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Article

Green catalytic oxidation of benzyl alcohol over Pt/ZnO in base-free aqueous medium at room temperature

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ABSTRACT

The selective oxidation of alcohol using molecular oxygen as an oxidant and water as a green solvent is of great interest in green chemistry. In this work, we present a systematic study of a Pt/ZnO catalyst for the selective oxidation of benzyl alcohol at room temperature under base-free aqueous conditions. Experimental observations and density functional theory calculations suggest that ZnO as a support can facilitate the adsorption of benzyl alcohol, which subsequently reacts with the activated oxygen species on the Pt catalyst, producing benzaldehyde. The resulting solid achieves a high conversion ($94.1 \pm 5.1\%$ in 10 h) of benzyl alcohol and nearly 100% selectivity to benzaldehyde with ambient air as the oxidant. In addition, by introducing a small amount of Bi (1.78 wt%) into Pt/ZnO, we can further enhance the activity by 350%.

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1. Introduction

The catalytic oxidation of alcohol into aldehydes/ketones is of great importance at both the laboratorial and industrial levels, and is one of the most challenging reactions to conduct in green chemistry [1–6]. To achieve environmental and economic acceptability, significant effort has been devoted to the development of advanced catalysts that can use molecular oxygen as an environmentally friendly oxidant [7]. Traditionally, most studies are conducted in organic solvents or under solvent-free conditions, and the resulting mixtures of the organic substrates, products, solvents, and molecular oxygen can be quite danger-

ous [8]. Anhydrous conditions, in contrast, are impractical because water is formed during the reaction [9]. Considering that water is a safe, cheap, and environmental friendly solvent, it is highly desirable to develop efficient catalysts under aqueous conditions. Owing to their ability to activate molecular oxygen and the C–H bonds of alcohol, Pt nanoparticles are generally acknowledged as effective catalysts for alcohol oxidation reactions [10–12]. In addition, the high performance of such nanoparticles in water, the most promising green solvent, is also appealing [13,14]. However, the reaction must be carried out at relatively high temperatures ($> 80\text{ }^{\circ}\text{C}$) [15,16] and oxygen pressures ($> 0.1\text{ MPa}$) [17] with the addition of bases (NaOH,

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K₂CO₃, etc.) [18], inevitably leading to severe problems such as undesirable side reactions, catalyst corrosion, and the requirement of an extra waste base treatment. From the viewpoint of green chemistry, it is of great interest to functionalize Pt catalysts for the selective oxidation of alcohol in the presence of atmospheric oxygen and the absence of a base at ambient pressure and room temperature.

Previous studies have mainly focused on the exploration of efficient structural or electronic modifiers for Pt nanoparticles [19–22]. Metal promoters, particularly Bi and Pb, have been demonstrated to drastically enhance the activity of Pt catalysts for alcohol oxidation by preventing an over-oxidation and poisoning of the Pt [23,24]. In contrast, relatively few studies have been devoted to the rational design of Pt catalysts based on a fundamental understanding of the elementary steps. Taking into account the fact that the adsorption and activation of molecular oxygen and alcohol are key steps in alcohol oxidation, it appears to us that the catalytic performance is able to be enhanced by introducing active components that facilitate the above important steps. Our previous study demonstrated that a partially reduced Bi₂O_{3-x} support can improve the activation of oxygen, which consequently enhances the catalytic performance of Pt nanoparticles for the selective oxidation of benzyl alcohol in a base-free aqueous medium with atmospheric oxygen as an oxidant [25]. To further prove this concept, effort should also be devoted to the fabrication and understanding of novel catalytic systems that can improve the activities of Pt nanoparticles by accelerating the alcohol adsorption and C–H activation.

