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A series of high-efficiency Pt/ZrO₂ catalysts were successfully prepared by simple methods on the basis of a ZrO₂ support with a mixed monoclinic/tetragonal phase structure. The activity test results showed that the mixed phase catalysts exhibited higher catalytic activity than pure monoclinic phase, and HCHO can be completely oxidized into CO₂ and H₂O at near ambient temperature. XRD, Raman and HRTEM results demonstrated that the monoclinic-tetragonal phase interface with abundant defects were formed due to the introduction of tetragonal phase. According to the results of TEM, XPS and H₂-TPR, the mixed phase interfacial structure can induce the formation of the active oxygen species, ionic Pt⁶⁺ species, strong metal-support interaction and low-temperature reducibility, which was vital for the significant improvement of the catalytic activity. Furthermore, the specific HCHO reaction rate of catalysts at 55 °C increased from 0.8×10^{-3} to 10.4×10^{-3} mmol h⁻¹ m⁻² and the activation energy decreased remarkably from 213.5 to 24.7 kJ mol⁻¹ with the increase of the biphase interface content. In situ DRIFTS spectra showed that the special interfacial structure can change the reaction pathway of HCHO oxidation and inhibit the formation of inert carbonate species, thus greatly enhacing the HCHO oxidation activity.

1. Introduction

Formaldehyde (HCHO) is a common toxic indoor air pollutant. Long-term exposure to this air pollutant, even at levels of a few ppm, may cause serious health problems such as skin irritation and nasal tumors.^{1, 2} The low temperature catalytic oxidation of HCHO into CO₂ and H₂O is regarded as the most promising HCHO removal technology, because this process is energy-saving, high efficient and environmental friendly.^{3, 4} To date, a series of transition metal oxides and supported noble metals have been extensively studied for HCHO oxidation. In general, the transition metal oxides exhibit low catalytic activity and high reaction temperature,^{5, 6} while the noble metal catalysts possess high specific activity and excellent lowtemperature oxidation performance, which are very desirable for indoor HCHO elimination.^{7, 8}

Zirconia (ZrO₂) has been extensively applied as supports in various fields, such as VOC oxidation,⁹ methane combustion,¹⁰ and hydrodeoxygenation of phenol,¹¹ because of its thermal stability, chemical resistance, redox surface property,

polymorphism and amphoteric nature.^{9, 12, 13} Zirconia contains three crystal phases: monoclinic (m-ZrO₂), tetragonal (t-ZrO₂) and cubic (c-ZrO₂). In general, m-ZrO₂ is stable below 1000 °C, and t-ZrO₂ and c-ZrO₂ structurally stabilize at high temperature or can be stable at room temperature by adding dopants, such as Y, La, Ce, etc..9, 14 However, ZrO2-based catalysts for HCHO oxidation frequently present low catalytic activity and require a high conversion temperature. For example, Huang et al. investigated the influence of different supports loaded Pt (i.e., TiO₂, Al₂O₃, CeO₂, ZrO₂, and MgO) on total HCHO oxidation, and found that Pt/ZrO2 catalyst showed the lowest Pt dispersion and the turnover frequency (TOF).¹⁵ Zhang et al. successfully synthesized a novel mesoporous ZrO₂ support with high specific surface area, and the lowest temperature for complete oxidation of HCHO by these ZrO₂-based Au catalysts was 157 °C, which is much higher than ambient temperature.¹⁶

It is well-known that the catalytic performance of a catalyst is often closely related to its polymorphism.^{12, 17} The crystal structure and corresponding structure transformation have a dramatically influence on the physicochemical and catalytic properties of samples.^{17, 18} Benefited from the understanding of crystal structure, some groups attempted to improve the catalytic performance of samples through changing crystal structure or introducing mixed phase structure. For instance, Zhang et al. investigated the HCHO catalytic activities over several manganese oxides with different crystal structures, and found that the δ -MnO₂ exhibited the best activity.¹⁹ Hurum et al. reported that the mixed-phase titania displayed high photocatalytic efficiency due to the coexistence of anatase and rutile phase structure.²⁰ Further studies have shown that the photocatalytic improvement of mixed phase

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system is probably attributed to the presence of the rutile/anatase interface and the rapid electron transfer through transition stages of the mixed phase system.²⁰⁻²² Up to the present, however, little attention has been devoted to the relationship between HCHO catalytic oxidation and interfacial structure of the mixed phase ZrO_2 catalysts.

Herein, we prepared a series of Pt/ZrO₂ catalysts with mixed phase structure and investigated the interface effect on HCHO catalytic oxidation. It was proved that the catalytic performance of catalysts could be vastly improved by the special monoclinic-tetragonal (m-t) phase interface of catalysts, and 100 ppm HCHO could be completely oxidized at near ambient temperature by the Pt/ZrO₂ catalyst with the maximum interfacial structure content. The reasons of the promotion effects by the mixed phase structure were studied profoundly by various characterizations, and the possible mechanism was also clearly elucidated.

