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Article

La-doped Pt/TiO₂ as an efficient catalyst for room temperature oxidation of low concentration HCHO

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ABSTRACT

Catalytic oxidation of formaldehyde (HCHO) is the most efficient way to purify indoor air of HCHO pollutant. This work investigated rare earth La-doped Pt/TiO₂ for low concentration HCHO oxidation at room temperature. La-doped Pt/TiO₂ had a dramatically promoted catalytic performance for HCHO oxidation. The reasons for the La promotion effect were investigated by N₂ adsorption, X-ray diffraction, CO chemisorption, X-ray photoelectron spectroscopy, transmission electron microscopy (TEM) and high-angle annular dark field scanning TEM. The Pt nanoparticle size was reduced to 1.7 nm from 2.2 nm after modification by La, which led to higher Pt dispersion, more exposed active sites and enhanced metal-support interaction. Thus a superior activity for indoor low concentration HCHO oxidation was obtained. Moreover, the La-doped TiO₂ can be wash-coated on a cordierite monolith so that very low amounts of Pt (0.01 wt%) can be used. The catalyst was evaluated in a simulated indoor HCHO elimination environment and displayed high purifying efficiency and stability. It can be potentially used as a commercial catalyst for indoor HCHO elimination.

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1. Introduction

Formaldehyde (HCHO) emitted from newly installed building materials, plastic cements and paintings is one of the main air pollutants in the indoor environment, which seriously affects people's health even at concentration lower than a few ppm [1–5]. As one of the most toxic air pollutants, HCHO has a negative influence on genetic material, respiratory tracts and cutaneous covering and also strongly affects the central nervous system [6]. Therefore, in order to improve indoor air qual-

ity and reduce public health risk, the abatement of HCHO at room temperature is a problem which should be urgently solved.

Over the past decades, many efforts have been made to investigate the removal of HCHO by environmental scientists [1]. Technologies that have been studied for the removal of HCHO are adsorption, photo-catalysis, plasma technology, and catalytic oxidation [3,7–11]. Adsorption is a useful method for indoor air HCHO removal. Some absorbents can successfully reduce indoor HCHO concentrations to very low levels [12–14];

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however, their effectiveness is limited by adsorption capacity and they produce secondary pollution during regeneration. Photo-catalysis has received wide attention over the past decades and has been widely applied in energy production and environmental protection [15–18]. However, the photo-catalytic process requires the assistance of light energy, which may not be available for the elimination of an indoor air pollutant and its wide application is limited. Catalytic oxidation can selectively decompose the toxic HCHO into harmless CO_2 and H_2O at ambient temperature [2,19–21]. Thus, the catalytic oxidation is regarded as the most promising method for indoor HCHO removal [1].

There are two major classes of catalysts for the complete oxidation of indoor HCHO: supported or unsupported transition metal oxides [7,8,22,23] and supported noble metal catalysts [3,9–11]. Of the former catalysts, the most efficient metal oxides that have been widely studied are MnO_x [7,24], CeO_2 [25], Co_3O_4 [26], and MnCeO_x [7]. Although they exhibit high activity at the beginning of the tests, these catalysts are easily deactivated in the presence of H_2O (H_2O can strongly adsorb on the surface of the active sites, especially at low temperature), which greatly influences its practical application [7]. For most supported noble metal catalysts, their activity and water-tolerance are superior for volatile organic compounds (VOCs) elimination. Supported catalysts, such as Pt/TiO_2 [3,27], $\text{Pt}/\text{Al}_2\text{O}_3$ [28], Pd/TiO_2 [29], and Au/CeO_2 [6], have been widely studied and demonstrated high activity for HCHO oxidation. However, due to limited sources and the high price of noble metals, it is currently an important task and hot research topic to design and prepare catalysts with smaller noble metal particle size to reduce their loading.

