Hydroxyapatite-Supported Low-Content Pt Catalysts for Efficient Removal of Formaldehyde at Room Temperature

Zhihua Xu,* Gang Huang,† Zhaoxiong Yan,* Nenghuan Wang,‡ Lin Yue,† and Qiongyu Liu†

ABSTRACT: Indoor environmental quality directly affects the life quality and health of human beings, and therefore, it is highly vital to eliminate the volatile organic compounds especially formaldehyde (HCHO), which is regarded as one of the most common harmful pollutants in indoor air. Hydroxyapatite (HAP)-supported Pt (Pt/HAP) catalysts with a low content of Pt (0.2 wt %) obtained via hydrothermal and chemical reduction processes could effectively remove gaseous HCHO from the indoor environment at room temperature. The influence of modifier in the preparation on the catalyst activity was investigated. The HAP and HAP modified by sodium citrate and hexamethylenetetramine-supported 0.2 wt % Pt could completely decompose HCHO into CO₂ and water, while HAP modified by sodium dodecyl-sulfate-supported Pt removed HCHO primarily via adsorption. The HAP modified by the sodium citrate catalyst exhibited superior catalytic performance of HCHO compared to the HAP and HAP modified by hexamethylenetetramine and sodium dodecyl-sulfate-supported Pt catalysts, which was mainly because of its higher surface Ca/P ratio providing more Lewis acidic sites (Ca²⁺) for co-operative capture of HCHO molecules and a larger amount of active oxygen species. Our results indicate that an optimized combination of functional supports and low-content noble metal nanoparticles could be a route to fabricate effective room-temperature catalysts for potential application in indoor air purification.

1. INTRODUCTION

Formaldehyde (HCHO), which could be released from adhesives, paints, and decorative materials for a long time in an airtight space, is well known for its harm to human health.¹⁻⁴ Efficient abatement of HCHO from indoor air is of great importance to air quality control and environmental safety purposes.⁵⁻¹⁰ In recent years, HCHO removal at room/ambient temperature over supported noble metals has attracted enormous attention because of its mild and “green” operation conditions, that is, no demand of extra energy and equipment.¹¹⁻¹⁷ Supported Pt catalysts have been considered as the most active catalytic materials for HCHO oxidation reaction at room temperature,¹⁸⁻²² whose activities are closely influenced by the supports. Oxides/hydroxides such as TiO₂,²³ CeO₂,²⁴ MnO₂,²⁵⁻²⁷ Co₃O₄,²⁸ SiO₂,²⁹ FeOOH,³⁰ and AlOOH³¹ have been intensively exploited to immobilize Pt nanoparticles (NPs) for HCHO decomposition, which take full advantage of stabilizing highly dispersed Pt NPs, generating active oxygen species (such as OH, O*, and O₂⁻) resulted from an metal-support interaction and enhancing the adsorption and subsequent oxidation of HCHO molecules because of the plenty of surface hydroxyls.³²⁻³⁶ However, the functional composite catalysts possessing distinct surface acid–base properties, which may exhibit unexpected HCHO capture and auxiliary oxidation performance, have not yet been systematically investigated for HCHO elimination at room temperature.

Hydroxyapatite (HAP, Ca₁₀[(PO₄)₆(OH)₂]) is one of the most stable forms of calcium phosphates, which is a major inorganic component of human body hard tissues like bones and teeth. The HAP nanomaterial has been widely investigated in the biomedical and catalyst-promoter applications because of its excellent chemical stability, bioactivity, and biocompatibility.³⁷⁻³⁹ Although HAP was previously reported as an efficient support for nano-gold (1 wt %) for HCHO oxidation at room temperature,⁴⁰ which was found to boost the stabilization of gold NPs against sintering. Nevertheless, the high content of noble metal (1 wt %) as one of the main defects hinders the practical application of the catalyst because of its depletable resource and high price. Since Huang et al. in 2011 reported the Pt/TiO₂ with 0.1 wt % loading of Pt for nearly 100% HCHO conversion at ambient temperature,⁴¹ some efforts have continued the exploitation of low-content noble metal NP catalysts for HCHO abatement at room temperature.⁴²⁻⁴⁴ However, it is still imperative to achieve functional composite catalysts with low loading of noble metal and without compromise of their catalytic performance.
Considering its environmental friendliness, rich resource and unique surface acid–base character, the HAP-supported low-content Pt (0.2 wt %) catalyst was prepared and explored for HCHO removal at room temperature; and the effect of the modifier introduced in the preparation process on the catalyst surface property and activity toward HCHO oxidation was investigated.

2. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-prepared HAP samples. All the major diffraction peaks of the samples were in line with those of the standard HAP (JCPDS no. 09-0432), suggesting successful synthesis of the HAP. However, the relative intensities of (210), (211), (112), and (300) peaks for the obtained samples were different from those of the standard HAP. This illustrates that the orientation of the crystal growth was somewhat different, primarily because of the different preparation conditions. HAP–sodium citrate (SC) presented an identical XRD pattern to that of HAP, indicating that the introduction of the modifier did not obviously change the phase structure. Moreover, no evident difference in the XRD pattern was observed for the supported Pt catalysts compared to the unsupported samples. This indicates that Pt deposition did not alter the crystal phase of the HAP support. No Pt phase was detected, mainly because of a small amount and/or high dispersion of Pt NPs.

Fourier transform infrared (FTIR) spectra (Figure 2) were used to characterize the functional groups of the samples. The bands at ca. 1023, 600, and 563 cm$^{-1}$ were because of the asymmetrical stretching and bending vibration of PO$_4$ groups, respectively. The band at ca. 962 cm$^{-1}$ was assigned to the symmetrical stretching vibration of PO$_4$ groups, and bands at ca. 3644 and 630 cm$^{-1}$ were attributed to the stretching and bending vibration of OH groups in the crystal structure of HAP, respectively.$^{45,46}$ This phenomenon manifests the existence of PO$_4$ and OH functional groups in the prepared samples. The bands at 1457, 1417, 872, and 713 cm$^{-1}$ were because of the vibration of CO$_3$$^{2-}$ groups,$^{17-49}$ implying that some PO$_4$$^{3-}$ ions in the crystal structure were replaced by CO$_3$$^{2-}$ ions. It also reveals that the as-prepared samples were the carbonate-containingapatites.$^{30}$ Moreover, the modified HAP (e.g., HAP–SC) and supported Pt samples presented similar FTIR spectra to those of the pure HAP. No modifier residues were observed, indicative of a relatively high purity of the obtained samples. Closer observation is found that the strong P–O band (ca. 1023 cm$^{-1}$) shifted to a lower wave number for Pt-loaded HAP compared to that of the pure HAP support (Figure 2b), while no obvious shift was observed for the OH band (not shown). This is an indication of an interaction between Pt NPs and PO$_4$$^{3-}$ groups.$^{40}$

The thermogravimetric (TG) analysis of the samples was conducted in a nitrogen atmosphere. As shown in Figure 3, three weight loss regions were observed in the investigated temperature. The first stage under 150 °C was attributed to evaporation of adsorbed water. The second region in the range of 150 and 500 °C was associated with the removal of chemical adsorbed/structural water.$^{51}$ The weight loss in the second region for HAP–SC, Pt/HAP–SC, Pt/HAP–SC-1, Pt/HAP–SC-2, Pt/HAP, Pt/HAP–HMT, and Pt/HAP–SDS. was 7.3, 1.41, 2.56, 1.28, 8.70, 2.86, and 1.50%, respectively. This result revealed that Pt/HAP–SC had the least amount of chemical adsorbed/structural water. The last step above 500 °C was because of decarbonation,$^{51}$ which originated from the CO$_2$ in air dissolved in the alkaline solution during the preparation process.

