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Article

High performance Pd catalysts supported on bimodal mesopore silica for the catalytic oxidation of toluene

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ABSTRACT

A series of bimodal mesoporous silica (BMS-*x*)-supported Pd catalysts were successfully prepared by a facile sol-gel approach, followed by an impregnation method. The synthesized catalysts were characterized by several analytical techniques and the oxidation of toluene was used to evaluate their catalytic performance. Textural analysis showed that all samples had high surface areas ($\sim 1000 \text{ m}^2/\text{g}$), large pore volumes ($\sim 1.2 \text{ cm}^3/\text{g}$) and uniform mesopore size ($\sim 2.6 \text{ nm}$). Defining the level of ammonia solution to within a certain range resulted in the catalysts possessing a typical bimodal mesoporous structure with an intraparticle framework mesopore and an interparticle textural mesopore (18–40 nm). Transmission electron microscopy observations and CO chemisorption results revealed that this unique bimodal mesoporous structure helped to decrease the particle size of Pd nanoparticles and could further enhance their dispersion. Activity tests revealed the Pd/BMS-5-Pd/BMS-20 catalysts with a bimodal mesopore structure possessed superior catalytic performance for the oxidation of toluene compared to Pd/BMS-30 with a unimodal mesopore structure. More importantly, compared with the Pd/MCM-41 and Pd/MCM-48 catalysts, Pd/BMS-15 had improved hydrothermal stability and catalytic performance at a high gas hourly space velocity of 70000 h^{-1} . These results indicate the potential application of the catalysts for the elimination of volatile organic compounds.

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1. Introduction

Volatile organic compounds (VOCs), an important class of air pollutants emitted from many industrial processes and transportation activities [1,2], are harmful to human health and the environment because of their toxic, carcinogenic, mutagenic, and teratogenic nature [3–5]. Several technologies are currently used to eliminate VOCs from the air. Among them, catalytic oxidation has been recognized as one of the most promising methods to address this matter [6]. A key issue in catalytic oxidation is the synthesis of high-performance cata-

lysts. Supported noble metal (e.g., Pd, Pt and Rh) and transition metal oxide catalysts have been extensively studied with regard to VOC oxidation.

Pd-based catalysts are abundantly used because of their superior activity, high thermal stability and hydrothermal tolerance [7,8]. Catalyst support design is an important factor when optimizing the performance of Pd-based catalysts. The morphology and textural characteristics of the support have a direct impact on the size, shape and loading level of the Pd particles supported on the catalyst [9]. In addition, the pore size of the support material is an important factor to consider when

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designing a catalyst as this property has a direct impact on the diffusion of the reactant/product molecules. Since the discovery of the mesoporous M41 family materials, especially MCM-41 and MCM-48, there has been a wealth of research using such materials as catalyst supports because of the ability to specifically tailor the physico-chemical and textural properties [10–13]. However, the pore size of these materials is often only several nanometers (2–5 nm), which dramatically limits ingress and diffusion of guest molecules to the active sites located inside the pore and resulting in low catalytic activity.

In recent years, solid materials with bimodal mesoporous distributions have received considerable attention [14–17]. Compared with traditional mesoporous M41s possessing a single pore distribution, the secondary pores in bimodal porous structure materials offer greatly improved access for molecules to diffuse into with less resistance [18,19]. At the same time, the advantage of bimodal porous materials has also been confirmed from simulations in the Knudsen diffusion regime, whereby molecules are able to ingress/egress mesopores but experience an attendant diffusion limitation [20–22]. The superiority of bimodal porous materials has been demonstrated in the areas of Fischer-Tropsch synthesis [23], photocatalysis [24], methane combustion [25] and CO preferential oxidation [26]; however, to the best of our knowledge, there are no reports linking the benefits of bimodal porous materials to catalytic oxidation of VOCs.

