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Article

Titania-supported Pt catalyst reduced with HCHO for HCHO oxidation under mild conditions

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ABSTRACT

A series of Pt/TiO₂(P25) catalysts were prepared by both impregnation (IM) and deposition-precipitation (DP) methods followed by reduction using either a HCHO solution or a H₂ stream. The effects of the preparation and reduction conditions and the Pt loading level on structural properties and performance during HCHO oxidation were then studied based on the assessment of adsorbed species on the catalyst surfaces using *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The results indicated that Pt/P25 prepared by DP and reduced with HCHO exhibited homogeneously dispersed Pt nanoparticles with appropriate particle size in addition to a high concentration of chemisorbed oxygen, and also showed high activity for HCHO oxidation. A HCHO conversion of 98% with stable performance over more than 100 h was achieved over Pt/P25 produced using DP and HCHO reduction at 30 °C, even with a 0.4% Pt loading. Pt/P25 synthesized using DP with H₂ reduction was less effective at promoting formate decomposition and thus showed less HCHO oxidation activity, likely because of lower levels of chemisorbed oxygen. The Pt/P25 made using IM and H₂ reduction had the highest amount of chemisorbed oxygen but also the largest Pt particles, resulting in the lowest activity for both the formation of formate species and formate decomposition into CO species, and thus showed low HCHO oxidation activity.

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1. Introduction

Formaldehyde (HCHO) is one of the most common toxic volatile organic compounds; it is known to be carcinogenic and may cause leukemia [1]. Consequently, many methods have been proposed to remove trace levels of HCHO in air, including adsorption, photocatalysis, and catalytic oxidation [2]. Among these, catalytic oxidation is one of the most effective and economically feasible technologies because HCHO can be oxidized to CO₂ over catalysts at much lower temperatures than those are required for thermal oxidation [3]. The catalytic decompo-

sition of HCHO at room temperature is particularly desirable because of the attendant environmentally friendly reaction conditions. Recently, significant progress has been achieved with regard to decreasing the reaction temperature necessary for HCHO oxidation by employing Pt catalysts with various supports [4–11], especially when using titania-supported Pt catalysts.

Despite this success, Pt/TiO₂ materials are frequently reported to exhibit inconsistent activity for HCHO oxidation even when identical Pt loadings and TiO₂ support structures are applied. As an example, Peng and Wang [7] reported that the

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optimal Pt loading in a series of Pt/TiO₂ catalysts reduced in H₂ at 450 °C was 0.6%. The room temperature HCHO conversions obtained in their study were 0.8%, 1.0%, and 41.5% over 0.01%, 0.1%, and 0.6% Pt/TiO₂, respectively, while the conversion obtained with 1% Pt/TiO₂ dropped to 14.3%, although this value increased to 97% at 120 °C. In contrast, Zhang and He [6] reported that HCHO could be completely oxidized into CO₂ and H₂O at room temperature over Pt/TiO₂ with a relatively high 1% Pt loading level. Recently, Huang et al. [12] found that nearly 100% conversion of HCHO was achieved over sodium borohydride-reduced Pt/TiO₂ catalysts even with a low Pt loading of 0.1%.

Differences in experimental parameters, such as the Pt loading method, the TiO₂ support properties, and the reduction procedure, have been suggested to account for such discrepancies. Huang et al. [12] prepared a series of Pt/TiO₂ catalysts by the impregnation and deposition-precipitation method while applying different reduction processes and evaluated their activity for the catalytic decomposition of HCHO at room temperature. This study showed that the reduction treatment had a significant effect on the structural properties and HCHO oxidation activity of the Pt/TiO₂ catalysts. The authors concluded that well-dispersed and negatively charged metallic Pt nanoparticles together with high levels of chemisorbed oxygen were likely responsible for the high catalytic activity of the NaBH₄-reduced Pt/TiO₂ catalysts. However, further study is still required to relate the catalyst preparation and reduction conditions to the structural properties of the catalyst, and to elucidate the detailed mechanism leading to the high catalytic activity and stability of these catalysts. Moreover, because some of the above catalysts were reduced in a NaBH₄ solution, the finished materials may have contained residual Na and B [12], which could have had various effects on the performance of the catalysts. Zhang et al. [3] reported that the presence of Na⁺ had a positive effect on the catalytic activity of Pt/TiO₂, to the extent that it changed the HCHO catalytic oxidation mechanism. Thus, in those catalysts contaminated with residual ions, it is difficult to ascertain which factors are actually affecting the performance of the catalyst. Recently, Qu et al. [13] reported that Ag/SBA-15 catalyst treated with a HCHO solution also showed high activity for HCHO oxidation. In comparison with NaBH₄ solution reduction, reduction with HCHO solution leaves no additional elements on the treated catalyst, which provides an opportunity to study the effects of the reduction conditions on the structure, properties, and catalytic performance of the catalyst. To the best of our knowledge, the open literature contains very few reports focusing on the HCHO reduction process and its effects on the structure, properties, and catalytic performance of Pt-based catalysts.

