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Efficient and stable platinum nanocatalysts supported over Ca-doped ZnAl₂O₄ spinels for base-free selective oxidation of glycerol to glyceric acid



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<i>Keywords:</i> High-surface-area spinel Platinum nanocatalysts Oxidation of glycerol Strong metal-support interactions Surface synergy	In the work, highly dispersed platinum nanocatalysts supported over undoped and Ca-doped zinc aluminate spinels were developed and applied for aqueous-phase selective oxidation of glycerol to produce glyceric acid under base-free conditions. As-fabricated Pt-based catalyst with the incorporation of an appropriate Ca/ $(Ca + Zn)$ molar ratio of 0.1 into the spinel exhibited a higher catalytic activity, along with a selectivity to glyceric acid (> 81%) and a high turnover frequency of 1160 h ⁻¹ , compared with other supported Pt-based ones over zinc aluminates, as well as most of supported Pt catalysts previously reported. The structural characterizations and catalytic experiments showed that surface synergy between highly dispersed metallic Pt ⁰ species and medium-strength basic sites mainly contributed to its enhanced catalytic efficiency for base-free glycerol oxidation. Moreover, the present Pt catalyst also presented high structural stability and good reusability. The work opens an alternative approach for constructing highly efficient and stable metal-base bifunctional catalysts for a wide range of heterogeneous oxidation processes without the addition of liquid alkalis.

1. Introduction

In order to make better use of biodiesel production, it is necessary to convert abundant glycerol into high value-added chemicals in the future. Commonly, glycerol can be selectively transformed into different important chemicals of industrial relevance, such as acrolein, 1,2-propanediol, glyceric acid, formic acid, and acrylic acid, through catalytic dehydration, hydrogenolysis, oxidation, and oxidehydration processes using some supported catalysts [1-5]. Among them, the oxidation of glycerol has received considerable attention since the oxidation is a facile method of activating molecules to synthesize chemical intermediates. Taking advantage of the presence of several hydroxyl groups, glycerol can be oxidized into a series of products including C1, C2, and C3 products (e.g. glyceric acid, tartronic acid, dihydroxyacetone, oxalic acid, glycolic acid, formic acid, and CO₂) [6]. Interestingly, many attractive noble metals (e.g. platinum, gold, and palladium) are active for the oxidation of biomass. For example, supported Pt nanoparticle catalysts have been applied for the oxidation of 5-hydroxymethylfurfural [7,8]. And, Pd and Pt nanoparticles (NPs) as highly efficient catalysts are explored in the oxidation of polyols using clean molecular oxygen as oxidant; however, the control of product selectivities is a challenging

task [9].

As we know, commonly, the catalytic activity of metal NPs is proportional to the loading of active metals, inversely being proportional to the particle size of NPs. In addition, the metal particle size also can govern the product selectivities [10–13]. Usually, the reduced particle size facilitates the increase in the metal particle edges, thus leading to the exposure of more active sites and promoting the oxidation processes [14]. Meanwhile, the basic solution medium (e.g. NaOH) promotes the elimination of β -H in glycerol as the rate-determining step, finally being in favor in the formation of the sodium salt of glyceric acid [15]. Moreover, the addition of homogenous bases can cause high cost of production, difficult separation, and environmental pollution issues.

On the other side, the surface acid-base property of catalyst supports can play a significant role in governing the catalytic performance of catalysts [16]. For example, Su and co-workers found that different functionalized carbon nanotubes and nanofibers supported Au catalysts exhibited different catalytic performance in the glycerol oxidation [17], and the enhanced basicity of the functionalized support was beneficial to the glycerol conversion and the production of C3 products. In addition, different supports including carbon materials (active carbon and graphite) [11,12] and metal oxides (e.g. TiO₂, MgAl₂O₄) [18,19] are

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employed in the above reaction. In most cases, homogenous NaOH was added into reaction systems with noble metal catalysts to promote the deprotonation of the hydroxyl group in glycerol [14,20], together with relatively high selectivity to glyceric acid (> 52%), although the products exist in the form of salts. Moreover, it was reported that supported gold-based catalysts were inactive for base-free glycerol oxidation [21]. Up to now, there are a few reports on supported noble-metal-based catalysts over basic supports applied in the base-free glycerol oxidation [19,22-25]. Although some basic layered double hydroxides and MgO were employed as supports for immobilizing noble metal NPs [26-28], the leaching of supports was serious in the course of glycerol oxidation under acidic reaction medium containing glyceric acid (pH could reach about 2), thus easily leading to rapid deactivation of catalysts. In this regard, it is highly desirable and a challenging task to develop efficient and stable metal-base bifunctional catalysts for base-free glycerol oxidation.

