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Article

Pt supported on octahedral Fe₃O₄ microcrystals as a catalyst for removal of formaldehyde under ambient conditions

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ABSTRACT

Several catalysts comprising Pt supported on octahedral Fe₃O₄ (Pt/Fe₃O₄) were prepared by a facile method involving co-precipitation followed by thermal treatment at different temperatures. A variety of characterization results revealed that this preparation process afforded highly crystalline octahedral Fe₃O₄ with a uniform distribution of Pt nanoparticles on its surface. The thermal-treatment temperature significantly influenced the redox properties of the Pt/Fe₃O₄ catalysts. All the Pt/Fe₃O₄ catalysts were found to be catalytically active and stable for the oxidation of low-concentration formaldehyde (HCHO) with oxygen. The catalyst prepared by thermal treatment at 80 °C (labelled Pt/Fe₃O₄-80) exhibited the highest catalytic activity, efficiently converting HCHO to CO₂ and H₂O under ambient temperature and moisture conditions. The excellent performance of Pt/Fe₃O₄-80 was mainly attributed to beneficial interactions between the Pt and Fe species that result in the formation of a higher density of active interface sites (e.g., Pt-O-FeO_x and Pt-OH-FeO_x). The introduction of water vapor improves the catalytic activity of the Pt/Fe₃O₄ catalysts as it participates in a water-assisted dissociation process.

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1. Introduction

Eliminating formaldehyde (HCHO) from indoor air is extremely important to meet stringent environmental regulations and preserve human health [1–4]. The catalytic oxidation of HCHO with oxygen at low temperature is an innovative and promising technique for this purpose owing to its high removal efficiency, low energy consumption, and lack of secondary pollution [5–8]. Among the numerous catalysts investigated for this process [9–19], those comprising Pt supported on iron-based oxides, such as Fe₂O₃, Fe₃O₄, and ferrihydrite, are extremely attractive owing to their remarkable activities in

HCHO oxidation at low temperatures [17–19].

It has been previously reported that Pt/Fe₂O₃ catalysts prepared by the colloid deposition method exhibit much higher catalytic activities for room-temperature oxidation of HCHO than those prepared by co-precipitation or impregnation method [17,18]. The effects of various factors on the catalytic performance of Pt/Fe₂O₃ catalysts have been studied, and the existence of beneficial interactions between the Pt and Fe species therein has been proposed to lead to the formation of highly efficient active interface sites. For example, Yan et al. [19] reported that mesoporous ferrihydrite and Fe₃O₄ nanoparticles obtained by a microemulsion-assisted method could

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be used as support materials in the preparation of highly active supported-Pt catalysts for HCHO oxidation. They suggested that the main features responsible for the superior catalytic activities of these supported-Pt catalysts were their surface hydroxyl groups, high Pt dispersions, and excellent adsorption performance.

Recently, significant progress has been made on the controlled synthesis of Fe_3O_4 materials with different crystallographic forms and morphologies, such as spheres, cubes, wires, nanorods, and octahedra [20–24]. Of these, well-defined octahedral Fe_3O_4 sub-microcrystal materials have drawn particular attention for their potential applications in environmental remediation and heterogeneous catalysis [25–27]. The thermodynamically stable octahedral Fe_3O_4 can provide an interface on which to assemble nanoparticles with high packing efficiency and structural stability. Furthermore, the bulky Fe_3O_4 crystallites are redox active, and their surface compositions can be adjusted by slight changes in oxygen partial pressure and substrate temperature. These features present numerous opportunities to develop highly efficient and thermally stable Fe_3O_4 -based catalysts for application in many important processes [28–31].

In the current study, Pt catalysts supported on octahedral Fe_3O_4 crystals ($\text{Pt}/\text{Fe}_3\text{O}_4$) were prepared by a simple co-precipitation/thermal treatment method, and their catalytic properties were investigated for the low-temperature oxidation of HCHO. The effect of thermal-treatment temperature on the physicochemical properties and catalytic performance of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts was investigated using a variety of characterization techniques. As a result, it was found that the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalyst thermally treated at a relatively low temperature (80 °C) exhibited very high catalytic activity and stability in HCHO oxidation under ambient temperature and moisture conditions.

