SBA-15(10) owns an absorption band with the maximum at 297 nm, indicating the presence of TiO_2 species [23]. Figure 5 shows that the Pd/SBA-15 sample possesses no desorption peak of NH_3 and the framework titanium could introduce the weak acid sites to the support, where intensities increase in accordance with increase of amount of NH_3 adsorbed, i.e., from 0.68 mol NH_3/kgcat for the sample having Si/Ti = 20, and up to 1.87 mol NH_3/kgcat for the sample with Si/Ti = 80 molar ratio (Table 2) due to the presence of unsaturated Ti^{4+} sites [28]. Moreover, the strong acid sites begin forming (1.21 mol $\text{NH}_3/\text{kg cat.}$) when the Si/Ti ratio = 10.

Table 2. Total acidity and density of acid sites of the catalysts.

Catalysts	S_q^* (mol NH ₃ /kgcat)	W_q^{**} (mol NH ₃ /kgcat)	$T^\dagger$ (mol NH ₃ /kgcat)
Pd/Ti-SBA-15(10)	1.21	0.31	1.52
Pd/Ti-SBA-15(20)	0.17	1.87	2.04
Pd/Ti-SBA-15(40)	—	0.98	0.98
Pd/Ti-SBA-15(80)	—	0.68	0.68

*Amount of desorbed NH₃ on strong acid sites.

**Amount of desorbed NH₃ on weak acid sites.

†Total amount of desorbed NH₃.

SEM and TEM

Figure 6A reveals that Pd/Ti-SBA-15(20) sample presents a large bunched, pipe-like structure with relatively uniform morphology, which is the typical morphology of ordered mesoporous SBA-15 [29]. Figure 6B shows that the Ti-SBA-15 (Si/Ti molar ratio = 20) possesses well developed parallel pore channels with uniform diameter of ca. 7 nm, indicating that the incorporation of titanium does not influence the original structure of SBA-15. Figure 6C shows the TEM image of Pd/SBA-15, which is easy to find that the Pd/SBA-15 shows straight pore channel with uniform pore diameter of ca. 5–6 nm, and the palladium particles are well dispersed on it with an average diameter of ca. 6.7 nm (Figure 6E). Figure 6D shows the TEM profile of Pd/Ti-SBA-15(20) and the palladium atoms are better dispersed on it with a mean diameter of ca. 5.5 nm (Figure 6F). On the other hand, the catalyst structure is unstable (BET surface area decreases from 729.6 to 565.4 m²/g) and the mean Pd particles over the support increase about 2 nm when the calcinations temperature increases from 600 to 800°C, as can be seen in Table 1 and Figure 6H.

Catalytic Oxidation of Benzene

The conversion values in the plot are calculated based on the concentration of benzene in the inlet and outlet gas. No benzene conversion was detected below 500°C in the absence of catalysts, and the products detected in the effluent are only CO₂ and H₂O. Figure 7A obviously reveals that all the Pd/Ti-SBA-15(x) samples possess higher activity than the Pd/TiO₂ and Pd/SBA-15, indicating that titanium is beneficial for enhancing the catalytic activity. Among these catalysts, Pd/Ti-SBA-15(20) owns the best activity (followed by Pd/Ti-SBA-15(10)), which can complete the elimination of benzene at 240°C, and this reaction temperature is lower than the other SBA-15 supported catalysts [3, 11, 12]. Some decrease could be observed when further raising the Si/Ti molar ratio from 20 to 80. This result can be explained as follows: Firstly, the TEM results reveal that the proper level of titanium can provide better dispersion of active phase, and this conclusion was gained on other catalysts [16–18, 30]. Secondly, the Pd/Ti-SBA-15(20) has the largest average pore diameter (Table 1). As a consequence, ben-

zene molecules are much easier to enter the pore channels and react on the active sites. On the other hand, the larger pore size is also beneficial for the diffusion and desorption of reaction products, such as CO₂ and H₂O, during catalytic reactions. Thirdly, the incorporation of titanium could generate lots of acid sites (see Figure 5), which are good for the active sites dispersion. As for the active phase in VOCs oxidation over Pd-supported catalysts, i.e., Pd⁰, Pd²⁺, or a mixed Pd⁰/Pd²⁺ phase, most investigators propose that Pd²⁺ is active in hydrocarbons combustion, and the presence of Pd⁰ can enhance the catalytic activity by providing more active sites for VOCs dissociation and allowing the overall reaction to proceed more rapidly [31, 32]. As known, the two-step redox model (according to the following Eqs. 1 and 2) was proposed for oxidation of hydrocarbons (HCs) over supported Pd catalysts [33]:

That is, the oxidized catalyst is reduced by HC, and HC is oxidized to CO₂ on the catalyst surface and then CO₂ is desorbed from the surface to the gas stream.

where k_i is kinetic constant for the reaction between chemisorbed oxygen and VOCs, k_{oi} is the kinetic constant for the non-equilibrium dissociative adsorption of oxygen on catalyst surface, and α stands for the stoichiometric coefficient for the total combustion reaction (mol O₂/mol VOC). In the second step, the catalyst redox center is oxidized by O₂ to recover the active oxidized centers through adsorption and dissociation of O₂ on the Pd surface. The larger pore size is proposed to promote desorption of CO₂ from the catalyst surface, therefore step (1) could be directly facilitated, and simultaneously more reduced catalytic centers are released and reaction (2) is speeded up. The evaluation result of Pd/Ti-SBA-15(y) and Pd/Ti-SBA-15(z) samples shows that the calcinations temperature has more obvious effect on catalytic activity

Figure 6. SEM, TEM patterns of catalysts, and Pd particle size distribution over the supports. SEM: (A) Pd/Ti-SBA-15(20); TEM: (B) Ti-SBA-15(20), (C) Pd/SBA-15, (D) Pd/Ti-SBA-15(20), (G) Pd/Ti-SBA-15(800), and (H) Pd/Ti-SBA-15(600); (E) Pd particle size distribution over Pd/SBA-15, (F) Pd particle size distribution over Pd/Ti-SBA-15(20), (I) Pd particle size distribution over Pd/Ti-SBA-15(600), and (J) Pd particle size distribution over Pd/Ti-SBA-15(800).

Figure 7. Conversion curves of benzene over various catalysts. (B: the Pd/Ti-SBA-15 catalysts with calcinations temperature and Si/Ti molar ratio were fixed to 500°C and 20, respectively; C: the Pd/Ti-SBA-15 catalysts calcinations time and Si/Ti molar ratio were fixed to 4 h and 20, respectively).

than calcinations time (Figures 7B and 7C), and the best calcinations time and temperature are 2–4 h and 600°C, respectively.

Stability Tests of Catalysts

The stability of the catalysts is crucial in application because the reaction products (such as water) could possibly cause the change of the catalysts surface, decreasing the catalytic activity. Further tests for the durability of Pd/SBA-15 and Pd/Ti-SBA-15(20) catalysts were performed (Figure 8). The reaction temperature kept at 240 and 200°C, respectively. The evaluation result reveals that the Pd/SBA-15 and

Figure 8. Stability tests with time-on-stream over different catalysts: (a) Pd/SBA-15; (b) Pd/Ti-SBA-15(20).

Pd/Ti-SBA-15(20) have no noticeable activity loss, indicating that the catalytic performance of both catalysts is well-sustained. As a consequence, the as-prepared Ti-modified mesoporous material is a promising catalyst for the potential application in catalytic oxidation of benzene-like VOCs.

CONCLUSIONS

Pd/Ti-SBA-15(x) catalysts with various Ti contents have been used for catalytic elimination of benzene, and the feasibility of Ti incorporation was explored in detail in this work. The characterization results reveal that all supports maintain their original structure after Ti incorporation and the framework Ti leads to a better dispersion of active redox Pd. Moreover, Pd/Ti-SBA-15(x) catalysts possess narrow pore size distribution, high specific surface area, and total pore volume. The framework titanium mainly located in the tetrahedral position and anatase TiO₂ forms in the pore channels of Pd/Ti-SBA-15(10). In addition, titanium could generate the strong and weak (Si/Ti = 10) acid sites in the catalysts. The evaluation results reveal that Pd/Ti-SBA-15(x) catalysts show higher activity than Pd/TiO₂ and Pd/SBA-15, and Pd/Ti-SBA-15(20) possesses the best activity and an excellent durability. Moreover, the calcinations temperature has more obvious effect on the activity than the calcinations time, and the best calcinations time and temperature are 2–4 h and 600°C, respectively.

ACKNOWLEDGMENTS

The support from the National Science Fund for Distinguished Young Scholars (No. 20725723), the National Basic Research Program of China (No. 2010CB732300), and National High Technology

Research and Development Program of China (No. 2006AA06A310) are gratefully acknowledged.

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