Recently, due to well-developed porous microstructure and large surface area, porous metal oxides and complex metal oxides have been widely employed as supports for metal-based catalysts in a variety of catalytic processes [29–31], because their high surface areas facilitate the active metal dispersion, thus promoting the occurrence of strong metal-support interactions (SMSIs) and enhancing the stability of metal NPs. Meanwhile, abundant pores of supports may be beneficial to the diffusion and transfer of reactants in the course of reactions, thus being in favor of the conversion of substrates. For instance, compared with single metal oxides, spinel-type zinc aluminate (ZnAl₂O₄) possesses the unique physicochemical properties including higher thermal/chemical stability and mechanical resistance [32,33]. Correspondingly, ZnAl₂O₄ supported metal catalysts exhibited superior catalytic property to single oxides supported ones [34,35].

In this contribution, a series of highly dispersed Ca-doped zinc aluminate spinels supported platinum catalysts were developed and applied in the base-free glycerol oxidation. It was revealed that the incorporation of a certain amount of Ca into the spinel structure could improve surface basicity of supported catalysts and promote the formation of SMSIs, thus synergistically enhancing catalytic performance of catalysts. Moreover, the as-fabricated Pt catalyst showed high structural stability and reusability with no significant loss of its activity after six consecutive runs.

2. Experimental section

2.1. Catalyst preparation

Undoped and Ca-doped zinc aluminates synthesized by our previously reported solution-phase method [29]. Typically, Zn $(NO_3)_2$ ·6H₂O (4.8 mmol), Ca $(NO_3)_2$ ·4H₂O (0.1 mmol), Al $(NO_3)_3$ ·9H₂O (10.0 mmol), and urea (50 mmol) were dispersed in a 100 ml of solvent consisting of methanol and deionized water (v/v = 1:1). Subsequently, the solution was aged at 180 °C overnight. Then, the resultant precipitate was washed with ethanol and deionized water several times. At last, the solid was dried at 70 °C overnight and denoted as ZCA-x (x = 0, 5, 10 and 15; x is Ca/(Ca + Zn) molar ratio in initial synthesis mixture).

Spinel support (0.5 g) was dispersed into a 100 mL of deionized water, and then 1.0 mL of $\rm H_2PtCl_6$ solution (19.3 mM) was added with stirring. Subsequently, 50 mL of NaBH₄ solution (80 mM) was added dropwise to the above suspension at room temperature, followed by aging for 4 h. The obtained precipitate was washed and dried at 70 °C for 12 h under vacuum. For comparison, other metal oxides supported Pt-based catalysts were synthesized based on the above same synthesis method.

2.2. Characterization

X-ray diffraction (XRD) patterns were gained on Shimadzu XRD-6000 diffractometer using a Cu-Ka source. Metal contents in samples

were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Shimadzu ICPS-7500). Transmission electron microscopy (TEM) experiments were operated on JEOL 2100 instrument. Micromeritics ASAP 2020 sorptometer was utilized to perform low-temperature nitrogen adsorption-desorption experiments. VG ESCALAB 2201 XL spectrometer (Al Ka X-ray radiation) was used to obtain X-ray photoelectron spectra (XPS) of samples. CO₂ temperatureprogrammed desorption (CO2-TPD) was tested on ChemiSorb 2720 instrument. The sample (50 mg) was outgassed under a He flow of 40 ml/ min at 200 °C for 1 h. Subsequently, a CO₂ flow (40 ml/min) was switched for 1 h at room temperature, and then purged with a He flow for 1 h. At last, the desorption of CO₂ was performed with the increasing temperature. FT-IR spectrophotometer (Thermo Nicolet 380) was applied to record Fourier transform infrared (FT-IR) spectra of CO2 adsorbed over samples. The self-supporting sample wafer was heated at 70 °C under N₂ flow for 1 h. After that, a CO₂ flow was switched for 1 h at room temperature and purged with a He flow for 1 h. Finally, FT-IR spectra of samples were collected under vacuum.

2.3. Catalytic oxidation of glycerol

The base-free oxidation glycerol was conducted in a stainless-steel reactor (100 ml), where glycerol (10 ml) and the catalyst (glycerol/Pt molar ratio = 590: 1) were charged. When the temperature of the reactor reached a certain temperature, the oxygen was fed into the reactor at a certain partial pressure. The oxidation began under stirring with a speed of 900 rpm. When the reaction finished, the reactor was placed into an ice bath and the reactants were centrifuged. the products were analyzed at 35 °C by a liquid chromatograph (Shimadzu LC-20A) using HPX-87H column and 5 mM H₂SO₄ aqueous solution as mobile phase with a flow rate of 0.6 ml/min with refractive index and ultraviolet detector by the external standard method.