2. Experimental

2.1. Catalyst preparation

$\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts were synthesized through a simple co-precipitation method previously reported in the literature with some modifications [25,32]. Typically, 5.189 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 10 mL water and then mixed with 1.33 mL of a solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (15 g/L) in a 250-mL three-neck round-bottom flask. The solution was then heated at 90 °C for 10 min to form a homogeneous solution. This mixture was then added to 100 mL KOH solution and vigorously stirred for 12 h. Finally, the resultant precipitate was washed with deionized water, separated via centrifugation, and dried at 80 °C for 6 h without any further thermal treatment. This as-prepared catalyst was labelled $\text{Pt}/\text{Fe}_3\text{O}_4$ -80. Two more catalysts were obtained by thermal treatment of the above material at 200 and 300 °C in static air, and denoted as $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300, respectively. The Pt loading was approximately 1.0 wt% for each catalyst. A reference sample of the Fe_3O_4 support alone was also prepared by the same method but without the addition of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained using a D/Max-rA X-ray diffractometer equipped with nickel-filtered $\text{Cu } K_\alpha$ radiation. ^{57}Fe Mössbauer spectra were obtained using an OIMS-500 Mössbauer spectrum instrument. ^{57}Co (Pd) was used as the γ -ray radioactive source and the velocity was calibrated against a standard α -iron foil. Magnetic measurements were performed on a SQUID-VSM magnetometer at room temperature. Transmission electron microscopy (TEM) images and high-angle annular dark field STEM (HAADF-STEM) images were acquired using a FEI Tecnai F20 EM operated at 200 kV and equipped with an energy-dispersive spectroscopy analyzer. N_2 -adsorption-desorption isotherms were obtained using a Micromeritics analyzer (ASAP 2010N). The Brunauer-Emmett-Teller (BET) model was used to calculate the surface areas. X-ray photoelectron spectroscopy (XPS) spectra were collected using an ESCALAB250 spectrometer with $\text{Al } K_\alpha$ radiation as the excitation source. All the elemental binding energies were corrected by adjusting the C 1s peak to 284.6 eV. Temperature-programmed reduction by H_2 (H_2 -TPR) analysis was performed by an adsorption instrument equipped with a thermal conductivity detector (TCD). For each analysis, the samples were purged in a flow of Ar at 100 °C for 30 min. The H_2 -TPR experiments were performed using a 5% H_2/Ar mixture (30 mL/min) over 0.1 g of catalyst at a heating rate of 10 °C/min. The Fourier-transform infrared (FTIR) spectra of the samples were recorded using KBr disks on a Nicolet 6700 spectrometer.

2.3. Catalytic tests

The HCHO oxidation tests were carried out in a quartz tube reactor containing 0.1 g of solid catalyst (40–60 mesh). The gas mixture consisted of 400 ppm HCHO, 20 vol% O_2 , a certain amount of water vapor chosen to provide a relative humidity (RH) of 0–80%, and balanced with N_2 . Gaseous HCHO was generated by flowing N_2 (coming from a mass flow controller) through aqueous formaldehyde kept in an incubator. Products and reactants were analyzed using a Techcomp GC-7900 gas chromatographer equipped with a TCD, and the catalytic activity of the catalyst under inspection was evaluated by the conversion of formaldehyde to CO_2 .