2. Experimental

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2.1 Preparation of ZrO₂ supports

Mixed phase ZrO₂ supports were prepared using different precipitation reactions. Briefly, ZrOCl₂·8H₂O (32 g) and urea (6 g) powders were dissolved in 70 mL of distilled water and vigorously stirred for 30 min. After that, the solution was transferred to a 100 mL autoclave with a Teflon liner at 150 °C for 12 h. The resulting precipitate was washed with deionized water until it reached pH 7 and dried in a vacuum oven at 60 °C for 12 h, which was denoted as ZrO₂-U. The other two supports were prepared by dropwise addition of an aqueous solution (50 mL) of ZrOCl₂·8H₂O (20 g) to 25 % ammonium hydroxide (50 mL) and a 1.8 mol/L potassium hydroxide solution (100 mL) at room temperature. The pure monoclinic phase ZrO₂ were synthesized according to the experimental procedure as reported by Witoon et al.²³ In detail, ZrOCl₂·8H₂O (9.7 g) powders were dissolved in 60 mL of distilled water, and then 25 % ammonium hydroxide was added dropwise until pH 1.5. After that, the mixture was transferred to a 100 mL autoclave with a Teflon liner at 140 °C for 24 h. Thereafter, the three white precipitates were washed with deionized water until they reached pH 7 and dried in a vacuum oven at 60 °C for 12 h. The obtained precipitates were denoted as ZrO₂-N. ZrO₂-K and ZrO₂-M, respectively. All supports were ground and calcined at 500 °C in the air for 4 h before using.

2.2 Preparation of Pt/ZrO₂ catalysts

The proper amount of the ZrO_2 support was uniformly dispersed into the $PtCl_4$ solution (1 wt % Pt). After impregnation for 30 min, NaBH₄ was added into the suspension as a reducing agent (NaBH₄ / Pt = 10, molar ratio) under vigorous stirring at room temperature for 3 h. Finally, the samples were centrifuged and dried in a vacuum oven at 60 °C for 12 h. The obtained samples were denoted as Pt/ZrO_2 -M, Pt/ZrO_2 -U, Pt/ZrO_2 -N and Pt/ZrO_2 -K, in which the actual loading of platinum was 0.84, 0.89, 0.79, 0.88 wt %.

2.3 Catalysts characterization

Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by N₂ adsorption-desorption isotherms at 77K using an autosorb-iQ instrument. X-ray powder diffraction (XRD) patterns were obtained by a D/max 2500 X-ray powder diffractometer with Cu K α radiation at a scan rate (2 θ) of 2° min⁻¹. The tetragonal phase zirconia (t-ZrO₂) content in the mixed phase samples was calculated by X'Pert HighScore Plus software. Raman spectra were recorded with a LabRAM Raman spectrometer using a 532 nm laser. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted using a JEM-2011, HT7700 and JEM-2100F. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB250XI with Al K α radiation. The samples were freshly prepared and dried in vacuum oven before the XPS measurement. Inductively coupled plasma mass spectrometry (Agilent 7700 Series ICP-MS) was carried out to determine the actual loading of platinum in the samples.

H₂ temperature-programmed reduction (H₂-TPR) and pulse CO chemisorption were measured by an AutoChem II 2920 apparatus. For H₂-TPR, the samples were first pretreated in an Ar flow of 20 cm³ min⁻¹ at 200 °C for 30 min. After that, reduction profiles were obtained by passing a flow with 10% H₂/Ar (50 cm³ min⁻¹) through the samples and the temperature was increased from 50 to 600 °C at a heating rate of 10 °C /min. For CO chemisorption, the samples were pretreated at 200 °C for 1 h in 10% H₂/Ar (50 cm³ min⁻¹) and then switched to an Ar flow (50 cm³ min⁻¹) for 40 min⁻¹. Next, 10% CO-He (50 cm³ min⁻¹) was introduced and the samples were measured at 50 °C.

The in situ diffuse reflectance FTIR spectroscopy (DRIFTS) was recorded in Nicolet iS50. Prior to the measurements, all samples were pretreated at room temperature in a gas flow of N₂ for 5 h to remove any adsorbed impurities. The all spectra scanned from 1000 to 4000 cm⁻¹ with 32 scans at a resolution of 4 cm⁻¹ and the background spectrum was subtracted from each spectrum, respectively. Samples were tested at room temperature under the following conditions: 100 ppm HCHO, 20 % O₂ and 74 % N₂ (balance). The total flow rate was 100 mL min⁻¹.

2.4 Activity test

The activity tests for the catalytic oxidation of HCHO over the samples (100 mg) were performed in a continuous flow fixedbed quartz tubular reactor (i.d. = 4 mm). Gaseous HCHO was generated by flowing nitrogen through the paraformaldehyde container in a water bath kept at 35 °C. The feed gas composition was 100 ppm HCHO and 20 % O₂ balanced by N₂. The total flow rate was 100 mL min⁻¹, corresponding to a weight hourly space velocity (WHSV) of 60 000 mL g_{cat}^{-1} h⁻¹. The concentration of HCHO in the inlet and outlet gas was measured by an online gas chromatograph of Agilent 7890B. The performance of the catalysts is presented in terms of HCHO conversion ($X_{\rm HCHO}$) as follows:²⁴

$$X_{\rm HCHO} = \frac{\left[CO_2\right]_{\rm outlet}}{\left[HCHO\right]_{\rm inlet}} \times 100\%$$

where $[^{\rm HCHO}]_{\rm inlet}$ and $[^{\rm CO_2}]_{\rm outlet}$ are the HCHO concentration in the inlet gas and the CO₂ concentration in the outlet gas, respectively.

2.5 Kinetic test

Kinetic data were measured by separate experiments, and the HCHO conversion was kept below 10 % to keep the reaction in the kinetic regime. That is, the experimental conditions were 425 ppm HCHO, 20 % O_2 , 62 % N_2 (balance) and WHSV 600 000 mL g_{cat}^{-1} h⁻¹. The total flow rate was 100 mL min⁻¹. The specific surface area and activation energy of catalysts were calculated from kinetic data.