Herein, we report a newly developed Pt/ZnO catalyst that enables efficient benzyl alcohol oxidation at room temperature under base-free aqueous conditions. Systematic experiments and density functional theory (DFT) calculations suggest that there is a synergistic effect between Pt and ZnO. Specifically, ZnO as a support can facilitate the adsorption of benzyl alcohol, which subsequently reacts with the activated oxygen species in a Pt catalyst to produce benzaldehyde. In addition, such activity showed an improvement of 350% with a small addition of Bi to the Pt/ZnO catalyst without any decrease in the selectivity.

2. Experimental

2.1. Materials

The materials used are as follows: deionized (DI) water, hexachloroplatinic acid (Sigma-Aldrich), sodium borohydride (Sigma-Aldrich), zinc oxide (Sinopharm Chemicals and Sigma-Aldrich), bismuth nitrate pentahydrate (Sinopharm Chemicals), and benzyl alcohol (Sinopharm Chemicals). All chemicals were used as received.

2.2. Preparation

Briefly, 1 g of ZnO powder was dispersed into 10 mL of DI water, followed by the addition of 2.66 mL of H₂PtCl₆·6H₂O (19.2 mmol L⁻¹) into the above mixture under vigorous stirring at room temperature. Next, 2 mL of cold DI water containing 8

mg of NaBH₄ was then slowly dropped into the above mixture. The color of the solution changed from light yellow to grey very quickly, indicating the successful formation of Pt nanoparticles. The mixture was further stirred for 2 h before being centrifuged, and then washed three times using ethanol and DI water. The solid obtained was dried at 65 °C overnight in a vacuum oven, and labeled as a Pt/ZnO catalyst. The actual content of the Pt was determined to be 0.80 wt% using ICP-MS.

One gram of ZnO powder, 2.66 mL of H₂PtCl₆·6H₂O (19.2 mmol L⁻¹), and 48.5 mg of Bi(NO₃)₃·5H₂O were mixed in 10 mL of DI water under vigorous stirring at room temperature. Then, 2 mL of cold DI water containing 8 mg of NaBH₄ was dropped into the above mixture. After stirring for 2 h, it was centrifuged, washed using ethanol and DI water three times, and then dried at 65 °C overnight in a vacuum oven. The as-synthesized solid was labeled as a Pt/Bi-ZnO catalyst. The actual contents of the Pt and the Bi were determined to be 0.80 wt% and 1.78 wt% using ICP-MS, respectively.

2.3. Characterizations

Wide-angle X-ray diffraction (WAXRD) patterns were recorded on a Rigaku Ultimate IV using Cu K_α radiation. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-1230 operated at 80 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a TECNAI G2 F20 operated at 200 kV. High-resolution X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultra-high vacuum (UHV) chambers. Nitrogen sorption data were obtained on a Micromeritics ASAP 2020 adsorption analyzer.

2.4. Catalytic reaction

In brief, 0.1 g of a catalyst, 0.2 mmol of benzyl alcohol, and 10.0 mL of H₂O were vigorously stirred together in a flask in the open air at room temperature (26 °C) in the dark. After several hours, 0.2 mL of the reactant was taken out with a plastic pipette, diluted with ethanol, and then analyzed using gas chromatography. Octane was utilized as the internal standard to quantify the reaction products. Because no byproducts such as benzoic acid or CO₂ were detected, the carbon balance = (moles of unconverted BA + moles of benzaldehyde)/moles of the total BA. The carbon balance was > 99%. For the Arrhenius plots, the catalytic reactions were conducted under identical reaction conditions except for the reaction temperature (35, 45, 55, and 65 °C). In O₂ partial pressure experiments, N₂ was employed as the balance gas. The partial pressure of O₂ was tuned by charging different amounts of N₂ and O₂ into the reaction flask using a mass flow controller. The total pressure for N₂ and O₂ was held at 1 bar.

The recycling tests were carried out as follows. After a catalytic reaction, the solid was separated from the mixture through centrifugation, followed by washing with DI water three times. The solid obtained was dried in an oven at 65 °C

overnight before being used for the next cycle.