The present paper reports the synthesis of a highly efficient Pt/TiO₂ catalyst intended for HCHO oxidation by a deposition-precipitation (DP) method followed by reduction via treatment with HCHO. A detailed study of the effects of the Pt/TiO₂ preparation and reduction conditions and the Pt loading amount on the structural properties and performance during trace HCHO oxidation is presented. The mechanism responsible for the high catalytic activity and stability of these materi-

als is examined using *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), which represents a powerful technique for the investigation of surface species in real-world conditions [6,14].

2. Experimental

2.1. Catalyst preparation

Two different Pt loading methods were used to prepare Pt/TiO₂ catalysts, the impregnation method and DP method, producing materials denoted as Pt/P25(IM) and Pt/P25(DP), respectively. The Pt/P25(IM) catalyst was prepared by uniformly dispersing P25 powder (Degussa) into a H₂PtCl₆ solution (H₂PtCl₆·6H₂O, Alfa Aesar) with the appropriate H₂PtCl₆ concentration. After vigorous stirring, the sample was washed with distilled water and centrifuged three times to remove any impurities on the surface of the catalyst. The catalyst was then dried overnight at 120 °C to evaporate the solvent. The Pt/P25(DP) catalysts were prepared by first dispersing the P25 support in deionized water, following which a H₂PtCl₆ solution was added dropwise into the P25 slurry with vigorous stirring at 70 °C. After stirring for 1 h, the pH of the solution was adjusted to 8 by adding an aqueous NaOH solution, and deposition by precipitation was allowed to continue for 2 h under vigorous stirring at 70 °C. The catalyst was subsequently washed and centrifuged three times to remove any surface impurity, and the resulting powder was dried overnight at 120 °C. Two different reduction methods were used when preparing catalysts, H₂ reduction and HCHO solution reduction, producing specimens referred to as Pt/P25(IM-H₂), Pt/P25(DP-H₂), and Pt/P25(DP-HCHO). During a typical H₂ reduction process, the as-prepared Pt/P25(IM) or Pt/P25(DP) was calcined in a H₂ stream (40 ml/min) at 300 °C for 3 h. Pt/P25(DP-HCHO) was prepared using a deposition-precipitation method similar to that described above, the only difference being that a HCHO solution (37%–40%, Guangzhou Reagent Company) was added to the DP solution after the pH of the solution was adjusted. Note that the Pt loading levels in this work are expressed as the mass percent of Pt in the catalyst, as confirmed by inductively coupled plasma (ICP, IRIS (HR)) elemental analysis.

2.2. Catalyst characterization

In-situ DRIFTS analyses were carried out using an EQVINOX-55 FFT instrument (Bruker) equipped with a diffuse reflectance accessory and an MCT detector. During each analysis, a finely ground sample (ca. 10 mg) was placed in a ceramic crucible within the *in-situ* chamber. A 100 ml/min flow of nitrogen gas containing HCHO was then passed through the chamber. Spectra under reaction conditions were recorded by averaging 64 scans with a resolution of 4 cm⁻¹. Metal nanoparticle size distributions were observed using a JEOL 2100F transmission electron microscope (TEM), and the compositions of the samples were characterized by an energy-dispersive spectrometer fitted to a JEM-2010HR TEM. BET surface areas of the samples were determined by N₂ adsorption at -196 °C

employing a Micromeritics ASAP 2020 instrument. Prior to these measurements, the samples were degassed at 300 °C for 2 h. CO chemisorption was performed using a Micromeritics ASAP 2020C automated system. Prior to CO chemisorption, approximately 0.2 g of freshly calcined catalyst was evacuated to 1.33×10^{-6} Pa at 110 °C for 30 min and then reduced under a flow of H₂ at 200 °C for 30 min. The catalyst was then evacuated again at 200 °C for 30 min to desorb any H₂, and the chemisorption analysis was carried out at 35 °C. An average CO/Pt stoichiometry of one was assumed for the dispersion calculations. X-ray photoelectron spectra (XPS) were recorded on a ESCALAB 250 spectrometer (Thermo Fisher Scientific, Al K α , $h\nu$ = 1486.6 eV) under a vacuum of approximately 2×10^{-7} Pa. Charging effects were corrected by adjusting the main C 1s peak to a position of 284.8 eV.