The effect of the modifier on HCHO removal is investigated in Figure 4. The HCHO concentration declined with the prolonging reaction time for all samples, and the HCHO removal performance followed the order: Pt/HAP–SC > Pt/HAP–HMT > Pt/HAP > Pt/HAP–SDS. That is, the HCHO removal efficiency after 60 min was 75, 73, 54, and 48% for Pt/HAP–SC, Pt/HAP–HMT, Pt/HAP, and Pt/HAP–SDS, respectively, which was much higher than that for Pt/TiO$_2$ (38%). This suggests the superiority of HAP support to TiO$_2$.
The relative CO₂ yield was 1.33, 0.76, 0.57, and about zero for Pt/HAP-SC, Pt/HAP-HMT, Pt/HAP, and Pt/HAP-SDS, respectively. Pt/HAP-SC, Pt/HAP-HMT, and Pt/HAP showed catalytic oxidation of HCHO into CO₂ and H₂O at room temperature. Surprisingly, Pt/HAP-SDS seemed to remove HCHO by adsorption because no product of CO₂ was observed. This result indicates that the modifier had an apparent influence on the catalytic activity of the catalysts. That is to say, we could achieve a highly efficient catalyst by tuning the modifiers in this work.

The Pt/HAP-SC sample showed the best catalytic performance for HCHO decomposition into CO₂ and H₂O at room temperature. Subsequently, the influence of Pt content on HCHO removal over Pt/HAP-SC is probed in Figure 5.

For HAP-SC and Pt/HAP-SC-1, a decline in HCHO concentration was observed, accompanied by a decrease in CO₂ concentration. The decrease of HCHO and CO₂ concentration in the reactor was mainly adsorbed by the two samples because of their basic surfaces. Moreover, incomplete oxidation of HCHO into formate species which cannot be monitored by the equipment, may also contribute to the decline of gaseous HCHO. As the Pt content increased to 0.2 wt % (Pt/HAP-SC), the decreased HCHO concentration and increased CO₂ concentration were seen, indicating the decomposition of HCHO into CO₂ and H₂O. With further increasing Pt loading to 0.4 wt % (Pt/HAP-SC-2), the HCHO removal and CO₂ yield further increased. In consideration of the relatively small specific surface area of the catalysts and Pt agglomeration, as well as the cost price of Pt in practical application, the Pt loading in this work was chosen as 0.2 wt %. This result also demonstrated that complete decomposition of HCHO at room temperature required an appropriate amount of dispersed Pt for activation of O₂ or generation of reactive oxygen species, which triggered the HCHO oxidation reaction and oxidized its intermediates into CO₂ and H₂O.

Figure 6 shows the scanning electron microscopy (SEM) images of HAP-SC, Pt/HAP-HMT, Pt/HAP-SDS, Pt/HAP, and Pt/HAP-SC. All samples displayed an appearance of particle agglomeration. However, the difference in the morphologies of the samples could apparently be recognized. For example, the mean particle size followed as: Pt/HAP-SC > Pt/HAP-HMT ≈ Pt/HAP-SDS > Pt/HAP. This implied that the modifier addition in the preparation process could change the morphology, which would lead to a difference in the catalytic performance. Compared to those of HAP-SC, the particle edges of Pt/HAP-SC became obscure. This was
presumably caused by Pt deposition, indicative of a strong interaction between the HAP support and Pt NPs. However, the samples in our work exhibited much lower surface areas (listed in Table 1) than those obtained via a hydrothermal method (31–43 m²/g).52 As seen from Table 1, the introduction of the modifier in the preparation process increased the specific surface areas. Pt/HAP–SDS possessed the largest \( S_{BET} \), which was similar to that of Pt/HAP–HMT and 1.72 times as large as that of Pt/HAP–SC. Based on the result of the performance tests, the specific surface area was not the decisive factor for the catalytic activity of the samples. The typical EDS spectrum of Pt/HAP–SC is shown in Figure 6f. Strong peaks attributed to Ca, P, and O elements and weak peaks because of Na and Pt elements were observed, indicative of the successful synthesis of HAP-supported Pt catalyst. TEM image (Figure 6g) confirmed that Pt NPs were immobilized on the HAP support companied by the lattice spacing of 0.222 nm and 0.33 nm associated with Pt (111) and HAP (002) lattice planes, respectively (inset of Figure 6g). The vague boundary between Pt and HAP was an indication of the strong interaction between them.