In this study, we synthesized a series of bimodal mesoporous silica materials (BMS-*x*) by a facile sol-gel approach. Thereafter, Pd/BMS-*x* catalysts were prepared via an impregnation method. Toluene was chosen as the VOC probe molecule because of its presence in industrial and automotive emissions, in addition to its high toxicity to human health. The primary purpose of the study was to investigate the relation between catalytic activity and the textural properties of the supports. Characterization was performed by X-ray diffraction (XRD), N₂ adsorption-desorption, field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and CO chemisorption.

2. Experimental

2.1. Catalyst preparation

The synthesis procedure has been reported elsewhere [27,28]. First, 2.1 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 40 mL of deionized water, with stirring at room temperature. After the solution became clear, 7 mL of tetraethyl orthosilicate (TEOS) was added dropwise to obtain a mixed solution. After 1 h, a desired amount of 2 mol/L ammonia solution was added to form a solution with a varying pH. The solution became progressively viscous and finally developed into a white gel, after which it was kept under static conditions for 5 h at room temperature for further silica condensation. Subsequently, the gel mixture was filtered and washed repeatedly with deionized water until a neutral pH was obtained. The white product was dried at 70 °C overnight to remove moisture and calcined at 550 °C for 6 h to remove the

surfactant CTAB at a heating rate of 3 °C/min. To study the effect of aqueous ammonia on the structure of synthetic silica materials, the same experiment was repeated with varying quantities (5–30 mL) of 2 mol/L aqueous ammonia. The samples were referred to as BMS-5, BMS-10, BMS-15, BMS-20 and BMS-30, wherein the numeric values refer to the amount (in mL) of 2 mol/L aqueous ammonia. For the purpose of comparison, MCM-41 and MCM-48 supports were synthesized according to procedures described elsewhere [11].

Pd-supported catalysts with a Pd loading of 0.5 wt% were prepared via an impregnation method with an aqueous solution of PdCl₂. The impregnated solids were dried at 100 °C overnight and calcined at 500 °C for 3 h (heating rate of 3 °C/min). Finally, the catalysts were reduced in a pure H₂ stream with a 50 mL/min flow rate at 400 °C for 2 h.

2.2. Catalyst characterization

XRD patterns were recorded on a PANalytical X'Pert PRO powder diffraction system using Cu K α radiation (λ = 0.15418 nm) in the 2 θ range of 0.7°–5° (scanning rate of 0.5°/min) and 10°–80° (scanning rate 4°/min), respectively. The textural properties of the samples were analyzed from N₂ adsorption-desorption isotherms using a Micromeritics ASAP 2020 gas absorption analyzer. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method and the pore volume and pore size distribution were estimated from the Barrett-Joyner-Halenda (BJH) model. FE-SEM micrographs were taken on a Hitachi S-4800 microscope. TEM micrographs were recorded on a Hitachi H-7500 microscope operating at an accelerating voltage of 80 kv. The exact Pd loading in all synthesized samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer OPTIMA 8300. Pd dispersion of catalysts was determined by CO chemisorption using a dynamic pulse method on a Micromeritics, AutoChem 2920. The samples (50 mg, 40–60 mesh) were reduced at 300 °C for 30 min in 5% H₂/Ar (50 mL/min), followed by flushing in He (50 mL/min) for 30 min. After cooling to room temperature under a He flow, a pulse of 5% CO/He were introduced to the catalyst.

2.3. Catalytic activity test

The activity tests of all catalysts were evaluated using a continuous-flow fixed-bed stainless steel reactor (6 mm i.d.) under atmospheric pressure. Each run contained a specific volume of catalysts in the form of 40–60 mesh particles. To create the stream containing toluene, one stream of pure air was passed through a boat-shaped saturator in an ice-bath to generate a mixed gas containing toluene of high concentration, which was then further diluted by another stream of pure air prior to reaching the catalyst bed. The total flow rate was set to 350 mL/min with a concentration of ca. 1000 ppm by adjusting the two flow rates. The reaction temperature was controlled by a tubular electric furnace and the temperature of the catalyst bed was monitored automatically by E-type thermocouples. In each test, the reaction bed temperature was raised to 80 °C with the

stream passing and the catalyst was pretreated in the reactant mixture flow for 1 h. Thereafter the reaction bed temperature was increased to the next desired temperature and stabilized for 30 min. The reactants and reaction products were monitored on-line using an Agilent 6820 gas chromatograph (GC), equipped with a TCD (TDX-01) column and a FID (AB-GASPRO capillary column). The stability tests of the catalysts were performed under similar conditions as the activities evaluation. In each run, the catalyst bed was first heated to a desired temperature, which was maintained for ~60 h. Regarding water vapor introduction, 11 vol% of H₂O was introduced by passing the feed stream through a water saturator at room temperature.