2.3. HCHO catalytic oxidation

The catalytic oxidation of HCHO was performed in a quartz tube (i.d. = 7 mm) fixed-bed reactor under atmospheric pressure using an apparatus constructed in-house. Approximately 0.2 g of the catalyst was packed into the reactor, and a simulated air stream (N₂ and O₂ at 4 and 100 ml/min) containing ~50 mg/m³ HCHO and water vapor (~35% relative humidity) was introduced as the reactant stream. Gaseous HCHO was generated by passing a stream of the simulated air through a bubbler containing a 35% HCHO solution. The gas hourly space velocity (GHSV, defined as the total flow rate of gas at STP per unit mass of catalyst) in the test apparatus was 30 000 ml/(h·g). The HCHO concentration in the reactant and product gas streams was analyzed by a phenol spectrophotometric method. In this method, the gas stream containing trace levels of HCHO was bubbled through 5 ml of a phenol reagent (C₆H₄SN(CH₃)C: NNH₂·HCl, Alfa Aesar) solution (1×10^{-6}) for 30 s to collect HCHO by absorption, following which 0.4 ml of an ammonium ferric sulfate (NH₄Fe(SO₄)₂·12H₂O, 1%, Tianjin Fuchen Chemical Reagent Company) solution was added as the coloring reagent. After shaking for 5 s and sitting for 15 min in the dark, the HCHO concentration was determined by measuring light absorbance at 630 nm with a spectrophotometer (UV-240, Shimadzu Co. Ltd., Japan). The conversion of HCHO was calculated based on the change in the concentration between the reactant and product gas streams.

3. Results and discussion

3.1. Structural properties

Because the Pt particles on the 0.4%Pt/P25 samples were too small to be detected by TEM, the TEM images and Pt particle size distributions of 0.8%Pt/P25 catalysts prepared by DP or IM followed by reduction with a H₂ stream or a HCHO solution are compared in Fig. 1. It can be seen that small, homogeneous Pt nanoparticles were uniformly present on all the reduced catalysts. Approximately 500 Pt nanoparticles were measured to obtain a histogram of the metal particle size distribution of each sample. In Fig. 1(b), a Pt nanoparticle size

Fig. 1. TEM images and Pt nanoparticle size distributions of 0.8%Pt/P25(DP-HCHO) ((a) and (b)), 0.8%Pt/P25(IM-H₂) ((c) and (d)), and 0.8%Pt/P25(DP-H₂) ((e) and (f)).

range of 1–6 nm was observed in the case of the 0.8%Pt/P25 (DP-HCHO) sample, with an average value of 3.2 nm; while a wider Pt nanoparticle size range of 3 to 8 nm with an average value of 7.0 nm was calculated for 0.8%Pt/P25(IM-H₂), as presented in Fig. 1(d). Fig. 1(f) shows that the 0.8%Pt/P25(DP-H₂) had a size range of 1 to 4 nm with an average value of 2.3 nm. The metal dispersions over the 0.4%Pt/P25(DP-HCHO) and 0.4%Pt/P25(DP-H₂) specimens determined by CO chemisorption were 27.7% and 34.5%, respectively, and their BET areas were 54.1 and 51.1 m²/g, respectively. These results indicate that both the preparation method and the subsequent reduction process have significant effects on the surface Pt distribution and the catalyst structure but not on the support properties, which has a great influence on the catalytic activity [6].