2.5. DFT calculations

DFT calculations were carried out using a plane-wave based program, Castep [26,27]. The Perdew-Burke-Ernzerhof (PBE) function [28] was used along with the ultrasoft-core potentials [29]. The cutoff energies were set to 300 eV for a geometry optimization, and 340 eV for an energy re-evaluation. The electron configurations of the atoms were H $1s^1$, C $2s^2 2p^2$, O $2s^2 2p^4$, Zn $3d^{10} 4s^2$, and Pt $5d^9 6s^1$. A $(\text{ZnO})_{48}\text{Pt}_{10}$ unit cell was employed as a model to interpret the Pt/ZnO interface, where the fcc (111) oriented Pt_{10} cluster is supported by a wurtzite $(2\bar{1}\bar{1}0)$ oriented three-layer ZnO slab. The lattice constants of the unit cell are $b = 12.9971 \text{ \AA}$, $c = 10.4109 \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$. The direction of the a -axis includes the vacuum region, and is set to $a = 40 \text{ \AA}$. The lower two layers of the ZnO slabs were fixed to the crystalline structure, and the top layer, Pt_{10} cluster, and ad-species were optimized.

3. Results and discussion

The microstructures of the Pt/ZnO catalysts were revealed using TEM and HADDF-STEM images. Clearly, the morphology and particle size of the ZnO (Fig. 1(b)) are almost the same as those of pure ZnO (Fig. 1(a)), suggesting that the microstructure of ZnO does not change during the loading of Pt. As shown in Fig. 1(c), the Pt particles are well dispersed in the ZnO framework with a narrow size distribution of $3.2 \pm 0.3 \text{ nm}$. The lattice distance of the individual Pt particle in Fig. 1(d) is ca. 0.23 nm, corresponding well with the lattice fringe spacing of the (111) plane in fcc Pt (0.228 nm, JCPDS 65-2868) [30]. WAXRD patterns (Fig. 2(a)), however, show no obvious diffraction peaks of Pt for either fresh or spent Pt/ZnO catalysts, presumably owing to the low loading amount, small crystalline size, and good dispersion of Pt on the ZnO support [31]. In all cases, the well-resolved diffraction peaks can be readily assigned to the ZnO crystalline phase (PDF 36-1451) [32].

XPS measurements were conducted to investigate the chemical states of the Pt and Zn elements. As depicted in Fig. 2(b), both fresh and spent Pt/ZnO catalysts share the same Zn $2p$ peaks with pure ZnO, where Zn $2p_{3/2}$ and Zn $2p_{5/2}$ are located at 1021.8 and 1044.9 eV, respectively, indicating that the

Fig. 1. (a) TEM image of commercial ZnO; HADDF-STEM (b), TEM (c) images of Pt/ZnO (size distribution of Pt particles shown in the inset); (d) HRTEM image of supported individual Pt particles on Pt/ZnO.

presence of Pt and the catalytic process do not influence the surface electron state of Zn^{2+} [33]. In contrast, two Gaussian doublets of the Pt peaks in the fresh/spent Pt/ZnO samples are clearly observed in Fig. 2(c), which can be ascribed to the Pt^0 (70.2/73.4 eV) [34] and Pt^{2+} (71.6/75.2 eV) species [35], respectively. The latter is likely due to the surface layer formation of Pt-O_{ad} bonds during the transfer of samples in air to the XPS chamber, as has been extensively studied in Ref. [36–38]. Notably, the $\text{Pt}^0/\text{Pt}^{2+}$ ratios calculated by the peak areas are around 80.8/19.2 for both fresh and spent Pt/ZnO catalysts (fresh, 80.8/19.2; spent, 80.9/19.1), demonstrating the Pt^0 species as the dominant form in the Pt/ZnO samples. In general, the Pt^0 species are accepted as the active sites for oxidative dehydrogenation reactions [11]. It is therefore expected that Pt/ZnO will exhibit an excellent catalytic performance in the selective oxidation of alcohol, as extensively discussed below.