The reaction rates normalized by the specific surface area (R_s) of the Pt/ZrO₂ catalyst were calculated using the following expression:²⁵

$$R_{s} = X_{HCHO} Q C_{f} / W S_{BE}$$

where Q is the volumetric flow rate (mL h⁻¹) and C_{f} is the inlet concentration of HCHO (mol mL⁻¹). W is the mass of the catalyst employed (g) and S_{BET} is the BET surface area of the catalyst (m² g⁻¹). The activation energy (*Ea*) was calculated from the slope of the Arrhenius-type plot of the HCHO oxidation rate.

3. Results and discussion

3.1 Catalyst characterization

Fig. 1 shows the XRD patterns of ZrO_2 supports and corresponding Pt/ZrO₂ catalysts. As shown in Fig. 1a, it was observed that all the diffraction peaks in the ZrO_2 -M could be assigned to monoclinic zirconia (JCPDS PDF No. 37-1484). No diffraction peaks of tetragonal zirconia (JCPDS PDF No. 50-1089) were detected, indicating that ZrO_2 -M consisted of pure monoclinic zirconia. For the ZrO_2 -U, ZrO_2 -N and ZrO_2 -K supports, distinct diffraction peaks of tetragonal zirconia appeared in addition to those of the monoclinic zirconia, implying the formation of the monoclinic-tetragonal (m-t) mixed phase. It should be pointed out that the special biphase structure might lead to the formation of more lattice disorder, oxygen vacancies or structure defects, especially around the transition stages of the mixed phase. ^{20, 26} As shown in Table 1, it was calculated that the amount of the tetragonal phase



Fig. 1 XRD patterns of as-synthesized ZrO_2 supports (a) and corresponding Pt/ZrO_2 catalysts (b).



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increased in the order of ZrO_2 -M, ZrO_2 -U, ZrO_2 -N and ZrO_2 -K supports, implying the increase of mixed-phase interfacial amount.

After Pt supported on the ZrO_2 , no Pt species could be detected, and the diffraction intensity of the tetragonal ZrO_2 decreased dramatically (Fig. 1b). This phenomenon was probably attributed to the low Pt contents, small Pt particles and/or special mixed phase structure of the catalysts.^{27, 28} Compared with the pure monoclinic phase Pt/ZrO₂-M catalyst, the presence of abundant defects on other samples might be beneficial to adsorb and stabilize platinum species.^{15, 27} Moreover, the geometrical similarity between the Pt cubic structure and ZrO₂ tetragonal structure also favored the formation of strong interactions and the stabilization of the Pt species on t-ZrO₂ or m-t phase interface.¹² The strong interactions might induce the distortion of the t-ZrO₂ crystal structure and then lead to a dramatic decrease of the diffraction intensity of t-ZrO₂ in the samples.

It is generally believed that Raman spectroscopy is sensitive to crystal defects such as lattice disorder and oxygen vacancies, which are not detectable by XRD.^{29, 30} Raman spectra of the Pt/ZrO₂ catalysts and corresponding supports are displayed in Fig. 2 and S1. For all Pt/ZrO₂ samples, the major bands located at ~179, 334, 476, 623 cm⁻¹ and the band at 476 cm⁻¹ were stronger than that at 623 cm⁻¹, which is a feature of m-ZrO₂.^{31, 32} As shown in the inset of Fig. 2, the Raman peak at 470 cm⁻¹ shifted to a higher frequency (477 cm⁻¹) with the introduction of tetragonal phase. The positive shift confirmed the presence of abundant defects in samples, and the defects were probably attributed to the special interfacial structure of the catalysts.^{33, 34}

Nitrogen adsorption-desorption isotherms and pore size distribution patterns of Pt/ZrO_2 catalysts and ZrO_2 supports are displayed in Fig. S2 and S3, and the corresponding parameters are listed in Table 1 and S1. Type IV isotherms (according to the IUPAC classification) were observed in all the samples, demonstrating the presence of mesoporous structure.³⁵ There was a big pore around 17.5 nm besides 3.4 nm for ZrO_2 -M sample as shown in Table S1, which might facilitate the dispersion of Pt species.³ The incorporation of Pt species further resulted in the disappearance of big pore in Pt/ZrO_2 -M.

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Table 1 Physical-chemical and HCHO catalytic properties of as-synthesized Pt/ZrO ₂ catalysts

samples	Surface area	Total pore volume (cm ³	Pore diameter	Pt content ^a	Pt dispersion ^b (%)	Tetragonal phase content ^c (%)		Rs ^d (mmol h ⁻¹ m ⁻²)	Ea ^e (kJ mol ⁻¹)
	(m ² g ⁻¹)	g ⁻¹)	(nm)	(wt %)		catalysts	supports		
Pt/ZrO ₂ -M	78.6	0.32	3.4	0.84	58.5	0	0	0.0008	213.5
Pt/ ZrO₂-U	54.4	0.16	7.8	0.89	9.00	6	7	0.0041	61.3
Pt/ ZrO₂-N	90.2	0.22	6.5	0.79	31.1	7	22	0.0056	38.2
Pt/ ZrO ₂ -K	70.3	0.12	4.9	0.88	51.3	9	30	0.0104	24.7

^a Determined by ICP-MS. ^bPt dispersion calculated by CO chemical adsorptions assuming a CO:Pt stoichiometry of 1:1. ^c The tetragonal phase content of samples were calculated by X'Pert HighScorePlus software. ^d Specific HCHO reaction rate of samples estimated at 55 °C under a kinetically controlled regime. The detail experimental conditions were shown in kinetic test. ^e The activation energy calculated from the slope of the Arrhenius-type plot of the HCHO oxidation rate.