**Table 1. Comparison of the Texture and XPS Results for Pt/HAP, Pt/HAP–SC, Pt/HAP–HMT, and Pt/HAP–SDS**

| samples         | \( S_{BET} \) (m²/g) \( ^a \) | \( V_{pore} \) (cm³/g) \( ^a \) | Ca/P ratio \( ^b \) | \( (O_{surf} + O_{bulk})/O_{total} \) (%) |
|-----------------|--------------------------------|-------------------------------|------------------|----------------------------------------|
| Pt/HAP          | 5.7                            | 0.04                          | 1.81             | 8.5                                    |
| Pt/HAP–SC       | 6.2                            | 0.04                          | 1.84             | 10.3                                   |
| Pt/HAP–HMT      | 10.3                           | 0.06                          | 1.80             | 8.5                                    |
| Pt/HAP–SDS      | 10.7                           | 0.06                          | 1.49             | 6.2                                    |

\( ^a \)Obtained from the nitrogen sorption isotherm result. \( ^b \)Obtained from the XPS result.

Figure 7a displays the hydrogen temperature-programmed reduction (\( \text{H}_2-\text{TPR} \)) patterns of Pt/HAP–SC, Pt/HAP–HMT, and Pt/HAP–SDS. Reduction peaks related to Pt oxides could not be discerned at relatively low temperature, indicating a negligible amount of Pt oxide and/or a small amount of Pt immobilized over the support. A strong band at 550–790 °C was observed, attributed to the reduction of bulk oxygen of the catalysts. It is clearly observed that Pt/HAP–SC shifted to a lower temperature compared to the other catalysts, presumably resulting from the strong interaction between Pt NPs and HAP–SC support. The addition of the modifier in the preparation process may alter the surface acidity/basicity of the catalysts, which may affect their catalytic activities toward HCHO removal at room temperature. To clarify the relationship between the additives and acidic/basic surface properties of the samples, temperature-programmed desorption of CO₂ (CO₂-TPD) measurements were carried out (Figure 7b). Some distinguished peaks appeared in the CO₂-TPD curves of the four samples, illustrating the existence of surface basic sites. For Pt/HAP–HMT, the CO₂ desorption peaks were seen at ca. 216, 385, and 706 °C, associated with the weak, moderate, and strong basic sites, respectively.53 For Pt/HAP, Pt/HAP–SC, and Pt/HAP–SDS, two peaks were observed at 370–390 and 700–712 °C, related to the moderate and strong basic sites, respectively. The number of basic sites is proportional to the intensity of the basic peak. The relatively weaker peak at 370–390 °C for Pt/HAP–SDS and Pt/HAP–SC indicates a smaller amount of moderate basic sites. Herein, the number of basic sites seemed to have no obviously positive effects on the catalytic performance of the catalysts by comparing the results of CO₂-TPD and the HCHO removal performance. This phenomenon is similar to the observation of the previous literature.53

The X-ray photoelectron spectroscopy (XPS) spectra for Pt/HAP–SC, Pt/HAP–HMT, and Pt/HAP–SDS are summarized in Figure 8. High-resolution XPS spectra of Ca 2p and P 2p peaks in Figure 8a,b confirmed the successful preparation of HAP. The atomic ratios of Ca/P are 1.81, 1.84, 1.80, and 1.49 for Pt/HAP, Pt/HAP–SC, Pt/HAP–HMT, and Pt/HAP–SDS, respectively. Pt/HAP, Pt/HAP–SC, and Pt/HAP–HMT presented a higher Ca/P ratio compared to that of the stoichiometric Ca₁₀(Z₃PO₄)₆(OH)₂. It manifests that Pt/HAP, Pt/HAP–SC, and Pt/HAP–HMT possessed calcium-enriched surfaces,54 with CO₃²⁻ anions introduced to compensate the charge caused by excess calcium cations in the apatite solids.50 However, Pt/HAP–SDS showed a lower Ca/P ratio than that of Ca₁₀(Z₃PO₄)₆(OH)₂ (Ca/P = 1.67), suggesting that it possessed a nonstoichiometric Ca-deficient surface with the introduction of H⁺ ions and depletion of OH⁻ ions denoted by the formula Ca₁₀-Z(HPO₄)₆(PO₄)₆-Z(OH)₂-Z (0 < Z < 1).55 That is to say, Pt/HAP, Pt/HAP–SC, and Pt/HAP–HMT acted as basic catalysts with the presence of acid sites, and Pt/HAP–SDS acted as an acid catalyst with the existence of basic sites.56,57