The selective oxidation of benzyl alcohol (BA) into benzaldehyde (BAD) over Pt-based catalysts was carried out in an aqueous medium without any base additives at room temper-

Fig. 2. (a) WAXRD patterns of ZnO, and fresh and spent Pt/ZnO samples; Zn $2p$ (b) and Pt $4f$ (c) XPS spectra in fresh and spent Pt/ZnO samples.

Fig. 3. Time course of alcohol oxidation on Pt/ZnO under aqueous conditions at room temperature. Reaction conditions: 0.1 g catalyst and 0.2 mmol benzyl alcohol in 10 mL H₂O at 26 °C.

ature. Ambient air is used as a green oxidant. Fig. 3 shows the time course of BA oxidation using a Pt/ZnO catalyst at room temperature. Control experiments demonstrate that neither the blank reaction without a catalyst nor the pure ZnO can produce a detectable conversion. Meanwhile, the conversion of benzyl alcohol using a Pt/ZnO catalyst can be as high as $94.1 \pm 5.1\%$ within 10 h, indicating that the presence of both Pt and ZnO is critical for alcohol oxidation. No benzoic acid or other side products were detected, implying that the selectivity required to produce BAD is nearly 100%. Meanwhile, we also prepared 0.81 wt% Pt/Al₂O₃, 0.81 wt% Pt/TiO₂, and 0.83 wt% Pt/MgO using the same method as for 0.80 wt% Pt/ZnO. TEM images suggest they achieve similar sizes for the PtNPs. The physicochemical properties and catalytic activities are summarized in Table 1. Interestingly, the TOF (h⁻¹) for BA oxidation within 10 h is 6.2 (Al₂O₃), 1.4 (MgO), 9.5 (TiO₂), 13.0 (ZnO), and 0 (SiO₂), respectively, clearly indicating that the activity depends on the oxide support. Among the various catalysts, Pt/ZnO shows the optimal activity. The TOF of Pt/ZnO is 3.5 times the reported 1.08 wt% Pt/Ca(Mg)-ZSM catalysts under similar experimental conditions (13.0 h^{-1} versus 3.69 h^{-1} per surface Pt atom) [39], which is likely due to the synergistic effect between the Pt and ZnO support.

Monitoring the reaction profiles and analyzing the reaction kinetics are very useful for illuminating the mechanistic details. Fig. 4(a) shows Arrhenius plots of Pt/ZnO. The apparent activation energy of BA oxidation over Pt/ZnO is as low as 23.7 kJ

mol⁻¹, similar to the value reported in Ref. [39]. The similar apparent activation energy and different TOF values suggest different pre-exponential factors for Pt/ZnO and Pt/Ca-ZSM-5. The higher TOF value for Pt/ZnO is likely due to the facilitated adsorption of reactants induced by the synergistic effect between the Pt and ZnO. Additionally, we also carried out kinetic studies to study the effect of the partial pressure of O₂ on the conversion of benzyl alcohol. As shown in Fig. 4(b), with the partial pressure of O₂ increasing from 0 to 0.10, the conversion of BA increases from 0 to 45.7%, indicating that the reaction is limited by the adsorption and activation of oxygen. Further increasing the O₂ partial pressure from 0.10 to 0.21, the conversion of BA remains steady (ca. 46%). The independence of the oxygen pressure on the reaction rate of Pt/ZnO implies that the O₂ adsorption and activation are no longer rate-controlled within this O₂ partial pressure range (0.10–0.21) [40]. Notably, our catalytic tests were conducted in ambient air, in which the O₂ ratio is ca. 0.21, corresponding to the point marked in light green in Fig. 4(b), suggesting that the activity of Pt/ZnO is most likely restricted by the alcohol adsorption and activation in the open air rather than the O₂ adsorption and activation [41].