3.2. XPS results

XPS analyses were carried out to identify the chemical states of surface elements, as shown in Fig. 2 and summarized in Table 1. Although the Pt 4f signal was somewhat weak because of the low levels of Pt loading and its wide dispersion, the negative binding energy (BE) shift of Pt 4f could still be observed at loadings over 0.4%, giving the 70.2, 70.3, and 70.9 eV values obtained for Pt/P25(DP-HCHO), Pt/P25(IM-H₂), and Pt/P25 (DP-H₂), respectively (Fig. 2(a)). These values may be compared with the BE of 71.2 eV of bulk metallic Pt [15]. Electron transfer from TiO₂ to the Pt core is believed to be responsible for this negative shift [16,17]. As can be seen in Fig. 2(b), the Ti 2p peak was also shifted to a lower BE compared with the BE of 458.9 eV previously reported for unreduced samples [12], suggesting the presence of oxygen vacancies [18,19]. Oxygen

Fig. 2. XPS spectra of reduced 0.4%Pt/P25 catalysts. (a) Pt 4f; (b) Ti 2p; (c) O 1s. (1) 0.4%Pt/P25(DP-HCHO); (2) 0.4%Pt/P25(DP-H₂); (3) 0.4%Pt/P25(IM-H₂).

vacancies and negatively charged Pt particles both show enhanced capacity for O₂ adsorption. A significant shoulder peak due to chemisorbed oxygen was present in the spectra of all the reduced Pt/P25 catalysts, as shown in Fig. 2(c). The amount of chemisorbed oxygen may be influenced by many factors, including the electronegativity and dispersion of the Pt and the presence of oxygen vacancies in the support [12,20–22]. It thus appears that both the preparation method and the reduction method have a significant effect on the surface Pt properties and chemisorbed oxygen concentrations, as listed in Table 1. The chemisorbed oxygen can be activated on the metal-support interface, forming highly active oxygen species that are involved in the oxidation reaction [23].

3.3. Catalyst activity

The catalytic activity of pure P25 and the Pt/P25 catalysts prepared using either the IM or DP methods followed by reduction with a HCHO solution or a H₂ stream was evaluated for HCHO oxidation, with the results presented in Fig. 3(a). It is evident that the Pt/P25 catalysts prepared by the DP method were more active than those prepared using the IM method. In the case of the Pt/P25 materials prepared by the DP method, reduction with the HCHO solution was also more effective than the H₂ stream reduction. The 0.4%Pt/TiO₂(IM-H₂) catalyst produced a HCHO conversion of 12.0% at 30 °C, and this value increased to 70.7% at 110 °C. Even those samples with lower Pt loadings, 0.16%Pt/TiO₂(DP-H₂) and 0.16%Pt/TiO₂(DP-HCHO), exhibited better activities, especially the 0.16%Pt/TiO₂(DP-

HCHO). With increasing Pt loadings, the HCHO conversion reached a maximum of ~98% over both 0.4%Pt/TiO₂(DP-H₂) and 0.4%Pt/TiO₂(DP-HCHO) even at room temperature, as shown in Fig. 3(b). These findings demonstrate that the preparation method and the reduction method both contribute to the activity of the catalysts.

Fig. 3(b) summarizes the results of long-term tests over

Fig. 3. (a) Dependence of HCHO conversion on reaction temperature for P25, 0.16%Pt/P25(DP-HCHO), 0.16%Pt/P25(DP-H₂), and 0.4%Pt/P25(IM-H₂) catalysts; (b) HCHO conversion over 0.4%Pt/P25(DP-H₂) and 0.4%Pt/P25(DP-HCHO) at 30 °C and 0.16%Pt/P25(DP-HCHO) at 70 °C over prolonged time periods.

Table 1

XPS data obtained for reduced 0.4%Pt/P25 catalysts.

Sample	BE (eV)			Surface atom ratio ^a	
	Pt 4f _{7/2}	O _{adsorbed} (O _{lattice})	Ti 2p	O _{adsorbed} /O _{lattice}	Pt/Ti
Pt/P25(DP-HCHO)	70.2	531.4 (530.0)	458.7	0.14	0.0010
Pt/P25(DP-H ₂)	70.9	531.4 (530.0)	458.7	0.11	0.0015
Pt/P25(IM-H ₂)	70.3	531.5 (530.0)	458.7	0.20	0.0010

^a Calculated from the corresponding areas of fitted peaks using XPSPEAK 4.1 with a Shirley background.

0.4%Pt/P25(DP-H₂) and 0.4%Pt/P25(DP-HCHO) at 30 °C and 0.16%Pt/P25 (DP-HCHO) at 70 °C. As shown, the 0.4%Pt/P25 (DP-HCHO) shows good stability over the 100 h test with a HCHO conversion of around 98%, while 0.16%Pt/P25(DP-HCHO) also presents good stability with a HCHO conversion of approximately 94%. The HCHO conversion over 0.4%Pt/P25 (DP-H₂), however, decreases rapidly from 94% to 87% during the long-term on-stream test.