3. Results and discussion

3.1. Characterization of the catalysts

The XRD patterns of the three $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts ($\text{Pt}/\text{Fe}_3\text{O}_4$ -80, $\text{Pt}/\text{Fe}_3\text{O}_4$ -200, and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300) as well as the Fe_3O_4 support alone are presented in Fig. 1. All the samples show diffraction peaks characteristic of inverse spinel magnetite iron oxide (Fe_3O_4 , JCPDS 65-3107) located at $2\theta = 30.2^\circ$, 35.6° , 43.3° , 53.8° , 57.3° , 63.0° , and 78.3° , which can be attributed to the (220), (311), (400), (422), (511), (531), and (533) planes of Fe_3O_4 , respectively [25,29]. For the three $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts, the intensity of the diffraction peaks as-

Fig. 1. XRD patterns of Fe_3O_4 (1), $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 (2), $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 (3), and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300 (4).

signed to the Fe_3O_4 crystal phase increases with increasing thermal-treatment temperature, indicating improved Fe_3O_4 crystallinity in the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts. No diffraction peaks related to Pt species could be detected by XRD for any of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts, indicating that the Pt species are highly dispersed on the Fe_3O_4 support.

The phase purity and crystal structure of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 were further studied by Mössbauer spectroscopy. As shown in Fig. 2 and Table 1, the spectrum of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 can be fitted to three six-line hyperfine sextets [29,33]. The two major signals (shown in purple and blue) can be attributed to the Fe^{2+} and Fe^{3+} ions in tetrahedral (A) and octahedral (B) sites of Fe_3O_4 , respectively, while the weak signal (green) is attributed to the Fe^{2+} ions in $\text{Fe}(\text{OH})_2$. Statistical analysis of the spectrum showed that the amount of magnetite in the sample was higher than 96.3%, suggesting that the phase purity of spinel Fe_3O_4 in the $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 catalyst is quite high.

The TEM and HRTEM images of $\text{Pt}/\text{Fe}_3\text{O}_4$ are displayed in Fig. 3. High-quality octahedral Fe_3O_4 crystals with well-defined facets, smooth surfaces, and straight edges can be clearly observed (Fig. 3(a)). Small Pt nanoparticles with a mean particle size of ≈ 2.5 nm are highly dispersed on the surface of the octahedral Fe_3O_4 (Fig. 3(b)–(d)). The lattice fringes with a d-spacing

Fig. 2. ^{57}Fe Mössbauer spectrum of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80.

Table 1

The fine parameters of the curves fitted to the Mössbauer spectrum of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80.

Component	IS ^a (mms ⁻¹)	QS ^b (mms ⁻¹)	Hf ^c (kOe)	WHWM ^d (mms ⁻¹)	AREA ^e (%)
Fe_3O_4 A	0.29 ± 0	0.02 ± 0	492.7 ± 0.3	0.24 ± 0	58.6
Fe_3O_4 B	0.60 ± 0.01	0.01 ± 0.02	455.0 ± 0.8	0.32 ± 0.01	37.7
Fe^{2+}	0.59 ± 0.04	2.31 ± 0.08		0.23 ± 0.04	3.7

^a The isomer shift relative to α -Fe at room temperature.

^b The quadrupole shift.

^c The magnetic hyperfine field at ^{57}Fe nuclei.

^d The half maximum linewidth.

^e The area of the spectrum component.

of 0.224 nm are consistent with the lattice spacing of the (111) plane of metallic Pt, while the lattice fringes with a d-spacing of 0.48 nm correspond to the (111) plane of Fe_3O_4 (Fig. 3(e) and (f)) [26]. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and EDS mapping analyses confirmed the uniform distribution of Pt nanoparticles over the surfaces of the Fe_3O_4 octahedral microcrystals (Fig. 4). The BET surface areas of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80, $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300, determined by N_2 adsorption-desorption measurement (Fig. 5), are ≈ 25 , 22 and 21 m^2/g , respectively, which are slightly higher than that of Fe_3O_4 support (19 m^2/g).

The XPS results for Fe_3O_4 and the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts are shown in Fig. 6 and Table 2. In the $\text{Fe } 2p$ XPS spectrum of Fe_3O_4 (Fig. 6(a1)), the peaks at 711.2 and 724.6 eV can be ascribed to $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$, respectively [34,35]. The spectrum can be fitted to three main peaks and two satellite peaks in the $2p_{3/2}$

Fig. 3. TEM images of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 (a, b), $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 (c), $\text{Pt}/\text{Fe}_3\text{O}_4$ -300 (d), HRTEM images of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 (e, f) and particle size distribution of the corresponding sample (the inset images).