3. Results and discussion

3.1. Structural analysis of Pt-based samples

XRD patterns of a series of undoped and Ca-doped ZnAl_2O_4 spinel supports and resulting supported Pt samples are shown in Fig. 1. Noticeably, in each case, spinel support shows several intensive (220), (311), (400), (422), (511) and (440) diffraction planes for cubic structure of zinc aluminate spinel phase (JCPDS No. 41-1745), reflecting the formation of the spinel structure with the good crystallinity. In addition, as for Ca-doped three spinel supports, a small amount of CaCO₃ impurity (JCPDS No. 05-0586) can be observed and is gradually enhanced in the intensity with the increasing content of ca. After loading Pt, XRD partners of all supported Pt samples are almost identical to those of pristine supports. Interestingly, one cannot observe any diffractions assignable to metallic Pt, probably because of the formation of highly dispersed small-sized Pt particles, as well as the low content of Pt (< 1.0 wt%) (Table 1).

As shown in Fig. 2, TEM images of representative two supported Pt samples (Pt/ZCA-0 and Pt/ZCA-10) depict an irregular porous microstructure of spinel supports, suggestive of the large specific surface area of samples. Meanwhile, it is noticed that many uniform small-sized particles of about 2–4 nm in size are evenly distributed on the surface of supports. For Pt/ZCA-10, a further HRTEM observation clearly reveals the lattice fringes of black NP and the support matrix, which correspond to the (111) and (311) planes of metallic Pt⁰ (JCPDS 04-0802) and cubic ZnAl₂O₄ spinel phase (JCPDS 05-0669), with an interplanar distance of 0.225 nm and 0.245 nm, respectively. Furthermore, based on the histogram of the narrow particle size distribution of Pt NPs on the Pt/ZCA-10, the average Pt particle size is determined to be 3.13 nm. Despite the composition of supports, small Pt NPs with a slight difference in the particle size (2.44–3.13 nm) and a 0.9 wt% Pt loading amount can be obtained in all cases (Table 1), indicating that the



Fig. 1. XRD patterns of undoped and Ca-doped ZnAl₂O₄ spinels (A) and supported Pt-based samples (B).

 Table 1

 Compositions and structural properties of Pt-based samples.

Samples	Pt ^a	Ca ^a	D _p ^b	Dis _M ^c	D _{BA} ^d
	(wt%)	(wt%)	(nm)	(nm)	(mmol/g)
Pt/ZCA-0	0.89	0	2.44	46.3	0.314 (0.269) ^e
Pt/ZCA-5	0.85	1.61	2.82	40.1	0.324 (0.297)
Pt/ZCA-10	0.92	2.99	3.13	36.1	0.479 (0.431)
Pt/ZCA-15	0.83	3.67	2.50	45.2	0.353 (0.296)

^a Obtained based on ICP-AES analysis.

^b Average size of Pt NPs obtained through TEM images.

^c Dispersion of Pt estimated based on the mean particle size of Pt from TEM results.

^d The amount of total basic sites obtained from CO₂-TPD curves.

 $^{\rm e}$ Data in parentheses: the amount of medium-strength basic sites obtained from CO2-TPD curves.

present ZnAl₂O₄ and Ca-doped ZnAl₂O₄ spinels are good supports for immobilizing and dispersing Pt NPs, probably because of the occurrence of strong metal-support interactions (SMSIs).

In addition, as shown in Fig. 3A, low-temperature nitrogen adsorption-desorption isotherms of samples are characteristic of I-type with no hysteresis loop, mirroring the main microporous character of all supported Pt samples. Such a porous structure can be further identified by pore size distribution curves (Fig. 3B), indicating that the pores mainly exist in the form of micropores. It is noted from Table 2 that all samples possess high BET surface areas (> 218 m² g⁻¹), where the micropore surface area occupies more than about 38% in total surface area. The above results clearly illustrate that well-developed interconnected porous network of spinels supported Pt catalysts can form, mainly originating from the voids formed by the aggregation of spinel particles.

3.2. Surface property of Pt-based samples

XPS characterization was carried out to determine the surface electronic states of Pt species in samples. As shown in Fig. 4, the binding energy values (BEs) of Pt $4d_{5/2}$ for all supported samples lie in the range of 314.2 to 314.8 eV, indicative of the character of metallic Pt(0) state

[36,37]. No peak signal related to Pt(II) species can be observed at the BE of about 317.4 eV. Meanwhile, it is interesting to note that a slightly negative shift in BE of Pt 4d 5/2 (about 0.6 eV) from Pt/ZCA-5 to Pt/ZCA-10 and Pt/ZCA-15, demonstrating the electron transfer from the support to Pt species with the incorporation of a certain amount of Ca cations and thus the formation of stronger metal-support interactions and electron-rich metallic Pt species. It is speculated that the Ca-O-Al structure should form in the tetrahedral interstitials of spinel, probably promoting the electron transfer from the support to Pt species and thus the formation of electron-rich metallic Pt species. In the case of Pt/ZCA-15, however, more surface impure CaCO₃ inversely inhibit electron transfer between Pt species and the support to some extent.