To test the proposed hypothesis, we explored the kinetic isotope effect (KIE) through the use of benzyl-d₇ alcohol (C₆D₅CD₂OH) and benzyl alcohol-OD (C₆H₅CH₂OD) as substrates in the selective oxidation. As shown in Fig. 4(c), by replacing C₆H₅CH₂OH with C₆H₅CH₂OD, the conversion remains almost unchanged (28.9 h^{-1} per surface Pt atom versus 27.5 h^{-1} per surface Pt atom). In contrast, the reaction was slowed down by a factor of 6.28 (28.9 h^{-1} per surface Pt atom versus 4.6 h^{-1} per surface Pt atom) once the C₆H₅CH₂OH was replaced with C₆D₅CD₂OH, clearly demonstrating that the cleavage of C–H is a rate-determining step. Moreover, we also tested the catalytic oxidation of substituted benzyl alcohol on Pt/ZnO to further confirm the result. In principle, benzyl alcohol substituted using electron-donating groups has a weak C–H bond, which might consequently lead to a high reaction rate. As shown in Fig. 4(d), 100% conversion of 4-methylbenzyl alcohol and 4-methoxybenzyl alcohol can be achieved within only 5 h, consistent with our hypothesis. On the other hand, when benzyl alcohol molecules were substituted using –NO₂ (the electron-withdrawing groups), the conversion of 4-nitrobenzyl alcohol after 5 h is only 3.3%, which is much lower than that of BA. No correlations were found between the reactivity and octanol-water partition coefficients [42] of aromatic alcohol (4-methylbenzyl alcohol > 4-nitrobenzyl alcohol > 4-methoxybenzyl alcohol ≈ benzyl alcohol), indicating that the electronic

Table 1
Physicochemical properties and catalytic activities of various supported Pt catalysts.

Catalyst	Pt loading (wt%)	d_{Pt}^a (nm)	Pt dispersion ^b	Surface area (m ² g ⁻¹)	Conv. (%)	TOF ^c (h ⁻¹)
Pt/ZnO	0.80	3.2 ± 0.3	0.35	5.0	94.1	13.0
Pt/Al ₂ O ₃	0.81	3.4 ± 0.4	0.33	149.9	43.0	6.2
Pt/MgO	0.83	2.5 ± 0.3	0.45	26.4	13.3	1.4
Pt/SiO ₂	0.83	2.9 ± 0.3	0.39	423.0	0	0
Pt/TiO ₂	0.81	3.5 ± 0.5	0.32	51.3	63.4	9.5

^a The average particle size of Pt determined using TEM.

^b dispersion = $1.13/d_{\text{Pt}}$ [11].

^c Defined as the amount of benzyl alcohol reacted per hour per surface Pt site.

Fig. 4. (a) Arrhenius plots for alcohol oxidation in the open air on Pt/ZnO catalyst; (b) Kinetic study of the O_2 partial pressure on the conversion for a Pt/ZnO catalyst at room temperature within 2 h (the O_2 pressure in ambient air is marked in light green); (c) Kinetic isotope effect observed for Pt/ZnO at room temperature within 3 h; (d) Conversion of substituted benzyl alcohol on the Pt/ZnO catalyst within 5 h. In all cases, the selectivity is > 99%.

properties of the substituent groups play a more significant role than the relative solubility of the reagents in water [43]. Taking all of these results together, it is clear that the C–H activation determines the catalytic oxidation of BA in Pt/ZnO in open air at room temperature.

DFT calculations were conducted to provide molecular level insight into the reaction pathways, as well as to elucidate the nature of the catalytic mechanism. In this case, a $(ZnO)_{48}Pt_{10}$ unit cell was employed as a model to interpret the Pt/ZnO interface. Similar simulations have been extensively reported in the literature as an investigation in the metal-oxide interface [44,45]. To calculate a possible reaction pathway, the entire oxidative dehydrogenation processes $2PhCH_2OH + O_2 \rightarrow 2PhCHO + 2H_2O$ are divided into two parts. Each part involves the production of a PhCHO molecule. The former half of BA-to-BAD is shown in Fig. 5. The individual optimized structures for the local minima (LMs) and the transition states (TSs)

are described using configuration numbers #1 to #10.