For noble metal-based catalysts, it is commonly accepted that their activity is closely related to their particle size [30–33]. When studying the water gas shift reaction on Pd/CeO_2 and Pt/CeO_2 , Gorte and coworkers [30] observed a linear relationship between activity and metal surface area. For methanol synthesis from H_2/CO on Pd/CeO_2 , Shen and coworkers [31] also found that there was a close correlation between activity loss and the growth of the Pd particle size. In our previous studies, we also found that on Pd supported on various supports for CO and CH_4 deep oxidation that the activity is closely related to the Pd crystallite size and its metal surface area [34–36]. The same effect was also observed for Ni supported on different supports for CH_4 reforming for hydrogen production [37–39]. Therefore, the preparation of ultra-small noble metal nanoparticles of Pd, Pt, and Au has recently received a great deal of interest in the field of catalysis due to their size dependent catalytic activity [40–42]. Meanwhile, many previous results have demonstrated that the addition of certain amounts of rare earth oxides can improve the dispersion of supported noble metal catalysts and give much smaller particle size of the active component compared with the non-modified ones [43–46]. Therefore, the metal-support interaction of noble metal supported catalysts can be enhanced by rare earth modification [44,46–48].

To improve the utilization efficiency of noble metal-based catalysts, in the present study, anatase TiO_2 was modified by La

first and then Pt was supported on it. This catalyst was applied for indoor low concentration HCHO oxidation at room temperature. To the best of our knowledge, there has been no report on the application of rare earth-modified Pt/TiO_2 for removing the low concentration HCHO at room temperature. The results demonstrated that La-doped TiO_2 remarkably reduced Pt particle size to below 2 nm. The La-modified TiO_2 was wash-coated on a cordierite monolith and then a very low amount of Pt (0.01 wt%) was supported on it. This catalyst was evaluated in a simulated indoor HCHO elimination environment, and it displayed high purifying efficiency and superior stability.

2. Experimental

2.1. Catalyst preparation

First, anatase TiO_2 was modified by various amounts of La (0, 1, 5, and 7 wt% La_2O_3) using a wet impregnation method. Typically, 0.4110 g $\text{La}(\text{NO}_3)_3$ was dissolved in an appropriate amount of deionized water. Then, 5 g TiO_2 (anatase, Aladdin) was added into the $\text{La}(\text{NO}_3)_3$ aqueous solution under constant stirring. After stirring for 2 h, excess water was removed in a rotary evaporator at 80 °C under vacuum. The samples were dried at 110 °C for 12 h and then calcined at 400 °C for 4 h. This catalyst was designed as 3 wt%La- TiO_2 . The other amounts of La-modified TiO_2 was denoted as x wt%/La- TiO_2 .

Second, Pt nanoparticles were supported on La-modified TiO_2 also by a wet impregnation method similar to that used for La-modified TiO_2 . The amount of Pt was fixed at 0.5 wt% of the final catalyst, and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ was the Pt source. In detail, the 0.5 wt% Pt/x wt% La- TiO_2 catalysts were prepared with an aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ instead of $\text{La}(\text{NO}_3)_3$ solution. An amount of the prepared x wt%La- TiO_2 support was measured and added into the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ solution. The mixture was constantly stirred overnight at 30 °C before removing excess water at 80 °C, and dried at 110 °C for 12 h and calcined at 400 °C in an air atmosphere for 4 h. The sample was reduced by 10% H_2/N_2 at 400 °C for 4 h to obtain Pt supported on La-modified TiO_2 , and designated as Pt/x wt% La- TiO_2 .