3.4. In-situ DRIFT analyses

In the following experimental trials, the differing activities of Pt/P25 catalysts prepared and activated with different methods were studied during HCHO oxidation with respect to the behavior of adsorbed species on the catalyst surface, using *in-situ* DRIFTS. Fig. 4 presents the dynamic changes in the DRIFTS spectra of the 0.4%Pt/P25 catalysts as a function of time in a flow of O₂ + HCHO + He at 30 °C. After exposing the catalyst to the O₂ + HCHO + He mixture, four bands appeared at 2062, 1657, 1570, and 1359 cm⁻¹. According to previous studies, the two strong bands at 1570 and 1359 cm⁻¹ are ascribed to $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ on catalyst sites [24,25], demonstrating that the adsorbed HCHO was converted into formate species. The very weak band at 2062 cm⁻¹ is assignable to linear CO adsorbed on Pt [6], and the band at 1657 cm⁻¹ is due to water adsorbed on the catalyst (originating from the water in the

reactant gas mixture) [6]. In our previous work [26], we found that adsorbed formate species and adsorbed CO were the main intermediate species, based on *in-situ* DRIFTS analysis. With increasing exposing time, the band intensities increase and reach a steady level after 60 min. A semi-quantitative analysis was performed by calculating the integrated area of the formate species band at 1570 cm⁻¹, and the results showed that, during the first 5 min of on-stream time, both the band intensities and the intensity increment over the Pt/P25(DP-HCHO) were the largest among these samples, while with increasing time both the band intensities and the intensity increment over Pt/P25(DP-H₂) became the largest, and Pt/P25(IM-H₂) exhibited the smallest values during the entire 60 min on-stream time. The amount of formate species over the catalyst surface is determined by two factors: the formation rate from adsorbed HCHO and the decomposition rate. The overall effect of the two factors can increase or decrease the formate species amount, depending on their relative dominance. Based on these results in combination with the activity test data provided in Fig. 3, we propose that the lower formate species amount over the Pt/P25(IM-H₂) is due to the slow formation of formate species on this material. Both the formate species formation rate and decomposition rate over the Pt/P25(DP-HCHO) are the fastest, resulting in a lower concentration of formate species but higher activity in comparison with the activity obtained over the Pt/P25(DP-H₂).

Fig. 4. *In-situ* DRIFTS spectra of O₂ + HCHO + He gas mixture adsorption over (a) 0.4%Pt/P25(DP-HCHO), (b) 0.4%Pt/P25(DP-H₂), and (c) 0.4%Pt/P25(IM-H₂) at 30 °C and (d) areas of 1570 cm⁻¹ peak over time for these same materials.

Fig. 5. *In-situ* DRIFTS spectra of $\text{O}_2 + \text{HCHO} + \text{He}$ gas mixture adsorption at various temperatures over (a) 0.16%Pt/P25(DP-HCHO), (b) 0.4%Pt/P25(DP-HCHO), (c) 0.4%Pt/P25(IM-H₂), (d) 0.8%Pt/P25(IM-H₂), (e) 0.4%Pt/P25(DP-H₂), and (f) 0.8%Pt/P25(DP-H₂).

Fig. 5 summarizes the changes in the DRIFTS spectra of the Pt/P25 catalysts made with different Pt loading amounts and different activation methods at various temperatures in a flow of $\text{O}_2 + \text{HCHO} + \text{He}$. As shown, the band ascribed to the adsorbed formate species at 1570 cm^{-1} varied with both temperature and Pt loading amount for all the samples.