Fig. 4. HAADF-STEM images of Pt/Fe₃O₄-80 (a) and corresponding EDX mapping images for Fe (b, c), O (d), and Pt (e, f).

region on the basis of the related literature [34–38]. The peak at 709.8 eV (together with the satellite peak at 715.4 eV) can be attributed to Fe²⁺, while the peaks at 711.3 and 713.0 eV are assigned to Fe³⁺ octahedral species and Fe³⁺ tetrahedral species, respectively. In addition, the Fe³⁺ shake-up satellite feature is observed at 718.9 eV. Compared with that of Fe₃O₄, the binding energies for Fe 2p_{3/2} for the Pt/Fe₃O₄ catalysts are shifted slightly toward higher values (Fig. 6(a2)), suggesting that the redox properties of Fe₃O₄ change somewhat upon introducing a small amount of Pt species, which indicates interaction between the Pt nanoparticles and the Fe₃O₄ support [25]. Additionally, the Fe²⁺/Fe³⁺ ratios for the three Pt/Fe₃O₄ catalysts (Table 2), estimated from the deconvoluted XPS spectra, are all around 0.5, which is quite consistent with the stoichiometry of Fe₃O₄.

The O 1s spectra obtained for Fe₃O₄ and the Pt/Fe₃O₄ catalysts are shown in Fig. 6(b). The spectrum can be deconvoluted into three peaks, peak I at ~529.8 eV can be assigned to O²⁻ ions in the lattice oxygen of Fe₃O₄ (denoted as O_L), peak II at ~531.3 eV can be attributed to the oxygen in the surface OH groups and/or oxygen vacancies of Fe₃O₄ (denoted as O_s), and peak III at ~532.4 eV originates from the adsorption of H₂O on the surface of the Fe₃O₄ support upon exposure to air [29,37]. As observed in Table 2, the percentage of O_s follows the order: Pt/Fe₃O₄-80 > Pt/Fe₃O₄-200 > Pt/Fe₃O₄-300, indicating that Pt/Fe₃O₄-80 possesses the largest amount of surface OH groups and/or oxygen vacancies.

Fig. 6(c) shows the Pt 4f XPS spectra for the Pt/Fe₃O₄ cata-

Fig. 5. Nitrogen adsorption-desorption isotherms of samples. (1) Fe₃O₄, (2) Pt/Fe₃O₄-80, (3) Pt/Fe₃O₄-200, (4) Pt/Fe₃O₄-300.

lysts. After curve fitting, the spectra comprise two pairs of peaks at 71.3 and 74.7 eV, and at 72.4 and 75.6 eV, which are assigned to Pt⁰ and Pt²⁺, respectively [17,39,40]. For Pt/Fe₃O₄-80, Pt⁰ is the major species (Pt²⁺/Pt⁰ = 0.36). However, increasing the thermal-treatment temperature results in an increase of Pt²⁺ concentration (Table 2).

The FTIR spectra of Fe₃O₄ and the Pt/Fe₃O₄ catalysts are shown in Fig. 7. The broad and strong absorbance peaks at 2800–3800 cm⁻¹ can be attributed to the stretching vibrations of OH groups and physically adsorbed water. The band centered at 1623 cm⁻¹ can be ascribed to the deformation vibrations of OH groups [25,41]. For the three Pt/Fe₃O₄ catalysts, the intensities of these bands decrease slightly with increasing thermal-treatment temperature, suggesting that a certain number of surface OH groups are present on the surface of the Pt/Fe₃O₄ catalysts. This is consistent with the XPS results discussed above.