3. Results and discussion

3.1. Textural properties of synthesized catalyst

Figure 1(a) displays the small-angle powder XRD diffractograms of all synthesized catalysts, which provide information on the long-range ordering of the mesopores. As shown in Fig. 1(a), all samples possessed a similar strong and broad diffraction peak at ~2.0°. This can be indexed as the (100) reflection on the basis of the existence of a MCM-41-like hexagonal cell [29], indicating the presence of uniform mesoporosity on all catalyst supports. Wide-angle XRD ($2\theta = 10^\circ$ – 90°) measure-

ments were performed and the diffractograms of all synthesized catalysts are shown in Fig. 1(b). Broad diffraction peaks at 2θ at ~22° can be observed in all samples, which are attributed to amorphous silica. No Pd species (Pd⁰, PdO) were observed in any samples, indicating that the Pd species were smaller and highly dispersed [30].

The porous structure and specific surface area of the catalysts were investigated based on N₂ adsorption measurements. The N₂ adsorption-desorption isotherms and their corresponding pore size distributions are shown in Fig. 2, and the relative structural parameters are summarized in Table 1. As shown in Fig. 2(a), all samples exhibited typical type IV isotherms, as expected for common mesoporous silica; however, they possessed variation in their capillary condensation steps. Only one obvious capillary condensation step in the region of p/p_0 0.3–0.45 is observed for the Pd/BMS-30 sample, suggesting that this support is largely composed of a single mesoporous structure (Fig. 2(b)). For the other samples, two capillary condensation steps are clearly observed in the p/p_0 regions of 0.4–0.75 and 0.8–0.95, respectively, indicating the presence of a bimodal mesopore. As indicated in the pore size distribution (Fig. 2(b)), the distribution of the textural mesopores is concentrated in the range of 18–45 nm. In addition, all samples had a high specific surface area greater than 1000 m²/g and no significant differences in the specific surface area and total pore

Fig. 1. Small-angle (a) and wide-angle (b) XRD diffraction patterns of Pd/BMS-*x* catalysts.

Fig. 2. N₂ adsorption-desorption isotherms (a) and pore size distribution curves (b) of Pd/BMS-*x* catalysts.

Table 1Physical and textural properties of Pd/BMS-*x* catalysts.

Catalyst	S_{BET}^a (m^2/g)	V_p^b (cm^3/g)	$D_{\text{p(small)}}^c$ (nm)	$D_{\text{p(large)}}^c$ (nm)	d_{100}^d (nm)	a_0^e (nm)
Pd/BMS-5	1024	1.24	2.64	22.36	4.59	5.30
Pd/BMS-10	1112	1.25	2.64	22.36	4.53	5.23
Pd/BMS-15	1232	1.46	2.64	18.91	4.34	5.01
Pd/BMS-20	1145	1.72	2.64	45.29	4.43	5.12
Pd/BMS-30	1243	1.08	2.66	—	4.32	4.99

^aBET specific surface area calculated. ^bTotal pore volume estimated at $p/p_0 = 0.99$. ^cBJH pore diameter calculated from the desorption branch. ^dInterplanar spacing of the (100) plane from XRD. ^eLattice parameter, $a_0 = 2d_{100} / \sqrt{3}$.

volume were observed between samples (Table 1).