The reaction is initiated through the dissociative adsorption of O_2 molecules, with the O species formed being bonded to Pt atoms (#1 to #3). The activation energy of this step is only 20.1 kJ mol⁻¹, indicating the good capability of Pt for O_2 activation. Meanwhile, $PhCH_2OH$ is adsorbed into the ZnO sites, followed by a cleavage of the O–H bond on the dissociated O species (#4 to #6) to form H–O(–Pt). The activation energy of this step is 44.1 kJ mol⁻¹ ($PhCH_2OH + O(-Pt) \rightarrow PhCH_2O + H-O(-Pt)$). Subsequently, the C–H proton is abstracted using the as-produced HO(–Pt) according to the reaction $PhCH_2O + H-O(-Pt) \rightarrow PhCHO + H_2O(-Pt)$ (#7 to #9), accompanied by the formation of a PhCHO molecule and a $H_2O(-Pt)$ molecule. The former half of the reaction is then completed through the desorption of the PhCHO and H_2O molecules (#10), leaving a single O atom on the Pt cluster of the catalyst surface. This O atom can reproduce the former half reaction with another $PhCH_2OH$ molecule ac-

Fig. 5. Energy changes and configurations for LM and TS along the former half of the BA-to-BAD reaction. Pt (dark blue), O (red), Zn (bluish gray), H (white), and C (grey).

Fig. 6. DFT calculations based on the flat Pt(111)/ZnO(2110) surface. (a) Energy profile; (b) Configurations for LMs and transition state TS.

cording to the whole oxidative dehydrogenation processes $\text{PhCH}_2\text{OH} + \text{O} \rightarrow \text{PhCHO} + \text{H}_2\text{O}$. In addition, $(\text{ZnO})_{48}\text{Pt}_{10}$ cells are regenerated for the next catalytic cycle after the desorption of the second produced benzaldehyde and H_2O molecules. Notably, the C–H proton abstraction through the dissociated O atom ($\text{HO}(-\text{Pt})$) possesses the highest activation energy ($186.5 \text{ kJ mol}^{-1}$), serving as the rate-determining step. Together with kinetic studies, particularly the KIE study in Fig. 4(c), the calculations have led to the belief that the C–H activation of the PhCH_2OH dominates the reaction rate.

In addition, we also conducted DFT calculations on a Pt(111)/ZnO(2110) flat surface (Fig. 6). In this case, ZnO is not directly involved in the catalytic cycle. The O–H bond of benzyl alcohol is cleaved through the pre-adsorbed O_2 , followed by the cleavage of the C–H bond to produce benzaldehyde. Interestingly, the corresponding activation energy E_a for a C–H cleavage ($E_a = 254.3 \text{ kJ mol}^{-1}$) is much higher than that of the $(\text{ZnO})_{48}\text{Pt}_{10}$ model ($E_a = 186.5 \text{ kJ mol}^{-1}$), confirming the importance of the Pt/ZnO interface. The excellent catalytic performance of Pt/ZnO for BA-to-BAD oxidation might result from the synergistic effects of Pt and ZnO. Specifically, a ZnO support acts as a site for PhCH_2OH adsorption, and Pt facilitates the adsorption and activation of O_2 , which consequently reacts with the adsorbed PhCH_2OH .

Fig. 7. Recycling tests for alcohol oxidation in the open air on the Pt/ZnO catalyst. Reaction conditions: 0.1 g catalyst, 0.2 mmol benzyl alcohol in 10 mL H_2O , 26 °C, 10 h.