The diversity in the surface chemical property could lead to distinct performances for HCHO adsorption and subsequent catalytic oxidation activity. Therefore, it is easy to understand a higher activity of Pt/HAP, Pt/HAP–SC, and Pt/HAP–HMT than that of Pt/HAP–SDS because the basic surface facilitates the capture of gaseous HCHO molecules.
The core level of Pt 4f7/2 (71.1−71.3 eV) and Pt 4f5/2 (74.4−74.6 eV) in Figure 8c illustrated the metallic state of Pt in the samples,58 further confirming the successful deposition of Pt NPs over the HAP supports. Three peaks at 531.2, 531.8, and 532.7 eV were deconvoluted in the O 1s spectra of the samples (Figure 8d), corresponding to oxygen of $\text{PO}_4^{3-}$, $\text{CO}_3^{2-}$, and OH anion ($\text{O}_\text{OH}$)/adsorbed oxygen species ($\text{O}_\text{ads}$) originated from the strong interaction between Pt and HAP support, respectively.59,60 The percentage of ($\text{O}_\text{OH} + \text{O}_\text{ads}$)/$\text{O}_{\text{total}}$ was 8.5, 10.3, 8.5, and 6.2% for Pt/HAP, Pt/HAP−SC, Pt/HAP−HMT, and Pt/HAP−SDS (listed in Table 1), respectively. Considering the lowest content of chemical adsorbed/structural water in the TG analysis, the obtained data indicated that Pt/HAP−SC had the largest amount of adsorbed oxygen species. Usually, a higher content of active adsorbed oxygen species is beneficial to catalytic oxidation of HCHO molecules, which could be the main reason for the superior performance of Pt/HAP−SC.

The electron paramagnetic resonance (EPR) of the catalyst before test and after test is shown in Figure 9. The signal at $g \approx 2.027$ for Pt/HAP−SC before HCHO oxidation test could be approximately attributed to surface-bound superoxide radical anions ($\text{O}_2^-$).61,62 The $\text{O}_2^-$ species presumably originated from surface anion vacancies located at or adjacent to the Pt and HAP interface,57,62,63 which were promoted by the strong interaction between Pt NPs and hydroxyl groups of HAP. After the Pt/HAP−SC catalyst was exposed in the HCHO gas, the signals attributable to superoxide radical anions disappeared, implying that the active oxygen species quickly participated in the oxidation reaction of HCHO molecules.

In situ diffused reflectance infrared Fourier transform (DRIFT) spectra in Figure 10 were used to study the possible reaction pathway of HCHO oxidation over the Pt/HAP−SC catalyst. After the reactant HCHO/O$_2$ gas was in contact with the catalyst (Figure 10a), some featured DRIFT peaks were observed, revealing the occurrence of HCHO oxidation over the catalyst. The broad band centered at ca. 3268 cm$^{-1}$ was related to the generated water in the HCHO oxidation reaction process. The peaks at 2979, 2987, and 2822 cm$^{-1}$ were caused by C−H stretching bands of adsorbed HCOO [(HCOO)$_\text{ads}$] and adsorbed HCHO, respectively.64 The peaks at ca. 1507 and 1340 cm$^{-1}$ were related to the vibration of adsorbed formate species, and peaks at 1457 and 1418 cm$^{-1}$ were associated with CO$_3^{2-}$ ions,50 resulted from the CO$_2$ product and/or CO$_2$ in the atmosphere reacting with the OH$^-$ of the catalyst. Some new small peaks at ca. 3853, 3750, 3649, and 3567 cm$^{-1}$ were observed with increasing the reaction time to 20 min. The peaks at 1771−1716 cm$^{-1}$ were because of the carbonyl group of adsorbed HCHO on different surface sites of the catalyst,65 and peaks at ca. 3853, 3750, 3649, and 3567 cm$^{-1}$ were because of the hydroxyl groups of the HCHO derivatives.66,67 Peaks at 1868 and 1844 cm$^{-1}$ were connected with the bridging CO bonded to the surface of the catalyst.68,69 It can be deduced that the adsorbed HCHO molecules were quickly
oxidized into formate or CO species. This phenomenon suggests that the further oxidation of formate and CO intermediates is the rate-determining step. In the HCHO/N2 gas flow (Figure 10b), a broad band at ca. 3276 cm$^{-1}$ could be discerned, indicative of the generation of water. Moreover, the peak related to adsorbed formate (1600 cm$^{-1}$) and small bands associated with the C–H stretching bands of adsorbed formate (2892 and 2801 cm$^{-1}$) appeared, which increased with increasing the reaction time to 40 min and remained almost constant with further increasing the reaction time to 60 min. Negative peaks at ca. 3569–3850 cm$^{-1}$ were related to the consumption of isolated surface hydroxyls. This phenomenon illustrated that the active surface hydroxyls directly participated in the decomposition of HCHO into formate species.