3.2. Catalytic activity and stability tests

The catalytic performances of the synthesized Pd/BMS-*x* catalysts for toluene oxidation at a gas hourly space velocity (GHSV) of 42000 h^{-1} are shown in Fig. 3 and Table 2. In all tests, CO_2 and H_2O were found to be the only products, indicating that toluene can be completely oxidized over these catalysts. The Pd/BMS-5–Pd/BMS-20 catalysts, with a bimodal mesopore structure, clearly had a higher catalytic activity than the Pd/BMS-30 catalyst with only a unimodal mesopore structure for the total catalytic oxidation of toluene. The T_{90} values (the reaction temperature at which toluene conversion was 90%) on the Pd/BMS-5–Pd/BMS-20 catalysts was $\sim 240^\circ\text{C}$. At the same reaction temperature, the Pd/BMS-30 catalyst could only achieve a conversion of $\sim 22\%$, demonstrating the important promotional role of the support pore structure in enhancing the catalytic performance. Among the bimodal mesoporous catalysts, Pd/BMS-15 produced a slightly better performance, with a T_{90} of 228°C for the oxidation of toluene.

The catalytic stability of Pd/BMS-15 was further tested at 250°C for 60 h, and the result is shown in Fig. 4. No significant deactivation in catalytic activity was observed within 60 h during the on-stream reaction experiments. In addition, the XRD pattern of the used Pd/BMS-15 catalyst was similar to that of the fresh one. No noticeable decrease was observed in the specific surface area ($1019 \text{ m}^2/\text{g}$) of the used catalysts. With re-

Fig. 3. Conversion profiles of toluene catalytic oxidation over Pd/BMS-*x* catalysts.

Table 2Properties and catalytic performances of Pd/BMS-*x* catalysts.

Catalyst	Pd loading ^a (wt%)	Dispersion ^b (%)	Toluene oxidation	
			T_{50}^c ($^\circ\text{C}$)	T_{90}^c ($^\circ\text{C}$)
Pd/BMS-5	0.30	41	226	247
Pd/BMS-10	0.34	41	223	246
Pd/BMS-15	0.41	69	218	228
Pd/BMS-20	0.35	39	220	238
Pd/BMS-30	0.40	27	259	286

^aPd actual content of samples determined by ICP-OES (wt%).

^bDispersion estimated from CO chemisorptions.

^cTemperatures at which 50% and 90% conversion of toluene.

gard to porosity, used catalysts still maintained bimodal mesoporous structure characteristics. These results demonstrate that the Pd/BMS-15 catalyst was catalytically stable.

3.3. TEM and FE-SEM images of catalysts

Figures 5 and 6 show the SEM and TEM images of BMS-15 and BMS-30 supports and the corresponding Pd/BMS-15 and Pd/BMS-30 catalysts. The SEM images (Fig. 5(a, b)) clearly show that BMS-15 support contains disordered sponge-like large mesoporous channels. TEM images (Fig. 5(c, d)) further show the coexistence of a bimodal mesoporous structure and illustrates that the formation of large mesoporous channels was mainly because of the packing of primary particles. Nevertheless, the BMS-30 support had a distinctly different morphology from the BMS-15 support, with particle-stacking characteristics (Fig. 5(e)) and the corresponding particle size also had a broad distribution (Fig. 5(f, g)).

For the Pd/BMS-15 catalyst, Pd nanoparticles with a uniform size and high density were homogeneously deposited on the BMS-15 support and no larger agglomerated particles were observed (Fig. 6(a, b)). The size of the supported Pd nanoparticles was $\sim 3 \text{ nm}$ on average. However, Pd nanoparticles displayed a different dispersion behavior on the Pd/BMS-30 catalyst. Irregular and relatively large particles were present on the BMS-30 support and the agglomeration of Pd particles is clearly discernable (Fig. 6(c, d)). Moreover, the Pd nanoparticles were significantly larger for Pd/BMS-30 ($\sim 8\text{--}17 \text{ nm}$) than Pd/BMS-15.

Fig. 4. Stability test for toluene catalytic oxidation over Pd/BMS-15 catalyst.

Fig. 5. SEM and TEM images of BMS-15 (a–d) and BMS-30 (e–g) supports.