For commercial application, 3 wt%La- TiO_2 was wash-coated on cordierite monoliths (256 cpsi, 15 cm (length) × 15 cm (width) × 1.2 cm (height)) first and then a calculated amount of Pt (0.01 wt% based on the weight of the monolith) was impregnated onto this modified monolith. Before impregnation, the 3 wt%La- TiO_2 powder, which was calcined at 400 °C for 4 h in air, was wash-coated on the cordierite monolith. Prior to wash-coating, the monoliths were calcined at 500 °C for 2 h (with a ramp rate of 5 °C/min) to remove adsorbed water. Then, a solid phase of 5 wt% boehmite (Disperal D) was dissolved in a slurry mixture consisting of liquid H_2O was first used for the impregnation of the calcined monoliths in order to enhance the attachment of the 3 wt%La- TiO_2 powder. The alumina-coated monolith was previously calcined at 300 °C for 1 h and then 500 °C for 1 h (heating rate 2 °C/min). Finally, the alumina-coated monoliths were immersed into a mixture of 3 wt%La- TiO_2 slurry (liquid to solid weight ratio = 80/20). The above procedure was repeated several times until the mono-

liths were coated with the desired amount of wash-coat. The La-TiO₂ coated monoliths were further calcined at 500 °C for 2 h at a heating rate of 5 °C/min. Afterwards, La-TiO₂ coated monoliths was impregnated by 0.01 wt% Pt by conventional impregnation, where the amount of Pt was just 0.01% of the mass weight of the monolithic catalyst. Finally, the Pt/La-TiO₂ coated monoliths were calcined at 400 °C for 4 h, and then further reduced by 10% H₂/N₂ at 400 °C for 4 h.

2.2. Catalyst characterization

N₂ adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 system. The specific surface area (*S*_{BET}) was estimated using the BET method. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method, which calculated the pore size based on the adsorption layer thickness in relation to the pressure and the average radius of the meniscus obtained using the Kelvin method. Each sample was analyzed after degassing in vacuum at 300 °C for 4 h.

The powder X-ray diffraction (XRD) patterns were obtained on a Bruker AXS D8 Focus diffractometer operating at 40 kV and 40 mA with a Cu target and *K*_α X-ray irradiation. Scans were collected over a range of 2θ from 10° to 90° with a step of 0.03°/s. The calculated experimental error for 2θ measurement of the peaks was ± 0.01°.

CO temperature-programmed desorption (CO-TPD) was measured on an Auto-Chem 2920 (Micromeritics Co.) to analyze the Pt dispersion of the catalyst. The sample (typically 50 mg) was reduced first in a flow of 10% H₂/Ar gas mixture (30 mL/min) at 300 °C for 30 min, and then purged by a ultra-high purity He flow (30 mL/min) at room temperature for 30 min prior to CO adsorption in a 4% CO/He flow (20 mL/min). Afterwards, the sample was purged again in He flow (30 mL/min) for 30 min to remove physically adsorbed CO. After getting a stable baseline, the temperature was increased to 500 °C at a rate of 10 °C/min. A CO desorption peak was generally detected for each sample at ~150 °C, and the relative CO desorption amount was monitored by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) experiments were carried out on an RBD upgraded PHI-5000C ESCA system using a single Mg-*K*_α X-ray source operating at 250 W and 14 kV. The spectra were obtained at ambient temperature. The binding energies were calibrated using the C 1s peak of graphite at 284.6 eV as reference.

The transmission electron microscope (TEM) and high angle dark field scanning transmission electron microscope (HAADF-STEM) images were taken on a Tecnai™ F30 field emission transmission electron microscope equipped with an energy dispersive spectroscopy (EDS) detector to determine the particle size of Pt.

2.3. Activity test

The activity test for the catalytic oxidation of HCHO over the catalysts (100 mg) was performed in a fixed-bed quartz flow

Fig. 1. Schematic of the procedure of using a powder catalyst for HCHO oxidation. A: Air; B: Formaldehyde solution; C: Detector; D: Quartz tube; E: Catalyst; F: Detector.

reactor (i.d. = 6 mm) in a chamber where the temperature was kept at 25 °C, as shown in Fig. 1. Gaseous HCHO was generated by flowing air through the formaldehyde solution container in a water bath kept at 25 °C. The feed gas composition was 0.5 ppm of HCHO, 21% O₂ and 50% RH balanced by nitrogen. The weight hourly space velocity (WHSV) was fixed at 60000 mL g⁻¹ h⁻¹. The inlet and outlet gases were monitored by INTERSCAN 4160 (detection range and limit are 0–19.99 and 0.01 ppm, respectively), which is a HCHO detector.