Fig. 6 shows changes in band intensity with temperature and Pt loading amounts. For the Pt/P25(DP-HCHO), the band intensity decreased with increasing temperature and Pt loading, and a similar trend is also observed over Pt/P25(DP-H₂), as shown in Fig. 6(b). Over Pt/P25(IM-H₂), however, the band intensity increased with increasing temperature and Pt loading. A comparison of the intensity changes over Pt/P25(DP-HCHO), Pt/P25(DP-H₂), and Pt/P25(IM-H₂), all with the same 0.4% Pt loading, is presented in Fig. 6(d). It is apparent that both the band intensity and the change of intensity with temperature over Pt/P25(DP-H₂) were the largest. These results are consistent with the activity test results in Fig. 3 and the dynamic changes in the DRIFTS spectra in Fig. 4. Pt/P25(DP-HCHO) was thus active with regard to both the fast conversion of adsorbed HCHO to formate species and the oxidation of formate species even at room temperature. Therefore, with the exception of the 0.16%Pt/P25(DP-HCHO), although a relatively high concentration of adsorbed formate species was detected, high activity for the oxidation reaction was observed over the Pt/P25(DP-HCHO) catalysts. In the case of the Pt/P25(IM-H₂) materials, the low concentration of adsorbed formate species together

with reduced activity during the oxidation reaction indicates that the generation of formate species is also a necessary step in the HCHO oxidation process, especially at a low reaction temperatures and reduced Pt loadings. With increasing Pt loading amounts or elevated reaction temperatures, the accumulation of adsorbed formate species over the Pt/P25(IM-H₂) catalysts indicates that the enhanced oxidation of formate species became the rate-determining step. The activity of the Pt/P25(DP-H₂) was between those of the Pt/P25(DP-HCHO) and Pt/P25(IM-H₂). The rapid generation of formate species over Pt/P25(DP-H₂) materials can evidently be realized even at room temperature. However, the rate of formate species oxidation over Pt/P25(DP-H₂) was lower than that over Pt/P25(DP-HCHO), and the accumulated formate species would therefore tend to block the active areas [25], resulting in lower HCHO oxidation activity. The results also indicate that the rate-determining step during HCHO oxidation over the 0.4%Pt/P25(DP-H₂) was the complete oxidation of formate species. With increasing Pt loadings or elevated reaction temperatures, the concentration of adsorbed formate species decreased while the activity rapidly increased.

Zhang and He [6] proposed a reaction scheme for HCHO oxidation over TiO_2 -supported noble metal catalysts involving the behavior of surface-adsorbed species, based on data obtained from *in-situ* DRIFTS. In this mechanism, HCHO is initially oxidized into formate surface species (step 1), following which the formate surface species decompose directly to produce ad-

Fig. 6. Intensity of the 1570 cm⁻¹ band as a function of temperature for (a) Pt/P25(DP-HCHO), (b) Pt/P25(DP-H₂), and (c) Pt/P25(IM-H₂) at various Pt loadings and (d) a comparison of these groups of catalysts.

sorbed CO species and H₂O (step 2) and, finally, these CO species react with O₂ to produce gas phase CO₂ (step 3). The conversion of surface formate species to adsorbed CO on the catalysts (step 2) is usually regarded as the rate-determining step for Pt/TiO₂ catalysts [6,13]. Based on the *in-situ* DRIFTS data from our recent work [20], however, we generally separated this process into two parts: a storage step and an oxidation step. In the storage step, HCHO is initially chemisorbed and reacts with chemisorbed oxygen to generate formate surface species and then decomposes into adsorbed CO species and H₂O. In the oxidation step, the adsorbed CO species react with O₂ or chemisorbed oxygen to produce gas phase CO₂, and gaseous O₂ is reactivated by the active sites to form chemisorbed oxygen. In the present study, we determined that both the Pt loading method and the reduction treatment have significant effects on the structural properties of the Pt/P25 catalysts and the resulting catalytic activity for HCHO oxidation, such that uniformly dispersed metallic Pt nanoparticles with smaller size were obtained on the Pt/P25(DP) compared with the Pt/P25(IM). Although the relatively large Pt particles resulted in greater quantities of chemisorbed oxygen over the Pt/P25(IM-H₂), which is considered an important factor with regard to instilling high activity in the reduced Pt/TiO₂ catalysts [12], the Pt/P25(IM-H₂) still exhibited lower catalytic activity. A semi-quantitative analysis based on the *in-situ* DRIFTS study indicated that the Pt/P25(IM-H₂) was much less effective for either the formation of formate species or formate decomposition, and so the activity of these materials for HCHO oxidation was very low. Although both Pt/P25(DP-HCHO) and Pt/P25(DP-H₂) were prepared with the same Pt loading method, the average Pt particle size, chemisorbed oxygen concentra-