3.4. Pd dispersion in catalysts

Pd dispersion was determined by CO chemisorption and the results are summarized in Table 2. The Pd/BMS-30 catalyst had a relatively low Pd dispersion (27%), while Pd/BMS-5-Pd/BMS-20 catalysts had dramatically improved Pd dispersion (39%–69%). The Pd/BMS-15 catalyst had the highest Pd dispersion (69%). In most cases, the specific surface area of the support is recognized as the crucial factor in metal dispersion. Moreover, metal dispersion has been reported to be closely related to the support structure [31,32]. Therefore, although having the highest specific surface area, the BMS-30 support with a unimodal mesopore structure still hinders uniform distribution of Pd during impregnation and suffers from sintering when subjected to subsequent thermochemical processing

[33]. Such factors are unfavorable for the dispersion of Pd particles. In contrast, the bimodal mesoporous structure supports provide both high surface area and pore volume sufficiently to enhance uniformity of the Pd precursor throughout the mesopore channels, limiting migration and agglomeration of the Pd nanoparticles. Clearly, increasing the dispersion of the Pd species exposes toluene to more Pd sites on the catalyst and therefore significantly improves catalytic activity.

3.5. Comparison of the catalytic performance of Pd/MCM catalysts

The catalytic activity of the Pd/MCM-41 and Pd/MCM-48 catalysts (their textural properties are shown in Fig. 7) was further evaluated and compared with that of Pd/BMS-15, and the results are shown in Fig. 8. Under a GHSV of 42000 h⁻¹, all three catalysts had a similar catalytic activity, with 90% toluene conversion at 225–230 °C (Fig. 8(a)). However, after increasing the GHSV to 70000 h⁻¹, Pd/BMS-15 exhibited a remarkably higher catalytic activity than the Pd/MCM-41 and Pd/MCM-48 catalysts, as shown in Fig. 8(b). The T_{90} over Pd/BMS-15 was 230 °C—an insignificant increase compared with the T_{90} value at a GHSV of 42000 h⁻¹. The catalytic activity of Pd/MCM-41 and Pd/MCM-48 clearly decreased at a GHSV of 70000 h⁻¹, with T_{90} increasing by 23 and 39 °C, respectively.

To examine the effect of water vapor on catalytic activity, 11 vol% of water vapor was introduced to the reaction system. As shown in Fig. 9, the introduction of water vapor at 250 °C under a GHSV of 42000 h⁻¹ had dramatic effects on the catalytic performance among the three catalysts. For the Pd/MCM-41 and Pd/MCM-48 catalysts, the conversion of toluene decreased by 14% and 9% respectively, while the catalytic activity of Pd/BMS-15 remained stable—the conversion of toluene remained at 99% during the 500 min on-stream reaction experi-

Fig. 6. SEM and TEM images of the Pd/BMS-15 (a,b) and Pd/BMS-30 (c,d) catalysts.

Fig. 7. XRD patterns (a) and N_2 adsorption-desorption isotherms (b) of Pd/MCM-41 and Pd/MCM-48.

Fig. 8. Conversion profiles of toluene catalytic oxidation over Pd/MCM-41, Pd/MCM-48 and Pd/BMS-15 at different GHSV: (a) GHSV = 42000 h^{-1} ; (b) GHSV = 70000 h^{-1} .

ments. In the presence of water vapor, a competitive adsorption of water vapor, toluene and oxygen molecules occurred on the surface of the catalyst. In relation to the Pd/MCM-41 and Pd/MCM-48 catalysts, toluene and oxygen molecules experience diffusion limitations when attempting to access the pores in the presence of a large amount of water vapor than for Pd/BMS-15, with its unique bimodal mesoporous structure. Furthermore, the continual decrease of catalytic activity of

Pd/MCM-41 and Pd/MCM-48 catalysts could be attributed to the collapse of MCMs structure.