To test the performance of the monolithic catalyst, Pt supported cordierite monoliths were placed in an air purifying machine. Then, the machine equipped with monolithic catalyst was located in a 2 m³ sealed box to evaluate the purifying efficiency of HCHO in a real environment. The initial concentration of HCHO was fixed at about 0.5 ppm and monitored by a HCHO detector. The procedure for testing the performance of the monolithic catalysts is shown in Fig. 2.

3. Results and discussion

3.1. Catalytic performance of the catalysts

Anatase TiO₂ was first doped with various amount of La₂O₃, and then 0.5 wt% Pt was supported on the La-modified TiO₂. The catalytic activity of Pt supported on La-modified TiO₂ powder catalyst for HCHO oxidation is shown in Figs. 3 and 4. The concentration of HCHO was fixed at 0.5 ppm, which is

Fig. 2. Schematic of the procedure of using a monolithic catalyst for HCHO oxidation. A: Air; B: Formaldehyde solution; C: Sealed chambers; D: Catalytic reaction apparatus; E: Fan; F: Detector.

Fig. 3. (a). Catalytic performance of Pt/La-TiO₂ and Pt/TiO₂ and durability test of Pt/3 wt%La-TiO₂ for HCHO oxidation (b). Reaction conditions: 25 °C, initial HCHO concentration 0.5 ppm, WHSV = 60000 mL g_{cat}⁻¹ h⁻¹.

about 5 times higher than the allowed upper limit (0.08–0.1 ppm). This concentration is similar to the amount of HCHO emission in newly decorated buildings. There has been no report on HCHO removal using a concentration lower than 1 ppm. It is observed that the catalyst activity was promoted by the doped La as compared with the unmodified one (Fig. 4). The Pt/TiO₂ catalyst presented the lowest HCHO conversion at room temperature, just 88%. However, the conversions for the La-modified samples were all above 90%. The highest activity of nearly 100% at a GHSV of 60000 h⁻¹ at room temperature was obtained when the loading of La₂O₃ was 3.0 wt% (Fig. 4). Furthermore, the stability of Pt/3 wt%La-TiO₂ catalyst in the long term was tested at 25 °C. As shown in Fig. 3(b), the sample exhibited excellent long term stability and catalytic activity, and the HCHO conversion was maintained at 100% for 40 h without any decrease. So, we concluded that anatase TiO₂ modified by La₂O₃ had a dramatic promotion effect for HCHO oxidation.

3.2. Characterization of the catalysts

The textural properties of the Pt/3 wt%La-TiO₂ and Pt/TiO₂ catalysts were investigated together with pure TiO₂ and

Fig. 4. Catalytic performance of Pt supported on various amount of La-modified TiO₂.

3 wt%La-TiO₂ by N₂ adsorption-desorption measurements. The results are shown in Fig. 5 and the quantitative results listed in Table 1. As can be observed in Fig. 5, all the catalysts displayed type IV isotherm with type H3 hysteresis. The capillary condensation step observed in the isotherms is the characteristic of the presence of mesopores. Moreover, pure TiO₂ showed an obviously larger N₂ adsorption amount than the others. This was in line with the surface area and pore volume results in Table 1. Among all the supports, pure TiO₂ possesses the highest surface area (67 m²/g) and pore volume, while the surface area and pore volume showed a slight decrease after modification by La₂O₃ and doping Pt. The pore size distribution of the catalysts can be seen from the inset image in Fig. 5. All the samples showed two similar groups of pore diameter distribution: one group at 20 nm and the other at 1.6 nm. The former was assigned to the secondary aggregation of the particles, while the latter was assigned to particle micropores.