The recycle performance for HCHO removal over the Pt/HAP–SC catalyst is shown in Figure 11a. The removal capacity of the catalyst decreased during the initial three runs and then remained almost unchangeable for the next runs with about a half of the first removal efficiency. It implies that the obtained catalyst with much low Pt content possessed a relatively stable activity toward HCHO removal. In order to uncover the reason of the catalyst deactivation, the FTIR spectra before and after HCHO test for the Pt/HAP–SC catalyst are investigated in Figure 11b. Some new peaks appeared in the spectrum after HCHO test. For example, the peak at 3572 cm$^{-1}$ was because of the intermolecular hydrogen bond resulted from the (HCOO)$_{ad}$ and peaks at 2979 and 2874 cm$^{-1}$ were attributed to the $\nu_s$(C–H) in (HCOO)$_{ad}$.$^{31,70}$ The small peak at 2513 cm$^{-1}$ is because of CO$_2$ substituting PO$_4^{3–}$ groups of HAP,$^{11}$ and peaks at 1795 and 1590 cm$^{-1}$ were ascribed to the $\nu_s$(CO) and $\nu_{as}$(COO) in (HCOO)$_{ad}$,$^{12,66}$ respectively. Moreover, a shift to a higher wavenumber was observed in the range of 900 and 1500 cm$^{-1}$ after the test, suggesting a strong interaction between adsorbed species and the catalyst. These phenomena implied that the formate species were strongly adsorbed on the surface of the catalyst, in agreement with the DRIFT result. Thus, the adsorbed species on the catalyst surface were presumed to be the main factor for the loss of the catalyst activity.

According to the above results, the pathway for HCHO removal over Pt/HAP–SC at room temperature is proposed in Figure 12. First, HCHO molecules were captured by HAP via hydrogen bonding between the H atom of HCHO and O atom of PO$_4^{3–}$ and simultaneously via weak electrostatic attraction between Ca of HAP and O atom of HCHO (step I). In the meantime, oxygen from air was adsorbed on the surface of Pt NPs which interacted with and stabilized by PO$_4^{3–}$ ions of the
support. The adsorbed oxygen molecules on the Pt surface interacted with hydroxyl ions (OH\(^-\)) nearby the Ca\(^{2+}\). Then, the adsorbed oxygen molecules and hydroxyl ions (OH\(^-\)) concurrently evolved into superoxide radical anions (O\(_2\)\(^{-}\)) and hydroxyl radicals ([OH]_{ads}), respectively, resulting to the formation of OH\(^-\) vacancies (δ\(^-\)) (step II).\(^{39,50}\) The active surface hydroxyls/generated (OH)\(_{ads}\) and/or superoxide radical anions (O\(_2\)\(^{-}\)) attacked the adsorbed HCHO (step III), leading to the formation of adsorbed HCOOH ([HCOOH]_{ads}) and/or [(CO)]_{ads} (step III),\(^{72}\) and the regeneration of hydroxide ion adjacent to Ca. Finally, the (HCOOH)\(_{ads}\) and (CO)\(_{ads}\) were further oxidized to CO\(_2\) and H\(_2\)O by the active oxygen species on the catalyst surface (step IV). It can be speculated that exposed Ca\(^{2+}\), PO\(_4\)^{3-}, and OH\(^-\) play co-operational roles in gaseous HCHO adsorption and decomposition. Therefore, it is one of the reasons that Pt/HAP−SC, Pt/HAP, and Pt/HAP−HMT displayed better catalytic performance for HCHO oxidation because of their higher surface Ca/P ratios compared to that of Pt/HAP−SDS based on the XPS analysis.