3.6. Discussion

3.6.1. Mechanism for the synthesis of bimodal mesoporous silica

The formation mechanism of the bimodal mesoporous silica can be simplified as follows. TEOS was first hydrolyzed to form monomeric and oligomeric silicate anions. The surfactant head group of the CTA micelle (positively charged) and the monomeric/oligomeric silicate ions (negatively charged) interact to form a micelle-encapsulated silica cluster. These micelle-encapsulated silica clusters react with existing adjacent particles to finally form a bridged interconnected textural mesostructure. The variation in the textural mesoporosity of samples is related to the relative rates of hydrolysis and condensation of TEOS, which influenced the size and packing geometry of the primary silica particles. Increasing the ammonia/silica molar ratio increases the hydrolysis and condensation rates accordingly resulting in the formation of larger silica primary particles, loosely bridged to other primary particles forming a larger textural porosity. From the N_2 adsorption-desorption isotherms of the Pd/BMS-5–Pd/BMS-20 catalysts, the first step in the p/p_0 region of 0.4–0.75 could be related to the capillary condensation of N_2 inside the intraparticle

Fig. 9. Effect of water vapor on toluene catalytic oxidation over Pd/MCM-41, Pd/MCM-48 and Pd/BMS-15. Reaction conditions: 250°C, 42000 h^{-1} , 11 vol% H_2O .

mesopores belonging to the typical surfactant-templated silica materials. The pores, with a diameter of ~ 2.6 nm, were predominantly constructed with negatively charged silicates and positively charged CTA micelles. The second sharp step, at a high relative pressure ($p/p_0 > 0.8$), implies the coexistence of textural mesopores, corresponding to the filling of the interparticle spaces among the nanoparticles. The secondary pore size was highly dependent on the rate of hydrolysis and condensation of TEOS and was mainly controlled by the ammonia/silica molar ratio [28,34]. As shown in Table 1, the size of textural mesopores changed from 18 to 30 nm with an increase in the ammonia/silica molar ratio.

3.6.2. Effect of the catalyst structure on catalytic performance

The oxidation of VOCs is a typical gas–solid catalysis reaction, which takes place at the interface boundary of the solid catalyst and gas reactants (O_2 , VOCs). In a typical gas–solid catalysis reaction, five steps are necessary: (1) external diffusion of reactants, (2) internal diffusion of reactants, (3) surface reaction and the formation of products, (4) internal diffusion of products and (5) external diffusion of products. During the whole process, the catalytic efficiency of the catalyst is strongly influenced by the structure and physical state of the catalysts. As the structural characteristics affect the dispersion of the active phase, Pd, determining molecular mobility is important to assess the diffusion of reactants and products. Therefore, in contrast to the Pd/BMS-30 catalyst, the reason that the bimodal mesopore catalysts have a higher catalytic activity is that they possess uniform intraparticle mesoporosity in addition to interconnected sponge-like interparticle mesoporous channels. This unique structure can facilitate the fast diffusion and transport of reactants and products, which reduces the diffusion limitations of reactants to the inner surface of the catalyst and increases the accessibility of the reactants to the active sites [33,35]. Under the higher GHSV, the diffusion of reactants and products on the catalyst was the main factor that deter-

mined the catalytic performance [36], which explains the excellent performance of Pd/BMS-15 compared with Pd/MCMs in the catalytic oxidation of toluene at the higher GHSV.

4. Conclusions

A series of bimodal mesoporous silica (BMS-*x*)-supported Pd catalysts were successfully synthesized. The synthesized catalysts possessed a bimodal mesopore distribution, including an intraparticle framework mesopore (~ 2.6 nm) and interparticle textural mesopore (18–40 nm). This unique bimodal structure had a significant effect on their catalytic performance. The Pd/BMS-15 catalyst exhibited enhanced performance in the oxidation of toluene, with a T_{90} of 228 °C. Compared with the Pd/MCM-41 and Pd/MCM-48 catalysts, Pd/BMS-15 displayed improved hydrothermal stability and catalytic performance at a high GHSV of 70000 h^{-1} . The superior catalytic activity was mainly related to the enhanced uniform dispersion of the active Pd species together with increased diffusion of reactants and products.