tion, and HCHO oxidation activity over the Pt/P25(DP-HCHO) were all greater than those over the Pt/P25(DP-H₂), indicating that the reduction treatment had a pronounced influence on the structural properties and catalytic activity of the Pt/P25 catalysts. The *in-situ* DRIFTS data indicated that the Pt/P25(DP-H₂) was less effective with regard to formate decomposition, and so its activity for HCHO oxidation was lower than that of the Pt/P25(DP-HCHO). All these results indicate that the presence of metallic Pt with an appropriate particle size in conjunction with an optimal concentration of chemisorbed oxygen leads to much more efficient HCHO oxidation. The site density of reactive surface oxygen, which is considered an important factor in the activity of Pt/TiO₂ catalysts [12], increases with larger Pt particles [21,27] such that overly small Pt particles (such as on the Pt/P25(DP-H₂) in this work) lead to poor activity, especially in the conversion of surface-adsorbed formate species. However, the overall activity of Pt/P25 diminishes with further increases in the Pt particle size because of the activity loss caused by the simultaneous decrease in the number of surface Pt atoms. Thus, although the Pt/P25(IM-H₂) had a high concentration of chemisorbed oxygen, it was less effective for HCHO oxidation.

4. Conclusions

We have demonstrated that both the Pt loading method and the reduction treatment have significant effects on the structural properties of the Pt/P25 catalysts, as well as the resulting catalytic activity for HCHO oxidation. Pt/P25 catalysts prepared by the DP method followed by HCHO reduction showed homogeneously dispersed Pt nanoparticles of appropriate size, as

Graphical Abstract

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Titania-supported Pt catalyst reduced with HCHO for HCHO oxidation under mild conditions

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A Pt/TiO₂(P25) catalyst was prepared by deposition-precipitation (DP) and reduction with HCHO. The catalyst exhibited homogeneously dispersed, appropriately sized Pt particles and a high concentration of chemisorbed oxygen and showed high activity for HCHO oxidation.

well as high concentrations of chemisorbed oxygen and high activity for HCHO oxidation. A HCHO conversion of 98% was achieved over the Pt/P25(DP-HCHO) at 30 °C even at a relatively low Pt loading of 0.4%, and this conversion was stable for more than 100 h. Pt/P25 prepared by the DP method but reduced with a H₂ stream was less effective in terms of the formate decomposition step and thus exhibited lower rates of HCHO oxidation, likely because of low levels of chemisorbed oxygen. Pt/P25 prepared by the IM method followed by reduction in a H₂ stream had the highest concentration of chemisorbed oxygen but the largest Pt particles, and thus showed the poorest activity for both the formation of formate species and the formate decomposition into CO species, and finally for HCHO oxidation. The activity barrier for HCHO oxidation over Pt/P25(DP-H₂) and Pt/P25(IM-H₂) can evidently be overcome by increasing both the Pt loading amount and the reaction temperature. In addition, the technique of reduction via a HCHO solution has been demonstrated to represent an effective means of reducing supported metal catalysts without introducing inorganic impurities.

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甲醛还原Pt/TiO₂催化剂用于温和条件下高效催化氧化甲醛

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摘要: 通过浸渍法(IM)和沉积-沉淀(DP)法制备了一系列Pt/TiO₂(P25)催化剂, 并分别用甲醛溶液和氢气还原处理催化剂。利用原

位红外监测催化剂表面吸附物种在反应过程中的变化, 探究了催化剂制备和还原条件及Pt负载量对催化剂结构和催化氧化甲醛活性的影响. 结果显示, 用DP法制备并用甲醛还原的Pt/P25催化剂中Pt颗粒分散均匀, 并具有合适的粒径和高浓度的表面活性氧, 显示出良好的甲醛氧化活性. 在空速30 000 ml/(g·h)、反应温度30 °C和甲醛初始浓度50 mg/m³的条件下, 0.4%Pt/P25(DP-HCHO)上的甲醛转化率达到98%, 并能稳定运行100 h以上. 相比之下, Pt/P25(DP-H₂)由于表面活性氧较少, 不利于甲酸盐氧化, 活性较低. Pt/P25(IM-H₂)虽然具有高浓度的表面活性氧, 却同时具有最大的Pt颗粒粒径, 在甲醛转化为甲酸盐和甲酸盐氧化两步反应中的活性均较差, 因而甲醛氧化活性最差.

关键词: 甲醛; 铂; 二氧化钛; 原位红外光谱; 沉积-沉淀法

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