Stability is one of the major concerns for a catalyst in practical applications. In this case, recycling experiments were carried out to assess the stability of a Pt/ZnO catalyst for BA-to-BAD oxidation under base-free aqueous conditions at room temperature. As shown in Fig. 7, there is only a slight change in the conversion, and the catalytic selectivity remains steady during the repetition of four continuous cycles. The conversion can reach up to about 95% within 10 h during the fourth successive run, affording the selectivity to BAD of higher than 99%. This suggests that a Pt/ZnO catalyst has greater stability than our reported efficient $\text{Pt}/\text{Bi}_2\text{O}_{3-x}$ catalyst, which can be quickly deactivated after the first run owing to an over-oxidation of $\text{Bi}_2\text{O}_{3-x}$ [25]. The good stability of Pt/ZnO is also confirmed based on the HADDF-STEM and TEM images. As shown in Fig. 8, there are no obvious changes in the morphology or particle size of the spent Pt/ZnO sample in comparison with the fresh version shown in Fig. 1. Apart from this, the Pt particles with a size distribution of $3.5 \pm 0.3 \text{ nm}$ are isolated and homogeneously distributed on the ZnO support without severe agglomeration, suggesting a good stability of the Pt/ZnO catalyst. Thus, it can be concluded that a Pt/ZnO sample can serve as a stable and efficient catalyst for practical alcohol oxidation at room temperature in an aqueous medium without any base additives.

In addition, p-electron metal, such as bismuth, has been acknowledged as an excellent promoter for a Pt catalyst [46,47]. Here, by introducing a small amount of Bi nitrate into a 0.80 wt% Pt/ZnO catalyst (1.78 wt% of Bi on the Pt/Bi-ZnO),

Fig. 8. (a) HADDF-STEM image of spent Pt/ZnO catalyst (HRTEM image of an individual Pt particle inset); (b) TEM image of spent Pt/ZnO catalyst (size distribution of Pt particles shown in the inset).

Fig. 9. (a) Time course of alcohol oxidation on Bi-ZnO and Pt/Bi-ZnO catalysts (XRD data inset); (b) Recycling tests for alcohol oxidation in the open air on Pt/Bi-ZnO catalyst. Experimental conditions: 0.1 g catalyst, 0.2 mmol benzyl alcohol in 10 mL H₂O, 26 °C, 3 h.

the activity is efficiently improved despite almost no change in the XRD pattern of the Pt/ZnO. As shown in Fig. 9(a), the conversion of alcohol using Pt/ZnO can be greatly enhanced from $94.1 \pm 5.1\%$ within 10 h to $98.1 \pm 1.6\%$ within 3 h without a decrease in selectivity. The TOF can be improved from 13.0 to 45.2 h^{-1} per surface Pt atom. To the best of our knowledge, this is the highest TOF ever reported for the selective oxidation of BA in an aqueous medium under identical reaction conditions. In addition, as shown in Fig. 9(b), no significant decrease in the activity or selectivity was detected even after the fourth cycle, indicating that Pt/Bi-ZnO is more stable than Pt/ZnO and Pt/Bi₂O_{3-x} during a catalytic reaction [25]. Its excellent performance and green-chemistry compatible process suggests that Pt/Bi-ZnO has significant potential as a catalyst in the selective oxidation of industrial alcohol. A preliminary investigation indicated that a Bi species is present separately on the support in the form of BiOCl, which is distinguished from previous reports [46]. Systematic studies of the promoting role of Bi on Pt/ZnO are ongoing.

4. Conclusions

We successfully fabricated a stable and efficient Pt/ZnO catalyst for benzyl alcohol oxidation under base-free aqueous conditions at room temperature. A high activity of $94.1 \pm 5.1\%$ with nearly 100% selectivity to benzaldehyde can be obtained with ambient air as an oxidant within 10 h. Kinetic studies indicate that C–H activation is a rate-determining step. DFT calculations further confirm that the high activity and selectivity result from the synergistic effect between the Pt and ZnO support. To be specific, ZnO provides sites for the adsorption of benzyl alcohol, and Pt facilitates the adsorption and activation of O₂, which consequently reacts with adsorbed benzyl alcohol to produce benzaldehyde. Furthermore, introducing a small amount of Bi species into 0.8 wt% Pt/ZnO (1.78 wt% of Bi on Pt/Bi-ZnO) can greatly enhance the conversion by 350% without changing the selectivity. This alcohol oxidation on Pt/ZnO is a green chemistry compatible process, which may further facilitate the design of environmentally friendly catalysts for oxidative reactions.