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Graphical Abstract

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Bimodal mesoporous silica supported Pd catalysts showed high activity and stability for the catalytic oxidation of toluene under high gas hourly space velocity making these catalysts promising for elimination of volatile organic compounds.

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双介孔硅基材料负载Pd催化剂上甲苯氧化性能的研究

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摘要: 催化氧化技术是挥发性有机物(VOCs)减排与控制的主流技术之一, 其关键之处在于高效催化材料的研究与开发, 负载型贵金属催化材料由于其低温下优越的VOCs催化氧化性能, 受到国内外研究者的广泛关注. 对于负载型催化剂而言, 载体的性质直接影响活性相的分散, 反应物和生成物的扩散与吸脱附, 是影响负载型催化剂性能的主要因素. 近年来, 多级孔结构硅基材料由于具有多级的孔道结构、高比表面积和大的孔体积, 逐渐成为VOCs催化氧化材料的研究热点.

本文采用溶胶凝胶法和浸渍法制备了系列双介孔结构硅基材料负载Pd催化剂(Pd/BMS-*x*), 通过控制合成过程中氨水的用量以调节催化剂的介孔结构分布. X射线衍射(XRD)结果表明, 所合成的Pd/BMS-*x*催化剂在~2.0°的衍射峰, 类似于MCM-41的(100)晶面衍射峰, 表明所有的样品均具有有序的介孔结构. N₂吸脱附实验表明所有样品的比表面积均高于1000 m²/g, 孔径分布表明Pd/BMS-30样品为单一介孔结构, 而Pd/BMS-5~Pd/BMS-20样品具有2.64 nm以及18–45 nm范围内的双介孔结构, 且Pd/BMS-15样品介孔分布较为集中. Pd/BMS-*x*催化剂上甲苯催化氧化性能测试表明, 双介孔结构的Pd/BMS-5~Pd/BMS-20催化剂上甲苯催化氧化活性远高于单一介孔结构的Pd/BMS-30催化剂, 表明载体结构对催化剂性能有重要影响. 其中, Pd/BMS-15催化剂性能最佳(*T*₉₀为228 °C)且具有较强的稳定性, 250 °C条件下, 反应持续60 h催化剂未见明显失活. SEM和TEM结果表明, Pd/BMS-15催化剂中Pd高度分散于载体上, 平均粒径在~3 nm左右. 而Pd/BMS-30催化剂中Pd颗粒间有明显的团聚, 平均粒径在8~17 nm之间. 分散度测试表明, 单一介孔结构的Pd/BMS-30催化剂, Pd分散度仅为27%, 而双介孔结构Pd/BMS-5~Pd/BMS-20催化剂介于39%到69%, 其中Pd/BMS-15催化剂中Pd分散度高达69%.

与常规单一介孔MCM-41和MCM-48负载Pd催化剂相比, 在低空速(42000 h⁻¹)条件下, Pd/BMS-15催化剂上甲苯催化氧化性能与Pd/MCM-41和Pd/MCM-48催化剂相当. 高空速(70000 h⁻¹)条件下, Pd/BMS-15催化剂的活性远高于单一介孔的Pd/MCM-41和Pd/MCM-48催化剂. Pd/BMS-15催化剂独特的双介孔结构, 有利于活性相Pd的分散、反应物的扩散和传输, 特别是在高空速条件下, 有利于反应物与活性相的接触, 提高了材料的氧化反应性能. 进一步考察了材料的水热稳定性, 将11 vol%的水蒸气引入到反应体系中, 测试结果表明水蒸气的加入导致Pd/MCM-41和Pd/MCM-48催化剂的甲苯催化氧化性能显著下降, 反应500 min后甲苯转化率分别从100%下降到76%和81%, 而对于Pd/BMS-15催化剂, 水蒸气的引入并未导致其活性明显下降, 从而表明Pd/BMS-15催化材料具有较高的水热稳定性.

关键词: 双介孔硅; 孔结构; 催化氧化; 甲苯; 钯

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