The H₂-TPR profiles of the three Pt/Fe₃O₄ catalysts and the Fe₃O₄ support are shown in Fig. 8. For all the samples, the high-temperature reduction peaks that appear at around or above 650 °C correspond to the reduction of Fe₃O₄ to FeO and then to Fe [17,42]. For the octahedral Fe₃O₄, the two weak reduction peaks centered at 340 and 450 °C are related to the reduction of trace amounts of surface Fe³⁺ to Fe²⁺. For Pt/Fe₃O₄-80, the low-temperature reduction peaks located at ca. 80 and 110 °C can be mainly assigned to the reduction of oxidized Pt species as well as to the reduction of some of the Fe³⁺ species located either at the interface of the Pt nanoparticles and the Fe₃O₄ support (i.e., Fe³⁺-O-Pt species) or close to the Pt nanoparticles via spillover of H atoms from the Pt species to Fe³⁺ species [17,42]. The enhanced reduction ability of the Fe₃O₄ support may be assigned to the increased density of lattice defects and surface oxygen vacancies caused by the introduction of Pt species. For Pt/Fe₃O₄-200 and Pt/Fe₃O₄-300, the low-temperature reduction peak shifts slightly to higher temperature and is much stronger in comparison with that of Pt/Fe₃O₄-80. The higher H₂ consumption for these two catalysts indicates that a larger number of their Fe³⁺ species can be reduced at low temperature, implying relatively strong interac-

Fig. 6. Fe 2p (a), O 1s (b), and Pt 4f (c) XPS spectra for all samples. (1) Fe_3O_4 , (2) $\text{Pt}/\text{Fe}_3\text{O}_4$ -80, (3) $\text{Pt}/\text{Fe}_3\text{O}_4$ -200, (4) $\text{Pt}/\text{Fe}_3\text{O}_4$ -300.

Table 2

Summary of the XPS data obtained for the catalysts.

Catalyst	Fe 2p	O_L (%)	O 1s	H_2O (%)	Pt 4f
	$\text{Fe}^{2+}/\text{Fe}^{3+}$		O_S (%)		$\text{Pt}^{2+}/\text{Pt}^0$
Fe_3O_4	0.75	60.5	26.5	13.0	—
$\text{Pt}/\text{Fe}_3\text{O}_4$ -80	0.47	57.0	30.3	12.7	0.36
$\text{Pt}/\text{Fe}_3\text{O}_4$ -200	0.51	62.2	25.7	12.1	0.56
$\text{Pt}/\text{Fe}_3\text{O}_4$ -300	0.54	63.2	24.6	12.2	1.52

O_L (%), O_S (%), H_2O (%), $\text{Fe}^{2+}/\text{Fe}^{3+}$, and $\text{Pt}^{2+}/\text{Pt}^0$ were calculated from the corresponding areas of the fitted peaks using XPSPEAK 4.1 with Shirley.

tions between the Pt species and the Fe_3O_4 support.

The above characterization results indicate that $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts can be obtained by a facile co-precipitation method in which small Pt nanoparticles disperse uniformly on the surface of the Fe_3O_4 octahedra. Relatively abundant surface OH groups or oxygen vacancies are present on the surfaces of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts. Interface species such as $\text{Pt-O(OH)}_x\text{-Fe}$ are formed during the preparation of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts. Changing the thermal-treatment temperature for the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts can

adjust the redox properties of the catalysts and can also influence the interface interactions between the Pt nanoparticles and octahedral Fe_3O_4 supports.

3.2. Catalytic activity

Fig. 9 shows the temperature dependence of HCHO conversion over the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts and Fe_3O_4 . Under the test conditions, the Fe_3O_4 support is inactive for HCHO oxidation in the

Fig. 7. FTIR spectra of Fe_3O_4 (1), $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 (2), $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 (3), and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300 (4).

Fig. 8. H_2 -TPR profiles of Fe_3O_4 (1), $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 (2), $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 (3), and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300 (4).

