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Synthesis of polymeric ionic liquids mircrospheres/Pd nanoparticles/CeO₂ core-shell structure catalyst for catalytic oxidation of benzyl alcohol

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ABSTRACT

New catalysts based on polymeric ionic liquids were synthesized and applied into selective oxidation of benzyl alcohol. Polymeric ionic liquid microspheres (PILM) were prepared by radical polymerization, and then the cations in the imidazole ring were exchanged with the metal anions. After that, the metal anions were reduced to Pd nanoparticles that was supported on the surface of PILM. This metal loading method favored the maximum amount of supported Pd nanoparticles that were uniformly distributed on the surface of PILM. In addition, the introduction of CeO₂ prevented the aggregation of Pd nanoparticles and finally formed PILM/Pd/CeO₂ catalysts with a core-shell structure. The performance of the PILM/Pd/CeO₂ catalysts was evaluated by changing the [K₂CO₃] : [alcohol] molar ratio, reaction temperature and oxygen flow rate in the oxidation reaction of benzyl alcohol. The conversion and selectivity under the optimal reaction conditions reached 48% and 98% respectively The catalysts were effective and reusable after 5 cycles of experiments. In the end, a mechanism underlying the reaction pathway in benzyl alcohol oxidation was put forward.

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1. Introduction

Metal nanoparticles (usually 1–100 nm in diameter or even 500 nm) have unique properties [1]. And thereby are widely used in catalysis, storage, sensing, energy, nonlinear photonics and medical functional materials [2–4]. Metal particles can significantly enhance the catalyst reactivity owing to their excellent atomic precision size and structural control, significant small size effects, quantum size effects and surface effects [5,6]. However, metal nanoparticles can easily agglomerate when applied directly [7]. This problem can be well solved by introducing a suitable carrier and surface modification. Among different carriers, polymer ionic liquid microspheres (PILM) can effectively inhibit the growth and agglomeration of metal nanoparticles and improve the stability of the nanodispersion system [8–10]. Furthermore, the loading of metal nanoparticles on the surface of PILM promotes a large num-

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ber of accessible surface active sites of the metal nanoparticles, and thus also strengthens the catalytic activity.

Polymeric ionic liquids are polyelectrolytes, that comprises an ionic liquid (IL) species in the polymer backbone and monomer repeating units [11–15]. They also are more advantageous in the field of catalysis because of higher mechanical properties, and thermal, chemical and electrochemical stability [16]. Polymeric ionic liquids with different catalytic effects can be obtained by selecting appropriate anions and cations, designing different molecular structures, and using different polymer processing techniques. They are also good carriers for metal nanoparticles and anion exchange reactions [17,18]. Furthermore, metal nanoparticles can be uniformly dispersed in the polymer backbone to prepare a highly efficient heterogeneous catalysts.

Metal and metal-oxide interactions are increasingly important for supported noble metal catalysts. The contact between metal nanoparticles and metal-oxides may induce charge redistribution and mass transfer at the interface [19]. Among different metaloxides, cerium dioxide (CeO₂) is an important rare earth oxide [20] with high oxygen storage capacity and thermal stability, so it attracts growing attention [21–24]. At the same time, due to the presence of Ce⁴⁺ \leftrightarrow Ce³⁺ redox switch in CeO₂. When Ce⁴⁺ is

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Fig. 1. Schematic diagram of the synthesis of PILM/Pd/CeO2 catalyst.

reduced to Ce^{3+} , it releases lattice oxygen. Therefore, CeO_2 has outstanding oxygen spillover capability [25,26]. For instance, the fabrications of Au/xCeO₂-Al₂O₃ and NiCu/CeO₂ catalysts were deposited by Louis et al. [27] and Varma et al. [28], respectively. As is well-known, metal nanoparticles easily aggregate at high temperature because of their high surface energy, thereby rapidly deactivating the catalyst. However, the aggregation of metal nanoparticles can be effectively prevented by their strong interaction with CeO_2 [29–32].

Herein, we reasonably proposed a simple method to synthesize PILM/Pd/CeO₂ core-shell catalysts. The specific structure and synthesis steps were shown in Fig. 1. Firstly, an ionic liquid 1-vinyl-3-butylimidazolium bromide (IL) was synthesized from appropriate amounts of 1-vinylimidazole and 1-bromobutane. Secondly, PILM based on the ionic liquid 1-vinyl-3-butylimidazolium bromide (IL) were prepared. Thirdly, the anion exchange occurred between PILM and metal precursor PdCl₄²⁻ from PdCl₂•2HCl aqueous solution, and subsequently PdCl₄²⁻ was reduced to Pd nanoparticles by NaBH₄ in ethanol solution. Finally, with cerium nitrate hexahydrate as a source of cerium, CeO₂ was encapsulated in the outer layer by homogeneous deposition to form a PILM/Pd/CeO₂ core-shell catalyst. The catalytic performance was evaluated by oxidation of benzyl alcohol to benzaldehyde as a model reaction. At the same time, the catalysts were evaluated by varying the reaction conditions.

2. Experimental

2.1. Materials

1-Vinylimidazole (99%), styrene (AR), Divinylbenzene (80%), azobisisobutyronitrile (AIBN; 99%), Palladium chloride (PdCl₂; AR, 98%) and 1-bromobutane (>98%) were purchased from Shanghai Macklin Biochemical Co. Ltd. Polyvinylpyrrolidone (K30), Benzyl alcohol (\geq 99%), ethanol (C₂H₅OH; \geq 99%) and cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O; \geq 99.0%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hexamethylenetetramine (HTMA; \geq 99%) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Sodium Borohydride (NaBH₄) was purchased from the China National Pharmaceutical Group Corp. Deionized water was used in all experiments. All chemicals were used as received without further purification.