Due to the surface cover and pore blockage by Pt species, the samples supported Pt exhibited the slightly decrease of surface areas and pore diameters compared with the supports.^{15, 36}

However, total pore volume somewhat increased. This could be attributed to the generated H_2 and the increase of pH during the preparation process.³⁷

The morphology and microstructure of Pt/ZrO_2 catalysts are further elucidated by transmission electron microscopy (Fig. 3). TEM analysis confirmed that small Pt species (ca. 3 nm) were uniformly dispersed on the surface or in the pores of the supports for all Pt/ZrO_2 samples, consistent with the measured Pt dispersion (Table 1). For the pure monoclinic phase Pt/ZrO_2 -M catalyst, the high dispersion might be due to the high surface area and big pore size. However, the special m-t interfacial structure in the mixed phase Pt/ZrO_2 samples should be beneficial to the stabilization of Pt species, resulting from abundant defects, strong interactions and geometrical similarity.

The chemical states of elements in the samples are investigated by X-ray photoelectron spectroscopy (XPS). The XPS spectra are shown in Fig. 4 and S4, and the binding



Fig. 3 TEM images of as-synthesized Pt/ZrO_2 catalysts. (a) Pt/ZrO2-M, (b) Pt/ZrO2-U, (c) Pt/ZrO2-N, and (d) Pt/ZrO2-K.

energies and the percentages of XPS peaks calculated are summarized in Table 2 and S1. It is reported that the Zr $3d_{5/2}$ binding energy of stoichiometric zirconia is in the range of 182.2-183.3 eV. 38 Table 2 shows that the Zr $3d_{5/2}$ binding energy of all Pt/ZrO₂ catalysts ranged from 181.9 to 182.0 eV, indicating that the supports were a non-stoichiometric oxide and that defects existed in the catalysts, in good agreement with the Raman results. As shown in Fig. 4b, three typical peaks were observed in the O 1s XPS spectra of the Pt/ZrO₂ catalysts. The binding energies at 529.6-530.1, 531.7-532.1 and 533.1-533.5 eV were assigned to the lattice oxygen (O_{latt}), adsorbed oxygen (O_{ads}), and oxygen-containing (hydro)carbons, respectively.^{39, 40}

Fig. 4c shows that all Pt/ZrO₂ catalysts displayed two Pt 4f_{7/2} peaks centered at 70.8-71.3 and 72.4-73.1 eV, which were assigned to metallic Pt⁰ and ionic Pt²⁺ species, respectively.^{3,41} From Table 2, the Pt^{δ+}/(Pt⁰⁺Pt^{δ+}) ratio of samples ranked in the following order: Pt/ZrO₂-M < Pt/ZrO₂-U < Pt/ZrO₂-N < Pt/ZrO₂-K, which coincided with the tetragonal phase content in the samples. The mixed phase structure might induce the partial flow of the 5d electrons of Pt into the 4d of Zr by the strong interactions, leading to the formation of cationic Pt^{δ+} species.^{42,43}

Considering that abundant defects in the samples were mainly caused by the lattice mismatch around the biphase interface, it was deduced that strong interactions probably only existed in the m-t phase interface and could affect the electronic structure of Pt adjacent to the special structure. Therefore, $Pt^{\delta+}$ cation species were dominant, and the ratio increased in the order of Pt/ZrO_2 -U, Pt/ZrO_2 -N and Pt/ZrO_2 -K. Nevertheless, there were some ionic $Pt^{\delta+}$ species in Pt/ZrO_2 -M,



Fig. 4 XPS spectra of Pt/ZrO₂ catalysts: (a) Zr 3d, (b) O 1s, (c) Pt 4f.

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Table 2 Surface chemical composition and element molar ratios of Pt/ZrO₂ catalysts

samples	Zr 3d _{5/2} (eV)	O_{ads}/O_{latt}	$Pt^{\delta +}/(Pt^{0}+Pt^{\delta +})$ (%)
Pt/ZrO ₂ -M	181.9	0.98	26.5
Pt/ZrO ₂ -U	181.9	1.41	76.9
Pt/ZrO ₂ -N	181.9	1.93	82.0
Pt/ZrO ₂ -K	182.0	1.79	84.7

though ZrO_2 -M is pure monoclinic zirconia. This is because Pt nanoparticles exposed on the surface of the support could be easily oxidized. On the basis of the above-mentioned results, we can speculate that Pt species in close proximity to the biphase interface are in the cation state and those around pure monoclinic or tetragonal phases are in the metallic state.

To visualize the lattice mismatch around the m-t phase interface and the relationship between the mixed phase structure and Pt species, the Pt/ZrO₂-K catalyst with the maximum tetragonal phase content was investigated by HRTEM. Fig. 5a shows that there were abundant defects around the transition stages of the two phases caused by the lattice mismatch, and the measured lattice spacing of the Pt nanoparticles adjacent to the interface structure was ca. 2.51 Å, consistent with the (200) plane of cubic platinum oxide $(Pt^{\delta^{+}})$. As shown in Fig. 5b and 5c, the measured lattice fringes of the Pt nanoparticles around pure monoclinic or tetragonal phase were ca. 1.98 Å, ascribed to the (200) plane of cubic platinum (Pt^{0}). For the pure monoclinic phase $Pt/ZrO_{2}-M$ catalyst, however, Pt nanoparticles mainly presented their metallic state (Fig. S5), in accordance with the XPS results. Accordingly, the mixed phase structure might induce the formation of $Pt^{\delta+}$ cation species at the interface, which cannot be caused by the pure phase structure. Moreover, the obscure boundary between the Pt nanoparticles and the support demonstrated the presence of a strong interaction.⁴⁴ More importantly, the strong interaction was essential for anchoring metal nanoparticles, weakening the Zr-O bond, and transferring interfacial electrons or oxygen atoms, which is



Fig. 5 HRTEM images for the Pt/ZrO_2 -K catalyst (a) Pt adjacent to the m-t phase interface, (b) Pt around the pure tetragonal phase, and (c) Pt around the pure monoclinic phase.