Fig. 9. Catalytic activities of the three $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts and the Fe_3O_4 support for HCHO oxidation. Reaction conditions: HCHO 400 ppm, O_2 20 vol%, N_2 balance, RH = 30%, and gas hourly space velocity: 60,000 $\text{cm}^3/(\text{g}\cdot\text{h})$.

temperature range 25–100 °C. However, all three $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts are catalytically active for HCHO oxidation in the presence of water vapor (RH = 30%) at relatively low temperatures. Among them, $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 exhibits the highest activity,

completely converting HCHO to CO_2 and H_2O at room temperature. The catalytic activities of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts decrease with increasing thermal-treatment temperature. Accordingly, complete oxidation of HCHO could only be achieved over $\text{Pt}/\text{Fe}_3\text{O}_4$ -200 and $\text{Pt}/\text{Fe}_3\text{O}_4$ -300 at 60 and 80 °C. These results suggest that inverse-spinel octahedral Fe_3O_4 can be used as a suitable support for the construction of a highly efficient supported Pt catalyst for low-temperature oxidation of HCHO. Its superior catalytic performance is comparable with those of even the most active iron oxide- (or ferrihydrite) -supported Pt catalysts, such as $\text{Pt}/\text{Fe}_2\text{O}_3$ and $\text{Pt}/\text{ferrihydrite}$, as well as those of the alumina-supported iron-promoted Pt catalysts ($\text{Pt}-\text{FeO}_x/\text{Al}_2\text{O}_3$) reported in the literature [17,19,43].

The effect of gas hourly space velocity (GHSV) on the catalytic activity of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 is presented in Fig. 10. For GHSV = 60,000 $\text{cm}^3/(\text{g}\cdot\text{h})$, complete oxidation of HCHO is achieved at room temperature. With increasing GHSV (i.e., decreasing contact time), the conversion of HCHO decreases to 93.5% and 84.1% for GHSVs of 90,000 and 120,000 $\text{cm}^3/(\text{g}\cdot\text{h})$, respectively.

In addition, the catalytic durability of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 was investigated by conducting a seven-day experiment in which a three-hour reaction was carried out on each day. As shown in Fig. 11, no obvious change in catalytic activity is observed, indicating the excellent stability of the catalyst.

As water vapor inevitably exists in the atmosphere for HCHO oxidation, the effect of RH on the catalytic activity of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 was also investigated at room temperature. As shown in Fig. 12, the conversion of HCHO increases from 81.2% to 100% when the RH increases from 0 to 30%. Upon further increasing the RH to 80% a slight decrease in catalytic activity (98.5% HCHO conversion) is detected. These results suggest that the catalytic activity of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 for HCHO oxidation is significantly improved by adding water vapor to the feed gas in a wide RH range (i.e. from 30% to 80%).

3.3. Discussion

Previous studies have demonstrated that iron-based oxides,

Fig. 10. Effect of GHSV on the catalytic activity of $\text{Pt}/\text{Fe}_3\text{O}_4$ -80 for HCHO oxidation. Reaction conditions: HCHO 400 ppm, O_2 20 vol%, N_2 balance, and RH = 30%.

Fig. 11. Stability study of Pt/Fe₃O₄-80 for HCHO oxidation in which the reaction was performed for 3 h each day over seven days. Reaction conditions: HCHO 400 ppm, O₂ 20 vol%, N₂ balance, GHSV = 60,000 cm³/(g·h), RH = 30%, 25 °C.

Fig. 12. Effect of RH on HCHO conversion over Pt/Fe₃O₄-80. Reaction conditions: HCHO 400 ppm, O₂ 20 vol%, N₂ balance, GHSV = 60,000 cm³/(g·h), 25 °C.

such as Fe₂O₃, Fe₃O₄, and ferrihydrite, can be used as efficient supports to prepare highly active supported Pt catalysts for low-temperature oxidation of HCHO [17–19]. However, the preparation processes for these iron-oxide-supported Pt catalysts are all multiple-step procedures that require organic solvents and/or surfactants. Furthermore, the resultant iron oxide supports (Fe₂O₃ or Fe₃O₄) usually comprise irregular spherical nanoparticles. Thus, they are not necessarily very attractive as materials for developing commercial catalysts owing to their relatively complicated preparation procedures and low structural stabilities.