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Graphical Abstract

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Green catalytic oxidation of benzyl alcohol over Pt/ZnO in base-free aqueous medium at room temperature

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ZnO as a support can facilitate the adsorption of benzyl alcohol, which subsequently reacts with an activated oxygen species on a Pt catalyst to produce benzaldehyde at room temperature under base-free aqueous conditions.

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Pt/ZnO 在室温水相无碱条件下绿色催化苯甲醇选择性氧化

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摘要: 醇类化合物选择性氧化是有机合成中一个非常重要的反应, 在精细化工领域具有重要应用。而水为绿色溶剂, 分子氧为绿色氧化剂实现醇类化合物选择性氧化是绿色化学领域的一大挑战。Pt 催化剂由于其优异的活化氧气和 C–H 键的能力在该反应中得到了广泛应用。但是, 常规的 Pt 催化剂通常需要在较高温度和较高氧气压力以及加碱的条件下才能发挥作用, 从而引起了催化剂腐蚀等一系列问题。从绿色化学角度出发, 进一步优化 Pt 催化剂, 让其能够在室温无碱条件下以空气为氧化剂选择性氧化醇类合成羰基化合物具有重要的研究价值和应用前景。

本文通过化学还原法制备了 Pt/ZnO 催化剂, 系统研究了该催化剂在水相无碱条件下选择性氧化苯甲醇生成苯甲醛反应中的催化性能. X 射线电子衍射和透射电镜等结果表明, Pt 颗粒较小(3.2 ± 0.3 nm), 均匀分散在 ZnO 载体上; X 射线光电子能谱表明 ZnO 载体能够稳定 Pt 纳米颗粒表面的 Pt⁰ 物种. 上述催化剂在水相苯甲醇选择性氧化反应中, 在室温下即可催化空气高选择性氧化苯甲醇到苯甲醛 (选择性>99%), 并表现出比 Pt/SiO₂, Pt/Al₂O₃, Pt/TiO₂, Pt/Ca(Mg)-ZSM-5 等催化剂更为优异的催化活性. 这可归结于 Pt 和 ZnO 之间的协同作用. 该协同作用通过动力学实验和密度泛函理论计算 (DFT) 得到了证实. 氧分压实验表明, 在以空气为氧化剂时, O₂ 的活化并不是限制 Pt/ZnO 催化活性的关键因素, 而动力学同位素效应实验则证实了苯甲醇的 C–H 键活化是整个反应的决速步骤. 通过构建不同的理论模型, 分别计算了 Pt/ZnO 界面处以及纯 Pt 位点上苯甲醇选择性氧化的反应过程. 结果表明, 苯甲醇和氧气分子倾向于分别在 ZnO 和 Pt 上进行吸附, 随后由吸附的氧气分子来活化苯甲醇中的 C–H 键, 进而生成苯甲醛和水. 而当 ZnO 不参与苯甲醇的吸附活化时, 整个反应的活化能会大大提高, 表明 ZnO 和 Pt 之间的协同作用对于整个反应至关重要. 此外, Pt/ZnO 表现出非常优异的稳定性, 循环使用 4 次后, 催化剂结构以及催化活性没有显著变化.

进一步向 Pt/ZnO 催化剂中引入少量 Bi 元素对 Pt 的电子结构进行修饰, 可以将 Pt/ZnO 的催化活性提高 3 倍. 所制备的 Pt/Bi-ZnO 复合物是目前报道的相同条件下催化苯甲醇选择性氧化反应转化频率 (45.1 h^{-1}) 最高的催化剂.

关键词: 铂/氧化锌; 选择性氧化; 苯甲醇; C–H 活化; 水相; 室温

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