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Fig. 6 H₂-TPR profiles of the Pt/ZrO2-M, Pt/ZrO2-U, Pt/ZrO2-N and Pt/ZrO2-K catalysts.

indispensable for high-efficiency catalysts.^{28, 45}

To gain the new insights into the interface effect on samples, H₂-TPR was performed and the results are displayed in Fig. 6. The mixed phase samples showed the three reduction peaks, assigned to the reduction of surface active oxygen interacting with Pt adjacent to the mixed phase interface (peak 3), the pure monoclinic or tetragonal phases (peak 2) and bulk oxygen in zirconia (peak 1), respectively.^{28, 38} It was noted that increasing the tetragonal phase content made the corresponding reduction peak shift to a lower temperature in the sequence of Pt/ZrO₂-U, Pt/ZrO₂-N and Pt/ZrO₂-K, which indicated the enhancement of the low-temperature reducibility. This result was consistent with previous reports that noble metal and mixed phase structures could accelerate the reduction of surface oxygen species and facilitate the activation or transfer of oxygen species.^{20, 26} For the Pt/ZrO₂-M sample, the reduction peaks might be related to the reduction of surface active oxygen around small Pt species (peak 3), large Pt species (peak 2) and bulk oxygen (peak 1), resulting from the weak crystallinity and small crystallite size of Pt/ZrO2-M sample (see Fig. 1b).³⁴

3.2 Catalyst Activity

The catalytic activities of the Pt/ZrO₂ catalysts and the corresponding supports toward HCHO oxidation are displayed in Fig. 7a and S6. All supports were inactive for HCHO decomposition at low temperature, and catalytic performance was improved significantly after Pt loading. It could be seen that the pure monoclinic phase Pt/ZrO2-M catalyst had the poor catalytic activity with HCHO complete convention temperature at 85 °C, while the as-prepared mixed phase Pt/ZrO₂ catalysts showed high catalytic activity, and HCHO could be completely oxidized into CO₂ and H₂O by Pt/ZrO₂-K at 30 °C, as well as Pt/ZrO₂-N and Pt/ZrO₂-U at 35 °C. Obviously, the Pt/ZrO2-M catalyst with relatively high surface area was even inferior to the as-prepared mixed phase Pt/ZrO2-U catalyst with lowest surface area for HCHO oxidation, which meant that the effect of surface area could be excluded as the main responsibility for the higher catalytic activity. However, the presence of the mixed phase could distinctly enhance the

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Fig. 7 (a) HCHO conversion ove ZrO₂ catalysts. Reaction conditions: 100 ppm HCHO, 20% O₂, WHSV = 60,000 mL g_{ca} ; (b) The relationship between the catalytic activity of Pt/ZrO2 catalysts at 25 °C a the tetragonal phase content in supports; (c) The stability test of Pt/ZrO2-K cata at 30 °C. Reaction conditions: 100 ppm HCHO, 20% O_2 , WHSV = 60,000 mL g_{cat}^{-1} h d) Arrhenius plots of reaction rates obtained from kinetic test over as-prepared Pt catalysts

low temperature cata ic performance of the samples. As shown in Fig. 7b, su an increasing tendency of catalytic activity for Pt/ZrO₂ alysts was directly related to the tetragonal phase con nt in the supports. Moreover, the $Pt^{\delta+}/(Pt^0+Pt^{\delta+})$ ratio o amples and corresponding catalytic activity increased dran cically in the sequence of Pt/ZrO₂-M, Pt/ZrO₂-U, Pt/ZrO₂-N a Pt/ZrO₂-K, probably attributed to the structure in the samples, because the formation of the bipha high surface area of P_2 -M did not result in the high Pt^{o+} content. The HRTEM in e of the Pt/ZrO₂-K catalyst confirmed thesis, and the defects caused by the the aforementioned hy lattice mismatch aro d the m-t phase interface were visualized. Combined v h the XRD, Raman and XPS results, it was presumed that th mixed phase structure might induce interfacial oxygen or ctron transfer among the Pt-biphase interface perimeters a anchor low coordinated Pt atoms in the form of $Pt^{\delta+}$ spec by means of strong interactions.⁴⁰ Consequently, we spe ate that Pt^{δ_+} species adjacent to the re active than Pt⁰ species around the biphase interface are pure phase and main ive sites of HCHO catalytic oxidation for mixed phase Pt/Zr catalysts. It must also be mentioned mance of the catalysts was closely that the catalytic per temperature reducibility.⁴⁶ The peak associated with the lo shift to a lower temperature with the increase of the tetragonal phase content (see Fig. 6) verified the speculation above. In addition, the stability of Pt/ZrO₂-K sample with the best catalytic performance was also checked by a long-term test at 30 °C. Figure 7c shows that the Pt/ZrO₂-K catalyst still exhibited 88% HCHO conversion after a 60 h long test in the same test conditions.