To identify the phase composition of the synthesized catalysts, all the samples were characterized by powder XRD. As the results show in Fig. 6, pure TiO₂ showed three diffraction peaks at $2\theta = 25.3^\circ$ (101), 37.8° (004) and 48.0° (200), which are typical for the anatase TiO₂ phase. La species peaks were not observed with modified TiO₂, indicating that the La₂O₃ species were highly dispersed on the TiO₂ support. At the same time, the introduction of Pt did not induce the appearances of the peaks of polycrystalline Pt, which can be attributed to the low loading of Pt (0.5 wt%) and manifested that Pt nanoparticles with an ultra-small size at very high dispersion on the supports were obtained, which was further confirmed by the HRTEM and HAADF-STEM images and CO adsorption-desorption studies described in the following.

To better understand how the La₂O₃ modification affected Pt dispersion and particle size, CO-TPD, HRTEM and HAADF-STEM analysis of the catalysts were performed. Pt dispersion was determined by CO chemisorption. The results are listed in Table 1. Without La addition, the Pt dispersion on Pt/TiO₂ sample was 51%. La₂O₃ addition to Pt/TiO₂ remarkably increased the Pt dispersion to 66%. Clearly, La addition induced a more dispersed Pt species on Pt/3 wt%La-TiO₂ catalyst that exposed

Fig. 5. N_2 adsorption-desorption isotherms and pore size distribution curves of TiO_2 and supported Pt catalysts. (a) TiO_2 ; (b) 3 wt%La- TiO_2 ; (c) Pt/ TiO_2 ; (d) Pt/3 wt%La- TiO_2 .

more Pt sites for HCHO oxidation, thus significantly promoting the activity of the catalyst.

Pt grain sizes were calculated based on the TEM and HAADF-STEM images shown in Figs. 7 and 8. The quantitative results are listed in Table 1. Fig. 7(a) and (b) showed that ultra-small Pt particles were well dispersed on the surface of the supports. The calculated Pt particle size was around 2.2 nm. Interestingly, the La_2O_3 -modified samples showed a smaller Pt size of around 1.7 nm as shown in Fig. 7(c) and (d). The results were further confirmed by HAADF-STEM, as shown in Fig. 8. The images and results were in accordance with the Pt dispersion determined by CO chemisorption. All the characterization

results demonstrated that the addition of La_2O_3 gave a dramatic improvement of Pt dispersion on TiO_2 support, leading to a smaller Pt particle size, more active sites exposed and superior activity for indoor low concentration HCHO oxidation. The turnover frequencies (TOFs) of the La-doped and undoped catalysts were 0.0776 and 0.0819 h^{-1} , respectively, which were very similar. This result further verified that the addition of La

Table 1

Physicochemical properties of Pt/ TiO_2 and Pt/La- TiO_2 measured by N_2 sorption isotherms.

Sample	S_{BET}^a (m^2/g)	Pore volume ^b (cm^3/g)	Pore size ^b (nm)	Pt dispersion ^c (%)	Pt particle size (nm)
Nano TiO_2	67	0.45	25.3	—	—
3 wt%La- TiO_2	65	0.31	19.7	—	—
Pt/ TiO_2	58	0.28	18.3	51	2.2
Pt/3 wt%La- TiO_2	59	0.27	16.4	66	1.7

^a Calculated by BET method.

^b Determined by BJH method.

^c Calculated by CO-TPD.

Fig. 6. Powder XRD patterns of TiO_2 and supported Pt catalysts.

Fig. 7. TEM images of Pt/TiO₂ (a, b) and Pt/3 wt%La-TiO₂ (c, d) and their Pt particle size.

can effectively increase the dispersion of Pt and decrease the particle size of Pt.