Our present work indicates that catalysts comprising Pt nanoparticles supported on octahedral Fe₃O₄ microcrystals (Pt/Fe₃O₄) with superior HCHO oxidation activities can be obtained by a facile co-precipitation method without using organic solvents or surfactants. It should be mentioned here that it is unusual to get the octahedral Fe₃O₄ microcrystals at such low preparation temperatures (90 °C). On the basis of a few related literatures [25,32,44], the formation of octahedral Fe₃O₄ mi-

crocrystals may be described with the so-called “oriented aggregation”. During the preparation process, Fe₃O₄ magnetite nuclei easily form when high concentration of KOH solution is added into the hydrothermal system containing Fe²⁺ cations. The main driving force for the oriented aggregation of nanoparticles is generally attributed to the tendency for reducing the high surface energy via the attachment (or rotation) of the primary Fe₃O₄ nanoparticles caused by various interactions, such as Brownian motion. The formation of uniform octahedral Fe₃O₄ microcrystals implies the fact that the growth rates of the Fe₃O₄ core in three axes directions are equivalent [32]. Besides, the crystal planes exposed on the surface of octahedral Fe₃O₄ seems quite suitable for uniformly dispersing small Pt nanoparticles, which can finally result in the formation of highly active Pt/Fe₃O₄ catalysts for the oxidation of HCHO.

The relatively high activity of Pt/Fe₃O₄-80 should be an indicative of the presence of more interface active sites (like Pt-O-FeO_x) through building suitable metal-support interaction between Pt species and octahedral Fe₃O₄. Furthermore, the relatively high structural and thermal stabilities of octahedral Fe₃O₄ microcrystals [44,45] suggest that the resultant active interface sites formed on the Pt/Fe₃O₄ surface catalysts should be highly stable, allowing long-term usage. According to the analysis results obtained in the current study, surface OH groups and/or oxygen vacancies are relatively abundant on the crystal planes of the octahedral Fe₃O₄ catalysts, indicating that highly active interface species like Pt-O-FeO_x and Pt-O(OH)_x-FeO_x are easily formed during the preparation of the Pt/Fe₃O₄ catalysts. Different thermal-treatment temperatures result in clear changes in the redox properties of the Pt/Fe₃O₄ catalysts by adjusting the strength of interface interactions between Pt nanoparticles and the Fe₃O₄ support, thus having a significant effect on the catalytic activities of the Pt/Fe₃O₄ catalysts. Our previous works have also revealed that such interface interaction between Pt nanoparticles and the oxide supports, like fumed SiO₂ and FeO_x modified Al₂O₃, indeed plays quite positive role in enhancing the catalytic activity of the supported Pt catalysts [43,46].

Considering the influence of water on the reactivity of the Pt/Fe₃O₄ catalysts, several recent studies have demonstrated that water participates in the catalytic oxidation process directly after dissociative chemisorption on the active interfacial sites of iron-oxide-supported Pt catalysts [47–49]. For instance, Ringleb et al. [49] reported that co-adsorption of oxygen and water on monolayer FeO(111)/Pt(111) transforms the film into a hydroxyl-terminated trilayer with a Pt-O-Fe-OH structural motif that shows activity in the low-temperature oxidation of CO, similarly to the non-hydroxylated counterpart. In another work, Chen et al. [50] reported that CO directly reacted with interfacial Pt-OH-Fe³⁺ sites of oxide-supported PtFeNi catalysts, and that the interfacial sites could be readily recovered upon contact with H₂O and O₂. In the present work, the existence of interfacial sites like Pt-O-FeO_x and Pt-O(OH)-FeO_x has been deduced based on XPS and FTIR analyses. Therefore, we propose here that the promoting role of water is due to the existence of active OH groups (i.e., in the form of Pt-O(OH)-FeO_x), which can directly participate HCHO oxidation

through a $\text{H}_2\text{O}/\text{O}_2$ -mediated oxidation process, at the surface/interface of the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts.