3. CONCLUSIONS

HAP-based catalysts with a low loading of Pt (0.2 wt %) synthesized by hydrothermal and NaBH\(_4\) reduction were investigated for HCHO removal at room temperature. The organic additive had a visible effect on the activity of the HAP-based catalysts. Pt/HAP−SC possessed a superior catalytic performance among the studied samples mainly because of its plenty of active oxygen species and high surface Ca/P ratio, which played a synergistic effect in HCHO capture. The formation of active oxygen species presumably induced by the strong interaction between Pt NPs and HAP support should be responsible for the catalytic performance for HCHO oxidation at room temperature. Gaseous HCHO molecules were first adsorbed and then oxidized into formate or CO species, which were finally decomposed into CO\(_2\) and H\(_2\)O on the Pt/HAP−SC surface. This work provides some insight into the design and fabrication of functional catalysts with low cost for environmental remediation.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation. HAP was synthesized as follows. 4.78 g of Ca(NO\(_3\))\(_2\)·4H\(_2\)O was dissolved in 100 mL of deionized water (solution I), and 1.58 g of Na\(_3\)HPO\(_4\)·12H\(_2\)O was dissolved in 40 mL of 2 mol/L NaOH solution (solution II). The solution I and II were mixed at 40 °C under magnetic stirring for 8 h. Then, the mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. Subsequently, the obtained precipitate was centrifuged and washed by deionized water several times and dried at 60 °C in a vacuum oven. Finally, the obtained powder was calcined at 700 °C for 2 h with a rate of 5 °C/min.

The modified HAP was obtained by using the above-mentioned procedure of pure HAP except that solution I consisted of Ca(NO\(_3\))\(_2\)·4H\(_2\)O (4.78 g) and the modifiers (0.1 g), for example, SC, SDS, or HMT.

The supported Pt catalysts were prepared according to our previous reports.\(^{24,31}\) Briefly, 0.4 g of HAP or modified HAP powder or TiO\(_2\) (Haining Fine Chemical Factory in Hebei district of Tianjin) was dispersed in 30 mL of deionized water, and then a H\(_2\)PtCl\(_6\) solution possessing varied nominal weight of Pt (0.4, 0.2, and 0.08 wt %) was added under magnetically stirring. Thereafter, 5 mL of a reducing mixture of NaBH\(_4\) (0.1 mol/L) and NaOH (0.1 mol/L) was immediately injected to the above suspension and stirred intensely for another 30 min. Finally, the resulting slurry was washed twice with deionized water and ethanol and dried at 60 °C in a vacuum oven. The nomenclature and concise information of the obtained samples are listed in Table 2.