CO₂-TPD curves of supported Pt-based samples were analyzed to reveal the effect of the incorporation of Ca into spinel structure on surface basicity of samples (Fig. 5). Commonly, the desorption temperature of CO₂ adsorbed on the sample surface can be correlated with the strength of surface basic sites. In all cases, there is a broad desorption region for adsorbed CO₂ between 50 and 700 °C. Further deconvolution of the desorption can give five or six components [38,39]. The first peak below 175 °C is associated with chemically adsorbed CO₂ on weak basic sites (WB.), as well as surface physically adsorbed CO2. In the CO2-TPD curves, three or four desorption peaks in the range of 175 to 580 °C can be ascribed to adsorbed CO2 on medium-strength basic sites (MSB.), which mainly result from surface hydroxyl groups, metaloxygen pairs in the supports or isolated Ca-O pairs [40,41], and coordinatively unsaturated O^{2-} ions, respectively. Meanwhile, the peak at higher desorption temperature of about 650 °C reflects the desorption of adsorbed CO₂ on strong basic sites (SB.). Based on the integrated desorption areas, one can note that among supported samples, the surface density of total basic sites on the Pt/ZCA-10 sample, as well as that of medium-strength sites, is largest (Table 1).

As we know, surface strong basic sites mainly originate from coordinatively unsaturated O^{2-} ions of oxides [38,39]. With the introduction of Ca^{2+} ions, the spinel structure of resulting ZCA-*x* supports may slightly change. Correspondingly, in the case of Pt/ZCA-5, the addition of a small amount of Ca^{2+} ions into the spinel structure probably leads to the decrease in the surface concentration of coordinatively unsaturated O^{2-} ions, thus giving rise a decreased density



Fig. 2. TEM and HRTEM images of representative Pt/ZCA-0 (a), and Pt/ZCA-10 (b,c) and the particle size distribution of Pt NPs (f) on the Pt/ZCA-10 sample.

of strong basic sites. With the increasing Ca content, inversely, the density of strong basic sites is increased gradually. It implies that the introduction of Ca²⁺ ions into the spinel structure of ZnAl₂O₄ can affect surface heterogeneity of supports in varying degrees. Despite the varied

density of strong basic sites among Pt/ZCA-*x* samples, the density of total basic sites or medium-strength basic sites increase gradually in the following order: Pt/ZCA-0 < Pt/ZCA-5 < Pt/ZCA-10. For Pt/ZCA-15 (Table 1), however, the presence of more surface impure CaCO₃ reduces



Fig. 3. Nitrogen adsorption-desorption isotherms (A) and pore size distributions (B) of Pt/ZCA-0 (a), Pt/ZCA-5 (b), Pt/ZCA-10 (c) and Pt/ZCA-15 (d).

Table 2

Textual property of supported Pt-based samples.

Samples	S _{BET} ^a	S _{micro} ^b	V _{total} ^c	V _{micro} ^d	D _{pore} e
	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(nm)
Pt/ZCA-0	229.3	101.7	0.116	0.0412	2.19
Pt/ZCA-5	230.4	108.9	0.119	0.0447	2.25
Pt/ZCA-10	218.5	83.1	0.111	0.0408	2.26
Pt/ZCA-15	222.7	106.2	0.104	0.0434	2.16

^a Specific surface areas calculated based on BET technique.

^b Micropore surface area determined based on t-plot model.

^c Determined from single-point total pore volume.

^d Micropore volume based on t-plot method applied to adsorption isotherm.

e Determined based on BJH method.



Fig. 4. XPS of Pt 4d region for Pt/ZCA-0 (a), Pt/ZCA-5 (b), Pt/ZCA-10 (c) and Pt/ZCA-15 (d) samples.



Fig. 5. CO_2 -TPD curves of Pt/ZCA-0 (a), Pt/ZCA-5 (b), Pt/ZCA-10 (c) and Pt/ZCA-15 (d) samples.

surface basicity of the sample. As a result, it can be concluded that the introduction of appropriate amounts of Ca can improve surface basicity of the present Pt/ZCA-x samples.

Furthermore, to identify the origin of surface basic sites on Pt-based samples, IR spectra of adsorbed CO_2 on two Pt/ZCA-0 and Pt/ZCA-10 samples were obtained in the range of 1200 to 1900 cm^{-1} (Fig. 6).