To further clarify the origin of this high efficiency, the reaction kinetics of the Pt/ZrO₂ catalysts were measured. The specific HCHO reaction rates (per unit surface area of catalyst), which represents the intrinsic catalytic efficiency of catalysts, were calculated to clarify whether the significant enhancement of the catalytic activity arised from the different

surface areas.⁴⁷ It was apparent from Table 1 that Pt/ZrO₂-M with relatively high surface area showed the lowest specific HCHO reaction rate $(0.8 \times 10^{-3} \text{ mmol h}^{-1} \text{ m}^{-2})$, indicating that the surface area was not key factor for the higher catalytic activity. As seen in Fig. 7d and Table 1, the activation energies decreased remarkably from 213.5 to 24.7 kJ/mol in the sequence of Pt/ZrO₂-M, Pt/ZrO₂-U, Pt/ZrO₂-N and Pt/ZrO₂-K, consistent with the tetragonal phase content. This result demonstrated that the higher the tetragonal phase content, the easier the HCHO complete oxidation, thus achieving a superior performance. Moreover, it is generally agreed that the activation energy is related to the reaction mechanism.^{35,} ⁴⁸ Therefore, we speculate that the mixed phase structure of Pt/ZrO₂ catalysts could significantly enhance the intrinsic catalytic efficiency and induce a new reaction pathway. This is different behavior compared to that of the pure monoclinic phase Pt/ZrO₂-M catalyst and results in an enormous decrease of activation energy. That is, there was an intrinsic relation between the mixed phase structure and high catalytic efficiency of the samples, thus further verifying the aforementioned hypothesis.

3.3 In-situ DRIFT test

In situ DRIFTS spectra of the Pt/ZrO₂-K and Pt/ZrO₂-M catalysts exposed to $HCHO/O_2$ were performed (Fig. 8) to detect the intermediates and investigate the catalytic mechanism of HCHO oxidation. As shown in Fig. 8a, formate species (1582, 1379 cm⁻¹ for ν (COO⁻) and 2986, 2862, 2765 cm⁻¹ for ν (CH))^{49,} ⁵⁰ were formed and dominant. Bands also appeared at 1479, 1324, 1180 and 1117 cm⁻¹, which were ascribed to the CH and CO vibrations of dioxymethylene species.^{36, 50} Therefore, it can be concluded that dioxymethylene and formate species were formed and accumulated during HCHO oxidation over Pt/ZrO2-K. Additionally, there was a negative band at approximately 3689 cm⁻¹ assigned to surface hydroxyl groups (-OH), indicating that the formation of dioxymethylene and formate species consumed -OH groups^{24, 51}. However, the DRIFTS spectrum of Pt/ZrO₂-M (Fig. 8b) was obviously different from that of Pt/ZrO₂-K. Formate species (1630, 1521 cm⁻¹ for ν (COO⁻) and 2938, 2895, 2831 cm⁻¹ for ν (CH))^{49, 50} and dioxymethylene (1456, 1409, 1337,1307 cm⁻¹ for CH vibrations and 1128,1096 cm⁻¹ for CO vibrations)^{36, 50} became weak. The bands of the hydroxyl groups appeared at 3764 and 3676 $\text{cm}^{\text{-1},\,^{24},\ 52}$ Interestingly, two new bands at approximately 1667 and 1178 cm⁻¹ appeared, which were assigned to v(C=O) and $v_{as}(COO)$ of



Fig. 8 Dynamic changes of in situ DRIFTS of (a) Pt/ZrO2-K and (b) Pt/ZrO2-M catalysts as a function of time in a flow of O₂ + HCHO + N₂ at room temperature. Reaction conditions: 100 ppm HCHO, 20 % O_2 and 74 % N_2 (balance). The total flow rate was 100 mL min

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 $\mbox{Scheme 1}$ The proposed catalytic mechanism of the $\mbox{Pt}/\mbox{ZrO}_2\mbox{-}K$ catalyst for HCHO catalytic oxidation

carbonate species, respectively.⁵¹

Herein, a possible mechanism for HCHO catalytic oxidation over Pt/ZrO₂-K and Pt/ZrO₂-M was proposed. From the aforementioned characterizations, there were two active sites (metallic and ionic Pt species) and Pt^{δ^+} species adjacent to the interfacial structure were the main active sites for the Pt/ZrO₂-K catalyst. However, for the Pt/ZrO_2 -M catalyst, Pt^0 species were the active sites and the activity of Pt^{δ^+} species was negligible, as reported in previous studies.^{3, 15, 37} According to the DRIFTS results of Pt/ZrO2-K, adsorbed formate and dioxymethylene (DOM) species were abundant and carbonate species were absent on the Pt/ZrO2-K catalyst. As shown in Scheme 1, when HCHO molecules were adsorbed on the surface of Pt/ZrO₂-K, DOM rapidly formed by the nucleophilic attack of the oxygen atom derived from PtO adjacent to the mt interface of the support, accompanying the formation of Pt^{0} . Then, the DOM was easily converted into formate species (HCOO⁻). Adsorbed oxygen species on the support of Pt/ZrO₂-K sample could be transferred rapidly to the perimeter of Pt nanoparticles in close proximity to the biphase interface, leading to the formation of active oxygen and Pt^{δ^+} species. This oxygen species could completely oxidize the adsorbed formate species into CO₂ and H₂O. However, the incomplete oxidation of HCOO⁻ might occur for Pt/ZrO₂-M in the form of inert carbonate species according to the DRIFTS results, which did not further decompose into CO₂ and H₂O (Scheme S1). More importantly, carbonate species probably occupied the active sites, resulting in low catalytic performance of Pt/ZrO₂-M.⁵³ By this cycle, HCHO was converted into CO₂ and H₂O for Pt/ZrO₂-K and inert carbonate species, CO_2 and H_2O for Pt/ZrO_2-M . Considering the coexistence of $Pt^{\delta+}$ and Pt^{0} species on the Pt/ZrO₂-K catalyst, there was another pathway for HCHO oxidation catalyzed by Pt⁰ species, which is similar to the pathway above. However, it was believed that this pathway is not the dominant process due to the low content and catalytic activity of Pt^0 species. Therefore, the Pt^{δ^+} species in close proximity to the mixed phase interface in the Pt/ZrO2-K catalyst dominated the efficiency of the HCHO conversion into CO₂ and H₂O. In addition, the low catalytic activity of Pt/ZrO₂-M was attributed to the absence of the interfacial structure

and the formation of inert carbonate species in HCHO oxidation.