XPS measurements were carried out to investigate the electronic state of the Pt species to reveal the effect of La₂O₃ on the Pt/TiO₂ catalyst. The results are shown in Fig. 9. Table 2 summarizes the binding energy (BE) values of Pt 4f, Ti 2p and O 1s and the atomic ratio of adsorbed O to lattice O calculated from the XPS results of the modified and unmodified catalysts. It is well known that the Pt 4f_{7/2} BE of Pt⁰, Pt²⁺ and Pt⁴⁺ are 71.1, 72.4 and 74.2 eV [10,11], respectively. For the Pt/3 wt%La-

TiO₂ catalyst, the peaks of Pt 4f were centered at 71.2 and 74.5 eV, so Pt⁰ and Pt⁴⁺ species simultaneously existed on this catalyst (Fig. 9(a)). It can be observed that the peaks of Pt 4f of unmodified Pt/TiO₂ were very similar to those of La-modified Pt/TiO₂. From Fig. 9(b), we can also see that the peak of Ti 2p centered very closely at 457.8 eV. Since the La-modified Pt/TiO₂ did not affect the electronic state of Pt and Ti, the Pt dispersion and Pt particle size would be the most important factors for the catalytic performance in HCHO oxidation.

The O 1s spectra of modified and unmodified Pt/TiO₂ are shown in Fig. 9(c). The O 1s spectra exhibited two peaks: a main peak at 529 eV, and a shoulder peak at 531.0 eV. These results indicated two types of oxygen species existed on the catalysts. The former can be assigned to lattice oxygen (O_{lat}), and the latter to chemisorbed oxygen (O_{ads}). The O_{ads}/O_{lat} ratio was calculated from the peak areas. The results are shown in Table 2. It was found that O_{ads}/O_{lat} was very different between modified and unmodified Pt/TiO₂. The O_{ads}/O_{lat} ratio of Pt/La-TiO₂ was higher than that of Pt/TiO₂. Thus the La-doped TiO₂ can create more oxygen vacancies than the unmodified one, and the metal-support interaction would be enhanced due to the generation and activation of more chemisorbed oxygen species.

3.3. Performance of the monolithic catalyst

For commercial application, 3 wt%La-TiO₂ was wash-coated on cordierite monoliths and then 0.01 wt% Pt was loaded on the monoliths by a conventional impregnation method. The monolithic catalyst was tested in a 2 m³ sealed box to simulate the air environment for HCHO decomposition. The results are shown in Fig. 10. The initial HCHO concentration was 0.55 ppm,

Fig. 8. HAADF-STEM images of Pt/TiO₂ (a, b) and Pt/3 wt%La-TiO₂ (c, d).

Fig. 9. XPS analysis of (1) Pt/TiO₂ and (2) Pt/3 wt%La-TiO₂ catalysts. (a) Pt 4f; (b) Ti 2p; (c) O 1s.

Table 2

XPS results of Pt/TiO₂ and Pt/3 wt%La-TiO₂ catalysts.

Sample	Pt 4f BE (eV)		Ti 2p BE (eV)	O 1s BE (eV)		O _{ads} /O _{lat}
	4f _{5/2}	4f _{7/2}		O _{ads}	O _{lat}	
Pt/TiO ₂	74.8	71.6	457.9	530.7	528.9	0.11
Pt/3 wt%La-TiO ₂	74.5	71.2	457.8	530.2	529.0	0.14

Fig. 10. Durability test of 0.01% Pt/3 wt%La-TiO₂ monolithic catalyst for HCHO oxidation.

which is close to the real high concentration in an indoor environment. For the fresh catalysts, the HCHO concentration was decreased to 0.08 ppm within 5 min. Surprisingly, the catalyst maintain high activity even after 3 months, and the HCHO concentration decreased to 0.08 ppm in less than 10 min with the help of this catalyst. The catalytic performance of the monolithic catalyst showed that the La₂O₃ modified Pt/TiO₂ catalyst possessed high activity and stability in practical application. It would be a superior catalyst in the oxidation of indoor low concentration HCHO at ambient temperature.