According to the shape of the broad absorption band, eight components can be fitted, indicative of the presence of surface diverse species originating from absorbed CO₂. Two intensive absorption bands at 1636/ 1416 cm⁻¹ for Pt/ZCA-0 and 1662/1416 cm⁻¹ for Pt/ZCA-10 are related to the asymmetric and symmetric O-CO- stretching vibrations of bridged carbonate (HCO_3^{-}) [42-44], indicative of the presence of Brønsted basic sites associated with surface hydroxyl groups. While two absorption bands at 1575/1302 cm⁻¹ for Pt/ZCA-0 and 1623/ 1291 cm^{-1} for Pt/ZCA-10 are due to the vibrations of bidentate carbonate $(b-CO_3^{2-})$ generated on metal-oxygen sites. Meanwhile, it is noted that two absorption bands at $1489/1375 \text{ cm}^{-1}$ for Pt/ZCA-0 and $1490/1364 \text{ cm}^{-1}$ for Pt/ZCA-10 are attributable to the vibrations of unidentate carbonate $(u-CO_3^{2^-})$ generated by interacting isolated O^{2^-} ions, mirroring the absorption of CO₂ on medium-strength or strong basic sites. Moreover, the other two bands at 1676/1535 for Pt/ZCA-0 and 1713/1538 cm⁻¹ for Pt/ZCA-10 correspond to surface polydentate carbonate species $(p-CO_3^{2^{-}})$. On the other side, one can evaluate the strength of basic sites according to the splitting of asymmetric and symmetric O-CO- vibration bands. A smaller value of band splitting presents a stronger interaction between CO₂ and basic sites. Correspondingly, the relative fraction of $u-CO_3^{2-}$ and $p-CO_3^{2-}$ species with smaller values of band splitting on the Pt/ZCA-10 determined by the integrated areas of vibration bands is about 53.4%, which is higher than that on the Pt/ZCA-0 (37.4%). It demonstrates that the incorporation of a certain amount of Ca into the spinel structure can induce more surface medium-strength or strong basic sites, well consistent with the results of CO₂-TPD experiments.

3.3. Catalytic performance of supported Pt-based catalysts

The reaction results in the oxidation of glycerol over different supported Pt catalysts are summarized in Table 3 under the same reaction conditions (60 °C, oxygen pressure of 0.5 MPa, and reaction time of 5 h). In the present reaction, no glycerol conversion is achieved in the absence of any catalysts. Significantly, the pure ZnAl₂O₄ supported Pt catalyst (Pt/ZCA-0) affords a glycerol conversion of 50.8% with a glyceric acid (GLYA) selectivity of 81%, besides the formation of other deep oxidation products including tartronic acid (TARA), dihydroxyacetone (DHA), glycolic acid (GLYCOA), oxalic acid (OXA) and CO₂ gas. Noticeably, in the case of Pt/ZCA-10, the incorporation of a Ca/ (Zn + Ca) molar ratio of 0.1 into the spinel leads to an obvious increase in glycerol conversion (61.8%), despite an identical GLYA selectivity. With the further introduction of Ca, the activity of Pt/ZCA-15 catalyst inversely is slightly decreased. Furthermore, in all cases, the selectivity to total C3 products can reach about 92.0%, reflecting the good catalytic performance of the present supported Pt catalysts in base-free glycerol oxidation. It is noted that compared with Pt/ZCA-0 with the higher dispersion of Pt species and a similar density of surface total basic sites, Pt/ZCA-5 shows a slightly reduced catalytic activity. Meanwhile, despite the higher dispersion of Pt species in the case of Pt/ ZCA-15, the catalytic activity of Pt/ZCA-15 is lower than that of Pt/ ZCA-10 catalyst with the larger density of surface basic sites. As for Pt/ ZCA-10 with the highest density of surface basic sites, the highest activity can be attained, despite the lowest dispersion of Pt species. The above results demonstrate that the catalytic activity of Pt/ZCA-x catalysts should be closely correlated with both the dispersion of active Pt species and surface basicity. Interestingly, Pt/ZCA-x catalysts with different Ca contents show very similar product selectivities, which probably originates from the similar spinel structure of ZCA-x supports, thereby leading to similar adsorption/activation behaviors for glycerol and intermediate molecules on the surface of catalysts during the oxidation process.

For comparison, several single oxides supported Pt catalysts with the similar Pt loading amount to that of Pt/ZCA-10 (*i.e.* Pt/ZnO, Pt/ Al₂O₃, Pt/CaO, Pt/ZrO₂, and Pt/CeO₂) were prepared for the application in the oxidation of glycerol. It is seen that these comparison



Fig. 6. IR spectra of CO₂ absorption on Pt/ZCA-0 (a) and Pt/ZCA-10(b).

Table 3 Catalytic reaction results over different Pt-based catalysts for the oxidation of glycerol.^a.