4. Conclusions

In this study, a series of mixed phase Pt/ZrO₂ catalysts were prepared by simple methods. Compared with a pure monoclinic phase Pt/ZrO₂-M catalyst, the catalytic activity of the mixed phase system was enhanced significantly, and HCHO can be completely oxidized into CO₂ and H₂O at near ambient temperature. XRD, Raman, TEM, XPS, HRTEM, and H₂-TPR characterizations revealed that the m-t phase interface can induce the formation of more defects and cationic $Pt^{\delta+}$ species. It was also proved that the Pt^{δ^+} adjacent to the interfacial structure was more active than the Pt⁰ around the pure monoclinic or tetragonal phases for HCHO oxidation. Moreover, the DRIFTS results of the Pt/ZrO₂-K and Pt/ZrO₂-M catalysts demonstrated that the special biphase structure can change the reaction pathway and inhibit the formation of inert carbonate species during HCHO oxidation. Thus, the enormous increase in the catalytic activity of the mixed phase system can be attributed to the presence of the m-t phase interface. Our findings shed light on the interface effect of the mixed phase Pt/ZrO₂ catalyst, which may afford guidance for developing high-efficiency catalysts to eliminate indoor HCHO by designing mixed phase systems.

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Notes and references

- Y. C. Huang, W. J. Fan, B. Long, H. B. Li, W. T. Qiu, F. Y. Zhao, Y. X. Tong and H. B. Ji, *J. Mater. Chem. A*, 2016, 4, 3648-3654.
- Y. Huang, B. Long, M. Tang, Z. Rui, M.-S. Balogun, Y. Tong and H. Ji, *Appl. Catal.*, *B*, 2016, **181**, 779-787.
 - L. Nie, J. Yu, X. Li, B. Cheng, G. Liu and M. Jaroniec, Environ. Sci. Technol., 2013, 47, 2777-2783.
- 4. Y. Huang, K. Ye, H. Li, W. Fan, F. Zhao, Y. Zhang and H. Ji, Nano Research, 2016, **9**, 3881-3892.
 - B. Y. Bai, Q. Qiao, J. H. Li and J. M. Hao, *Chin. J. Catal.*, 2016, **37**, 102-122.
 - C. Zhang, Y. Li, Y. Wang and H. He, *Environ. Sci. Technol.*, 2014, **48**, 5816-5822.
 - L. Nie, A. Meng, J. Yu and M. Jaroniec, *Sci. Rep.*, 2013, **3**, 3215.
 - H. B. Huang, Y. Xu, Q. Y. Feng and D. Y. C. Leung, *Catal. Sci. Technol.*, 2015, **5**, 2649-2669.
 - F. Wyrwalski, J. F. Lamonier, S. Siffert and A. Aboukais, Appl. Catal., B, 2007, **70**, 393-399.
 - V. G. Milt, E. A. Lombardo and M. A. Ulla, *Appl. Catal., B*, 2002, **37**, 63-73.