4. Conclusions

This work demonstrated that La-modified TiO₂ had a dramatic promotion effect on a Pt/TiO₂ catalyst for ambient HCHO oxidation. The grain size of the Pt nanoparticles was reduced to below 2 nm after the TiO₂ support was modified by La₂O₃,

which led to a higher Pt dispersion, more exposed active sites and thus superior activity for indoor low concentration HCHO oxidation. The XPS results showed that the amount of chemisorbed oxygen was more than on the unmodified support, so an enhanced metal-support interaction would be another reason for its higher activity. The La-modified TiO₂ was wash-coated on a cordierite monolith and then a very low amount of Pt (0.01 wt% of the total catalyst) was supported on it. This catalyst was evaluated in a simulated indoor HCHO elimination environment, and it displayed superior purifying efficiency and stability. Therefore, it is potentially a commercial catalyst for indoor HCHO elimination

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Graphical Abstract

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La-doped Pt/TiO₂ as an efficient catalyst for room temperature oxidation of low concentration HCHO

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La-doped TiO₂ was used to support Pt and the catalyst displayed superior catalytic performance in the removal of low concentration HCHO at room temperature.

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La 掺杂 TiO₂ 负载 Pt 催化剂制备及其室温氧化低浓度甲醛

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摘要: 甲醛是室内装修污染的重要组分, 已严重危害到人们身体健康, 在室温条件下消除甲醛引起了人们的广泛兴趣。目前室温清除甲醛主要有物理吸附法、光催化法、等离子体技术及催化氧化技术。物理吸附法主要采用活性炭等作为吸附剂, 其初期吸附效果较好, 但当吸附饱和之后会重新释放甲醛造成二次污染; 光催化法和等离子体技术需要特殊装置, 不适合室内室温环境脱除甲醛; 而催化氧化技术则可直接将甲醛转化为无毒无害的水和CO₂, 因而备受关注。Pt/TiO₂被认为是目前消除甲醛最有效的催化剂。为进一步降低贵金属 Pt 的用量及增强其稳定性 (Pt 被氧化后其活性会降低), 本文首次

采用稀土 La 掺杂锐钛矿型 TiO_2 , 负载少量 Pt 后用于室内低浓度 (0.5 ppm) 甲醛的催化氧化.

活性测试结果表明, 纯 TiO_2 催化剂上甲醛转化率在 5% 以下, 有可能是物理吸附或可见光催化所致. 负载 0.5% Pt 后, Pt/TiO_2 和 Pt/La-TiO_2 甲醛转化率均高于 80%, 尤其是 La 掺杂活性高达 96% 以上, 且在连续反应 8 h 甚至延长至 40 h 后其活性均未见下降趋势. 电镜结果表明, La 掺杂 Pt/La-TiO_2 催化剂中 Pt 粒径从未掺杂的 2.2 nm 降至 1.7 nm; CO 程序升温脱附测试表明, $\text{Pt/La-TiO}_2/\text{Pt}$ 的分散度达 66%, 而未掺杂样品仅为 51%; X 射线光电子能谱测试表明, Pt/La-TiO_2 的表面氧化物高于 Pt/TiO_2 催化剂, 说明 La 掺杂增强了 Pt 和载体间的相互作用. 为探讨 Pt/La-TiO_2 商业化应用前景, 将粉体 Pt/La-TiO_2 涂覆在堇青石蜂窝陶瓷上制备成整体催化剂. 该整体催化剂在容积为 2 m^3 的密室测试中 5 min 内即可将浓度为 0.5 ppm 的甲醛将至 0.02 ppm 以下. 该催化剂在存放 3 个月后活性略有下降, 但在 10 min 内仍可将甲醛浓度降至 0.08 ppm, 达到室内甲醛排放标准.

综上, 本文成功制备了 La 掺杂 Pt/La-TiO_2 用于室内低浓度甲醛催化氧化, 该催化剂表现出优异的催化性能. 通过多种表征手段表明, La 修饰后贵金属 Pt 纳米粒子尺寸减小、分散度提高及 Pt 与载体间相互作用增强是其活性优异的主要原因. 以 Pt/La-TiO_2 粉体制备的整体催化剂同样表现出了高的催化性能, 具有工业应用前景.

关键词: 低浓度甲醛; 室温氧化; 稀土; 镧掺杂; 铂; 二氧化钛; 整体催化剂

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