Entry	Samples	Conv.	Selectivity ^b (%)					
		(%)	GLYA	TARA	DHA	GLYCOA	OXA	Others ^c
1	Pt/ZCA-0	50.8	81.0	3.1	11.7	2.0	1.8	0.4
2	Pt/ZCA-5	48.7	82.2	0.7	11.4	2.0	2.0	1.7
3	Pt/ZCA-10	61.8	81.1	1.9	10.6	3.9	2.6	0
4	Pt/ZCA-15	55.7	81.4	2.0	10.7	3.3	2.6	0
5	Pt/ZnO ^d	31.8	45.9	1.2	44.7	3.2	1.1	3.9
6	Pt/Al ₂ O ₃ ^d	18.8	72.1	0	21.6	2.6	3.7	0
7	Pt/CaO ^d	16.9	69.3	0	0	6.2	5.8	18.7
8	Pt/ZnO-CaO-	16.6	60.3	0	28.7	1.2	1.5	8.3
	Al ₂ O ₃ ^e							
9	Pt/CeO ₂	26.9	78.8	0.3	12.7	1.0	4.0	3.2
10	Pt/ZrO ₂	28.1	80.7	1.3	11.0	1.4	2.5	3.1

 $^{\rm a}$ Reaction conditions: glycerol/Pt = 590/1; 60 °C; oxygen pressure of 0.5 MPa; 5 h.

 $^{\rm b}$ Selectivity was determined as: mol of product formed \times the number of carbon atoms for product / (mol of glycerol converted \times 3).

^c Other deep oxidation C1 products mainly including formaldehyde, formic acid and CO₂.

^d 1.0 wt % Pt loading amount.

 $^{\rm e}$ Pt NPs supported over a physical mixture of three kinds of single metal oxides.

catalysts afford much low glycerol conversions (< 32%), along with changing selectivities to GLYA in the range of 45.9–80.7%. Meanwhile, supported Pt one over the physical mixture of CaO, ZnO, and Al_2O_3 delivers a much lower glycerol conversion of 16.6%, indicative of a poorer activity. The above results further confirm the significant promotion of ZnAl₂O₄ spinel supports on the glycerol oxidation.

Fig. 7 shows the change in the conversion and product selectivities with the reaction time over the Pt/ZCA-10. Notably, the GLYA selectivity is slightly decreased by about 0.9% with the prolonged reaction time from 0.5 to 6 h, together with a gradually increased conversion from about 25.8% after a short reaction of 0.5 h up to 63.1% after 6 h. Selectivity to DHA shows a quite slight decrease from 11.9 to 10.6% as the reaction time is prolonged from 0.5 to 6 h. Meanwhile, more C2 products (GLYCOA, OXA) are produced with the elongated reaction time, despite relative smaller amounts of C2 products, due to further scission of CC– bond in GLYA and DHA. Furthermore, the effects of reaction temperature and oxygen pressure on the oxidation of glycerol over the Pt/ZCA-10 were evaluated (Fig. 8). Note that with the reaction temperature from 40 to 100 °C, the rate of glycerol conversion is enhanced progressively due to the endothermic character of



Fig. 7. Change in the conversion and product selectivities with the reaction time over the Pt/ZCA-10 in the glycerol oxidation. Reaction conditions: $60 \degree$ C; 0.5 MPa oxygen partial pressure.

oxidation reaction, together with a remarkable decrease in the GLYA selectivity at higher reaction temperatures of 80 and 100 °C because of the deep oxidation of GLYA and the formation of more other by-products (GLYCOA, OXA, and C1 products). Meanwhile, noticeably, raising oxygen pressure from 0.1 to 1.0 MPa promotes the conversion of glycerol. Like the reaction temperature, the increase in oxygen pressure leads to a slight decrease in GLYA selectivity. while that of total C2 and C1 products increases with the raised reaction pressure. According to above product distributions in the glycerol oxidation, it can be concluded that in the Pt/ZCA catalyst system, glycerol can easily be oxidized to produce GLYA, accompanied by a possible simultaneous conversion of glycerol to DHA, and DHA and GLYA are separately formed probably through two different pathways [45]. In our case, however, glyceraldehyde cannot be detected, probably due to the fast oxidation of glyceraldehyde as a reaction intermediate to generate GLYA (Scheme 1). The slightly decreased selectivities to GLYA and DHA with the prolonged reaction time and the elevated oxygen pressure demonstrate that the transformation modes of glyceraldehyde intermediate into two main GLYA and DHA products probably keep unchanged in the course of oxidation reaction, and the further conversion of GLYA and DHA into other products does not easily take place at the low reaction temperatures (< 80 °C).

On the other side, to under the instinct catalytic activity of Pt-based catalysts, the turnover frequency values (TOFs) of glycerol converted also were calculated according to the conversion rate of glycerol per surface metallic Pt sites per hour at the initial reaction stage of 15 min



Fig. 8. Change in the conversion and product selectivities over the Pt/ZCA-10 in the glycerol oxidation with the reaction temperature (A) and the oxygen partial pressure (B). Reaction conditions: (A) 0.5 MPa (O₂) and 5 h; (B) 60 °C and 5 h.