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DOI: 10.1039/C7TA03888G

Journal Name

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- 11. P. M. de Souza, R. C. Rabelo-Neto, L. E. P. Borges, G. 40. Jacobs, B. H. Davis, U. M. Graham, D. E. Resasco and F. B. Noronha, ACS Catal., 2015, 5, 7385-7398.
- 12. V. P. Pakharukova, E. M. Moroz, D. A. Zyuzin, A. V. Ishchenko, L. Y. Dolgikh and P. E. Strizhak, J. Phys. Chem. C, 2015, 119,28828-28835.
- 13. I. Das and G. De, Sci. Rep., 2015, 5, 18503.
- 14. A. Nandy, C. S. Tiwary, A. Dutta, K. Chattopadhyay and S. K. Pradhan, Electrochim. Acta, 2015, 170, 360-368.
- 15. H. B. Huang and D. Y. C. Leung, J. Catal., 2011, 280, 60-67.
- 16. Y. Zhang, Y. Shen, X. Yang, S. Sheng, T. Wang, M. F. Adebajo and H. Zhu, J. Mol. Catal. A-Chem., 2010, 316, 100-105.
- 17. J. A. LaVerne, J. Phys. Chem. B, 2005, 109, 5395-5397.
- 18. S.-H. Guan, X.-J. Zhang and Z.-P. Liu, J. Am. Chem. Soc., 2015. 137. 8010-8013.
- 19. J. Zhang, Y. Li, L. Wang, C. Zhang and H. He, Catal. Sci. Technol., 2015, 5, 2305-2313.
- 20. D. C. Hurum, A. G. Agrios, K. A. Gray, T. Rajh and M. C. 47. Thurnauer, J. Phys. Chem. B, 2003, 107, 4545-4549.
- 21. J. Zhang, Q. Xu, Z. Feng, M. Li and C. Li, Angew. Chem., Int. Ed., 2008, 120, 1790-1793.
- 22. V. Likodimos, A. Chrysi, M. Calamiotou, C. Fernandez-Rodriguez, J. M. Dona-Rodriguez, D. D. Dionysiou and P. Falaras, Appl. Catal., B, 2016, 192, 242-252.
- 23. T. Witoon, J. Chalorngtham, P. Dumrongbunditkul, M. Chareonpanich and J. Limtrakul, Chemical Engineering Journal, 2016, 293, 327-336.
- L. Ma, D. S. Wang, J. H. Li, B. Y. Bai, L. X. Fu and Y. D. Li, 24. Appl. Catal., B, 2014, 148, 36-43.
- 25. D. Y. Yoon, E. Lim, Y. J. Kim, J. H. Kim, T. Ryu, S. Lee, B. K. Cho, I. S. Nam, J. W. Choung and S. Yoo, J. Catal., 2014, 319. 182-193.
- 26. G. N. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G. P. Petrova, N. Tsud, T. Skala, A. Bruix, F. Illas, K. C. Prince, V. Matolin, K. M. Neyman and J. Libuda, Nat. Mater., 2011, 10. 310-315.
- C. B. Zhang, H. He and K. Tanaka, Appl. Catal., B, 2006, 65, 27. 37-43
- Q. Xu, W. Lei, X. Li, X. Qi, J. Yu, G. Liu, J. Wang and P. 28. Zhang, Environ. Sci. Technol., 2014, 48, 9702-9708.
- J. Li, X. Liu, W. Zhan, Y. Guo, Y. Guo and G. Lu, Catal. Sci. 29. Technol., 2016, 6, 897-907.
- 30. Y. Huang, H. Li, W. Fan, F. Zhao, W. Qiu, H. Ji and Y. Tong, ACS Applied Materials & Interfaces, 2016, 8, 27859-27867.
- 31. M. Li, Z. Feng, G. Xiong, P. Ying, Q. Xin and C. Li, J. Phys. Chem. B, 2001, 105, 8107-8111.
- 32 C. Li and M. Li, J. Raman Spectrosc., 2002, 33, 301-308.
- 33. Q. Zhu, Y. Peng, L. Lin, C. M. Fan, G. Q. Gao, R. X. Wang and A. W. Xu, J. Mater. Chem. A, 2014, 2, 4429-4437.
- 34. F. Yang, J. J. Wei, W. Liu, J. X. Guo and Y. Z. Yang, J. Mater. Chem. A, 2014, 2, 5662-5667.
- 35. S. P. Mo, S. D. Li, W. H. Li, J. Q. Li, J. Y. Chen and Y. F. Chen, J. Mater. Chem. A, 2016, 4, 8113-8122.
- 36. B. Y. Bai and J. H. Li, ACS Catal., 2014, 4, 2753-2762.
- 37. H. B. Huang and D. Y. C. Leung, ACS Catal., 2011, 1, 348-354.
- 38. O. A. Bulavchenko, Z. S. Vinokurov, T. N. Afonasenko, P. G. Tsyrul'nikov, S. V. Tsybulya, A. A. Saraev and V. V. Kaichev, Dalton Trans., 2015, 44, 15499-15507.
- 39. M. Lin, X. Yu, X. Yang, K. Li, M. Ge and J. Li, Catal. Sci. Technol., 2017, 7, 1573-1580.

- A. Y. Klyushin, M. T. Greiner, X. Huang, T. Lunkenbein, X. Li, O. Timpe, M. Friedrich, M. Hävecker, A. Knop-Gericke and R. Schlögl, ACS Catal., 2016, 6, 3372-3380.
- P. Bera, K. R. Priolkar, A. Gayen, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, V. Jayaram and G. N. Subbanna, Chem. Mater., 2003, 15, 2049-2060.
- 42. Z. Hao, L. An, H. Wang and T. Hu, React. Kinet. Catal. Lett., 2000, 70, 153-160.
- C. Li, Y. Shen, M. Jia, S. Sheng, M. O. Adebajo and H. Zhu, 43. Catal. Commun., 2008, 9, 355-361.
- 44. Z. Yan, Z. Xu, J. Yu and M. Jaroniec, Appl. Catal., B, 2016, 199. 458-465.
- 45. A. Bruix, J. A. Rodriguez, P. J. Ramírez, S. D. Senanayake, J. Evans, J. B. Park, D. Stacchiola, P. Liu, J. Hrbek and F. Illas, J. Am. Chem. Soc., 2012, 134, 8968-8974.
- 46. J. G. Deng, S. N. He, S. H. Xie, H. G. Yang, Y. X. Liu, G. S. Guo and H. X. Dai, Environ. Sci. Technol., 2015, 49, 11089-11095.
 - J. T. Hou, L. L. Liu, Y. Z. Li, M. Y. Mao, H. Q. Lv and X. J. Zhao, Environ. Sci. Technol., 2013, 47, 13730-13736.
 - Y. Chen, Z. Huang, M. Zhou, Z. Ma, J. Chen and X. Tang, Environ. Sci. Technol., 2017, 51, 2304-2311.
 - C. B. Zhang, F. D. Liu, Y. P. Zhai, H. Ariga, N. Yi, Y. C. Liu, K. Asakura, M. Flytzani-Stephanopoulos and H. He, Angew. Chem., Int. Ed., 2012, 51, 9628-9632.
 - G. Busca, J. Lamotte, J. C. Lavalley and V. Lorenzelli, J. Am. Chem. Soc., 1987, 109, 5197-5202.
- 51. J. Wang, P. Zhang, J. Li, C. Jiang, R. Yunus and J. Kim, Environ. Sci. Technol., 2015, 49, 12372-12379.
- 52. D. W. Kwon, P. W. Seo, G. J. Kim and S. C. Hong, Appl. Catal., B, 2015, 163, 436-443.
 - B. C. Liu, C. Y. Li, Y. F. Zhang, Y. Liu, W. T. Hu, Q. Wang, L. Han and J. Zhang, Appl. Catal., B, 2012, 111, 467-475.

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High-efficiency Pt/ZrO₂ catalysts with mixed phase were successfully prepared. The catalysts exhibited high activity and interfacial structure can change reaction pathway.