4. Conclusions

Octahedral- Fe_3O_4 -microcrystal-supported Pt catalysts have been prepared by a facile precipitation method. The resultant $\text{Pt}/\text{Fe}_3\text{O}_4$ catalysts showed high activity and stability for the low-temperature oxidation of HCHO. A variety of characterization techniques revealed that the Pt nanoparticles were well dispersed on the surface of the octahedral Fe_3O_4 , and abundant active interface sites were present on the $\text{Pt}/\text{Fe}_3\text{O}_4$ catalyst thermally treated at a lower temperature. We believe that these catalysts have considerable potential for practical application to the removal of formaldehyde under ambient conditions.

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Graphical Abstract

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Pt supported on octahedral Fe_3O_4 microcrystals as a catalyst for removal of formaldehyde under ambient conditions

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An octahedral- Fe_3O_4 -supported Pt catalyst ($\text{Pt}/\text{Fe}_3\text{O}_4$ -80) obtained by a facile co-precipitation method exhibits unprecedented catalytic performance in the oxidation of low-concentration formaldehyde under ambient temperature and moisture conditions.

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八面体四氧化三铁亚微米晶负载铂催化剂用于室温催化氧化甲醛

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摘要: 空气中低浓度甲醛的治理和消除一直备受关注. 在较低的反应温度下将甲醛转化为 CO₂ 和 H₂O 的催化氧化法具有能耗低、效率高和环境友好等优点, 被认为是一种最具应用发展前景的甲醛消除技术. 在各种催化剂体系中, 一些铁基氧化物 (Fe₂O₃, Fe₃O₄ 或 ferrihydrite) 负载的 Pt 催化剂表现出较为优异的催化性能, 能够在室温下实现甲醛的完全氧化. 越来越多的研究表明, 载体材料的结构及形貌是影响贵金属催化剂性能的主要因素. 因此, 深入研究 Pt 物种在不同类型铁基氧化物表面的分散情况及界面间相互作用, 对理解催化剂活性中心的性质, 设计制备性能更加优异的负载型贵金属催化剂具有重要科学意义.

本文采用共沉淀法一步合成出八面体 Fe₃O₄ 亚微米晶负载 Pt 催化剂 (Pt/Fe₃O₄), 考察了不同热处理温度对催化剂催化甲醛氧化反应性能的影响. 结果表明, 在 80 °C 下热处理的催化剂 (Pt/Fe₃O₄-80) 具有很高的催化活性, 在室温下甲醛的转化率可接近 100%. 随着催化剂热处理温度的升高, 催化剂活性有所降低. 此外, Pt/Fe₃O₄ 催化剂还表现出良好的稳定性, 经长时间存放或连续运行后催化剂的活性基本保持不变. 此外, 在一定湿度范围内 (RH = 30%–80%), 水的存在能够显著提高 Pt/Fe₃O₄ 催化剂的甲醛催化氧化性能.

采用各种表征技术对 Pt/Fe₃O₄ 的结构、形貌、价态及氧化还原性等物理化学性质进行了研究. 结果表明: 采用该合成方法能够得到粒径较为均一、具有尖晶石结构和八面体形貌的 Fe₃O₄ 亚微米晶, 尺寸较小的 Pt 纳米粒子 (平均 2.5 nm) 均匀分布在八面体 Fe₃O₄ 晶体的表面, 且 Fe₃O₄ 载体表面还存在一定量的羟基物种. 随着热处理温度的升高, 催化剂表面的 Pt 物种和 Fe 物种的价态均发生明显变化. 结果证实, Pt 纳米粒子与 Fe₃O₄ 载体间的相互作用力会随着热处理温度的升高而发生明显变化. 对于性能较为优异的 Pt/Fe₃O₄-80 催化剂, Pt 纳米粒子与 Fe₃O₄ 载体之间存在着强度适宜的相互作用, 能够产生相对较多的 Pt-O-FeO_x 和 Pt-OH-FeO_x 界面活性位, 从而使其能够在较低的反应温度下表现出较强的活化分子氧的能力. 此外, 反应体系中引入的水分子能够与氧分子在界面活性位上共同活化, 形成表面活性-OH 物种, 从而有效促进催化剂反应性能的提升.

关键词: 八面体四氧化三铁; 铂纳米粒子; 界面作用; 催化氧化; 甲醛

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