(< 30% conversion of glycerol). It is interestingly noted from Fig. 9 that Pt/ZCA-10 presents the largest TOF value of about 1160 h⁻¹ among supported Pt catalysts. In terms of TOF values, the instinct activity of Pt/ZCA-10 is better than or comparable to those of the most monometallic Pt catalysts previously reported using molecular oxygen for base-free glycerol oxidation (Table S1) [23,46-52], further mirroring its superior catalytic activity of Pt/ZCA-10 in base-free glycerol oxidation. Previously, many researchers have proven that additional homogeneous base (e.g.NaOH) can facilitate the O-H bond activation viaproton transfer, thus accelerating the oxidation of glycerol [21,26,53,54]. Under base-free reaction conditions, it is difficult for OH- to participate in the oxidation due to its quite low concentration. In the present catalyst system, the catalytic activity of Pt/ZCA catalysts are superior to those of other single metal oxides supported Pt ones. Especially, the as-fabricated Pt/ZCA-10 catalyst with the highest TOF value of 1160 h⁻¹ shows the best catalytic performance. The structural characterizations demonstrate that the Pt/ZCA-10 possesses the higher surface density of total basic and medium-strength basic sites originating from surface uniformly dispersed M-OM- structure (M = Ca, Zn or Al) in the spinel, probably promoting electron transfer from basic sites (lattice oxygen species) to Pt NPs and thus the lower binding energy of Pt 4d_{5/2} region and the formation of SMSIs, as evidenced by the above XPS results.

In order to reveal the adsorption mode of the hydroxyl group on supported Pt-based catalysts, *in situ*FT-IR spectra of glycerol adsorbed over Pt/ZCA-0 and Pt/ZCA-10 catalysts were analyzed. The results are shown in Fig. 10. Typically, glycerol can interact with a coordinatively unsaturated metal site on the surface of metal oxide to form a polydentate alkoxy species. Noticeably, when glycerol is adsorbed on the surface of Pt/ZCA-0, two intensive peaks at 1088 and 1049 cm⁻¹ can be attributed to the C–O vibrations of primary alcohol groups of glycerol adsorbed on the surface, due to Lewis acid/base interactions between alcohol groups of glycerol and metal atom on the spinel surface, in



Fig. 9. Change in the initial TOF values over different supported Pt catalysts.

addition to two weak should peaks (1109 and 1014 cm⁻¹) related to physically adsorbed and bulk glycerol molecule [55], respectively. In the case of Pt/ZCA-10, the absorption bands of the C–O vibration related to alcohol groups appears at about 1156 and 1076 cm⁻¹, respectively, which are assignable to hydrogen-bonding and Lewis acid/ base interaction between secondary or primary hydroxyl groups of glycerol and surface metal atoms, indicating stronger surface adsorption of glycerol. Meanwhile, several characteristic absorption peaks corresponding to the splitting of the C–H vibrations for Pt/ZCA-0 (2926 and 2858 cm⁻¹) also shift to higher frequencies for Pt/ZCA-10 (2976 and 2889 cm⁻¹), due to the difference in their electronic effects induced by stronger surface adsorption of glycerol [56]. The above results suggest that surface strong basicity can greatly promote the adsorption and activation of hydroxyl groups in glycerol during glycerol oxidation. According to the above comprehensive characterizations and



Scheme 1. Pathways of oxidation of glycerol over Pt/ZCA catalysts.



Fig. 10. In situFT-IR spectra of glycerol adsorption over Pt/ZCA-0 (a) and Pt/ZCA-10 (b).

catalytic reaction results, obviously, a surface synergy between highly dispersive Pt species and basic sites should contribute to the improved catalytic performance of Pt/ZCA-10 catalyst. Here, we tentatively propose a mechanism for glycerol oxidation to produce GLYA on as-fabricated Pt/ZCA catalysts (Scheme 2). Previously, it was reported that the deprotonation of hydroxyl group with the help of base was one of the rate-determining steps for the glycerol oxidation [14,20]. Furthermore, noble metals were responsible for the deprotonation of β-hydrogen in the oxidation of alcohols, which was another rate determining step [57]. In our case, glyceraldehyde intermediate can first form from glycerol oxidation [44,58,59]. Thereupon, two primary and secondary hydroxyls in glycerol may be simultaneously adsorbed and activated on basic sites (e.g. MO- pairs), adjacent to metallic Pt sites. Subsequently, the β -hydrogen in the primary hydroxyl group adsorbed on the surface can be abstracted by surface active O^{2-} sites to form an alkoxy compound intermediate. Secondly, the formed intermediate interacts with adjacent Pt species to generate a metal-hydride through the H-metal bond, while molecular oxygen can be activated on Pt atoms. Here, the electron transfer from electron-rich Pt atoms to adsorbed oxygen cannot only promote the activation of molecular oxygen but also facilitate the formation of metal-hydride because of the nature of β hydrogen with partial negative charge in the alkoxy intermediate [60]. Then, further eliminating β-hydrogen in metal-hydride may produce glyceraldehyde intermediate, while the eliminated hydrogen can be captured by surface oxygen species. Finally, active oxygen species can oxidize surface hydrogen adsorbed on basic sites to release water [43]. In our present Pt/ZCA-x catalyst system, surface basic sites are responsible for the first rate-determining step (the abstraction of α -hydrogen in terminal hydroxyl group of glycerol), while metallic Pt species can assist in the second rate-determining step (the \beta-hydrogen abstraction). Further, glyceraldehyde formed can be rapidly oxidized to