4.2. Catalyst Characterization. Powder XRD diffractograms were recorded on an XPERT powder diffractometer (PANalytical), and Cu Kα radiation (λ = 0.15419 nm) was applied. Nitrogen sorption was determined on a Micromeritics ASAP 2020 system, and the samples were pretreated under vacuum at 120 °C for 4 h. The adsorption branch of the adsorption—desorption isotherm was used to obtain the pore-size distribution. SEM and transmission electron microscopy (TEM) images were obtained using an S-4800 microscope (Hitachi, Japan) equipped with an energy-dispersive X-ray spectrometer, and a JEM-2100F microscope (JEOL, Japan), respectively. XPS spectra were achieved on an ESCALAB 250xi spectrometer (Thermo Scientific). Binding energy of all elements was referenced to the C 1s peak energy of the contaminant carbon at 284.8 eV. EPR spectra were collected at room temperature using a Bruker E500 instrument operating at the X band (~9.853 GHz). The center field was 3510 G, and the g value was determined from precise frequency and magnetic field values. TG analysis was performed on a DTG-60H analyzer (SDT Q600, USA) in a flow of N\(_2\) at a heating rate of 10 °C/min. H\(_2\)-TPR tests were carried out on a BELCAT-B (Japan) apparatus equipped with a TCD. In a typical experiment, the catalysts were first pretreated at 300 °C for 1 h with a He atmosphere and cooled to room temperature. Next, the temperature was ramped to 800 °C with a ramp of 10 °C/min with the introduction of the reducing gas (10% H\(_2\)/Ar). In the experiment of CO\(_2\)-TPD, the catalysts were pretreated at 300 °C with a He atmosphere for 1 h. After being cooled to room temperature, the catalysts were exposed in CO\(_2\) for 30 min. Then, the catalysts were purged with He at room temperature for 30 min to remove the physically adsorbed molecular CO\(_2\). Finally, CO\(_2\)-TPD profiles were recorded with a ramp of 10 °C/min from room temperature to 800 °C under a He stream. FTIR spectra and in situ DRIFT spectra were collected using a Thermo Fisher 6700 instrument. In the in situ DRIFT spectra experiments, the catalysts in the in situ cell reactor were pretreated in a nitrogen flow at room temperature for 1 h. Subsequently, a mixed gas of HCHO/O\(_2\) or HCHO/N\(_2\) was introduced into the DRIFT reactor at room temperature via an individual mass flow meter at a flow rate of 30 mL/min.

Table 2. Preparation Information of the Obtained Samples

| samples modifier         | Pt content (wt %) | HCHO removal efficiency (1 h) (%) |
|-------------------------|-------------------|----------------------------------|
| Pt/HAP                  | 0.2               | 54                               |
| HAP−SC                  | sodium citrate    | 0                                | 10                               |
| Pt/HAP−SC               | sodium citrate    | 0.2                              | 75                               |
| Pt/HAP−SC−1             | sodium citrate    | 0.08                             | 33                               |
| Pt/HAP−SC−2             | sodium citrate    | 0.4                              | 84                               |
| Pt/HAP−SDS              | sodium dodecyl sulfate 0.2 | 48                               |                                  |
| Pt/HAP−HMT              | hexamethylenetetramine | 0.2                         | 73                               |
| Pt/TiO\(_2\)            |                   | 0.2                              | 38                               |
4.3. Catalytic Performance Test. The performance experiments were conducted in a 6 L organic glass reactor as reported in our previous work. A specified amount of the sample (0.1 mg) was first scattered in a glass Petri dish and placed into the chamber followed by covering with a glass slide. After the reactor was sealed, a certain amount of condensed HCHO (38%) was injected into the reactor. Then, the liquid HCHO was quickly volatilized to the gaseous phase. condensed HCHO (38%) was injected into the reactor. Then, the liquid HCHO was quickly volatilized to the gaseous phase assisted by a 5 W fan at the bottom of the reactor. The test started by removing the cover from the Petri dish until the concentration of gaseous HCHO reached a stable value. Concentrations of gaseous HCHO, CO₂, CO, and H₂O were online monitored using the Photoacoustic IR Multigas Monitor.

The catalytic performance of the samples was expressed by HCHO removal (Cᵢ/Cₒ) and CO₂ generation (ΔCO₂/Cₒ), where ΔCO₂ is the difference between CO₂ concentration at a reaction time t and initial CO₂ concentration and Cₒ is the equilibrium HCHO concentration before the test which was set at ca. 180 ppm in this work. Cᵢ and Cₒ are the HCHO concentration at reaction time t and 60 min, respectively. The formaldehyde removal efficiency was obtained as follows:

\[ \eta = \frac{C₀ - Cᵢ}{C₀} \times 100\% \]

AUTHOR INFORMATION

Corresponding Authors
*E-mail: xuzhihua78@sina.com. Phone: 86-13409925284. Fax: 86-027-84226806 (Z.X.).
*E-mail: zhaoxiangyan75@163.com. Phone: 86-13720263625. Fax: 86-027-84226806 (Z.Y.).

ORCID
Zhihua Xu: 0000-0001-4711-9482

Notes
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