GLYA product *via*the following processes. Firstly, the water molecule interacts rapidly with glyceraldehyde adsorbed on surface basic sites, thus forming a surface intermediate [61]. Secondly, Pt species interact with adsorbed intermediate to form a metal hydride *viaa* metal-hydrogen bond. Thirdly, two protons are abstracted from metal hydride and further adsorbed on basic sites to generate GLYA product. At last, adsorbed hydrogen was oxidized by active oxygen species on Pt sites to release water.

Obviously, in the present catalyst system, undoped and Ca-doped ZnAl₂O₄ supports can provide high surface areas and porous microstructure for dispersing and stabilizing active Pt species, while surface basic sites mainly originating from M–O pairs (M = Ca, Zn or Al) in the ZnAl₂O₄ spinel structure can facilitate the adsorption and activation of alcohol hydroxyl groups in glycerol and greatly promote the abstraction of protons in glycerol or glyceraldehyde intermediate from O–H and/or CH– groups under base-free reaction conditions, like NaOH. In the case of Pt/ZCA-10 catalyst, a larger surface density of basic sites may facilitate the activation of glycerol and further following elimination of β hydrogen in alkoxide. In addition, surface electron-rich Pt⁰ species can promote the activation of molecular oxygen and C–H bond in reaction intermediates. Thereupon, a surface synergy between highly dispersed electron-rich Pt species and medium-strength basic sites mainly contributes to its higher catalytic performance of the Pt/ZCA-10 catalyst.

At last, for as-fabricated Pt/ZCA-10 catalyst, the reusability and stability were further examined. Note that the conversion and selectivity to GLYA still keep stable after six consecutive runs (Fig. S1), indicative of excellent structural stability of the Pt/ZCA-10 under actual reaction conditions. The ICP-AES analysis of filtrates shows neglectable leaching of Pt after six cycles, while the TEM observation of used catalyst reveals no obvious aggregation and growth of Pt NPs (Fig. S2). Such exceptional stability of the catalyst should be assigned to the strong metal-basic sites interactions, as well as well-developed porous framework, thereby tightly anchoring NPs on the support surface and thus preventing the growth or aggregation of Pt particles during the reaction process.

4. Conclusions

In summary, a series of supported Pt nanocatalysts over high-surface-area and porous undoped and Ca-doped zinc aluminate spinels were employed for base-free glycerol oxidation. The results showed that Pt NPs could be evenly distributed and tightly immobilized on the support surface, thus forming the strong interactions between Pt species and the support. Comprehensive characterizations including XPS analysis, CO₂-TPD, and FT-IR spectra of CO₂ adsorption experiments revealed that introduction of an appropriate amount of Ca into the ZnAl₂O₄ resulted in the enhanced surface density of medium-strength basic sites and the strengthened metal-support interactions. As-fabricated Pt catalyst having a Ca/(Zn + Ca) molar ratio of 1:10 exhibited a superior catalytic activity to other supported Pt ones, with a high TOF value of 1160 h⁻¹. Compared with pristine ZnAl₂O₄ supported Pt one,



Scheme 2. The proposed mechanism of base-free oxidation of glycerol to glyceric acid over Pt/ZCA catalysts.

the instinct activity of Pt/ZCA-10 catalyst is nearly one time higher with the introduction of ca. It was believed that a surface synergy between highly dispersed electron-rich metallic Pt species and medium-strength basic sites greatly promoted the hydroxyl group activation in glycerol, as well as the activation of molecular oxygen, thus leading to its enhanced catalytic efficiency. Moreover, for the present supported Pt catalysts, the several advantages of high surface area, acid-resistance of the spinel supports, abundant surface basic sites, and SMSIs guaranteed the effective stabilization and dispersion of Pt NPs and thus prevented the aggregation of metal particles during actual reactions. The present findings provide a new way to construct supported metal-base catalysts applied in practical catalytic processes through the immobilization of other noble metal or non-noble metal NPs on the as-formed high-surface-area spinel-type Ca-doped zinc aluminate spinel supports with appropriate surface basicity.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110559.

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