2.2. Synthesis

2.2.1. Synthesis of 1-Vinyl 3-butyl-imidazolium Bromide (IL)

The synthesis method of 1-vinyl-3-butylimidazolium bromide was appropriately modified based on a previous report [33]. In the experiment, 1-bromobutane and 1-vinyl-3-butylimidazolium bromide were placed in a 100 ml three-necked flask at a molar ratio of 1:1 and refluxed in an oil bath of 50 °C for 24 h under a nitrogen atmosphere with stirring. The product was washed three times with ethyl acetate and vacuum-dried at 60 °C for 12 h.

2.2.2. Synthesis of Polymeric Ionic Liquid Microspheres (PILM)

PILM were prepared through a typical precipitation polymerization. 80 mg of 1-vinyl-3-butylimidazolium bromide, 0.75 g of divinylbenzene (DVB), 0.75 g of styrene, 70 mg of AIBN, 0.2 g of PVP and 20 ml of ethanol were added into a 50 ml three-necked flask. Multiple nitrogen purges were performed to remove oxygen so that the entire reactor was performed under a nitrogen atmosphere. The polymerization was conducted at 75 °C and under magnetic stirring for 12 h. After the reaction system was cooled to room temperature, the product obtained was centrifuged, purified by washing with ethanol and water, and vacuum-dried at 60 °C for 12 h.

2.2.3. Synthesis of Pd nanoparticles immobilized onto Polymeric Ionic Liquid Microspheres (PILM/Pd)

Pd nanoparticles was immobilized onto PILM. Firstly, 50 mg of the PILM and 7 ml of PdCl₂•2HCl aqueous solution were dispersed ultrasonically in a 25 ml three-necked flask containing 15 ml of ethanol. After that, the mixture was stirred at room temperature for 3 h to convert Br⁻ to PdCl₄²⁻.Ten times the excess of fresh NaBH₄ solution was added to the mixture under vigorous stirring at room temperature for 6 h. The product obtained was centrifuged,washed with ethanol several times and finally vacuumdried at 40 °C for 12 h.

2.2.4. Synthesis of PILM/Pd/CeO₂

30 mg of PILM/Pd microspheres were ultrasonically dispersed in a 100 ml three-necked flask containing 40 ml of water/ethanol solution with volume ratio of 1:1. Then 0.15 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 0.085 g of Hexamethylenetetramine (HTMA) were added to the mixed solution. The mixture was condensed and refluxed at 60 °C for 6 h, and then cooled to room temperature. Finally, the product

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obtained was centrifuged, washed several times with ethanol and water and vacuum-dried at 60 $^\circ C$ for 12 h.

2.3. Characterization

A Fourier transform infrared spectrometer (FTIR) were obtained with a tensor 27 spectrometer. The sample was placed in KBr at room temperature and subjected to solid tableting. And the wavelength range of the infrared spectrum were recorded at 4000 to 400 cm⁻¹. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance diffractometer (Germany) with Cu K α radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA. On a Hitachi S-3400N microscope, the scanning electron microscopy (SEM) could be used to measure the surface appearance of the sample. The Scanning electron microscopy (SEM) was carried on under a Hitachi S-3400 N microscope. Before measuring the sample with SEM, place the sample on the copper paste and spray the gold powder. The internal shape was observed using transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and selected area electron diffraction (SAED) on a JEM-1230 microscope operated at 100 kV. Samples for TEM measurements were suspended in ethanol and 2-3 drops were dropped onto a Cu grid. Zeta potentials of samples dispersed in ethanol and adjusted to pH 7.0 were detected on a NanoBrook Omni analytical instrument. The X-ray photoelectron spectroscopy (XPS) was implemented on an Axis Ultra DLD spectrometer operated at energy of 150 W using a Al K α (mono) anode.

2.4. Procedure for benzyl alcohol catalytic oxidation

The performance of the catalysts were detected through the oxidation reaction of benzyl alcohol. Oxygen at different flow rates was bubbled into a 25 ml double-necked flask containing benzyl alcohol (2.08 g, 20 mmol) in a different molar ratio of K_2CO_3 to benzyl alcohol molar ratio, 25 mg of catalyst and 20 ml of H_2O . The mixed solution was magnetically stirred for 6 h under different temperature gradients. After 6 h, the mixtures were separated through centrifugation. The reaction rate and yield of the substrate were determined by gas chromatography. The solid mixture separated by centrifugation was washed several times with ethanol and distilled water. Then it was vacuum-dried at 60 °C and used for the next cycle.

3. Results and discussion

3.1. Characterization of spherical PILM/Pd/CeO₂ catalyst

The zeta potential value of the PILM carrier were measured by multiple times. The average value of the potential of ~ 36.37 mv (Fig. 2) indicated the PILM were positive. This reason was that the imidazole ring was a π -electron-deficient non-center symmetrical structure, which made it easy for the N atom in the imidazole ring to introduce the alkyl chain into the imidazole ring. This made the imidazole ring a positive cation. And the synthesized PILM contained an imidazole group and were therefore positive. This further demonstrated that PdCl₄²⁻ can be more easily immobilized on PILM by ionic exchange. Furthermore, more Pd nanoparticles were loaded on the PILM.

The characteristic peaks of the samples were confirmed by FTIR. As shown in Fig. 3, the characteristic peaks around 1650 and 1570 cm⁻¹ were attributed to C=C and C=N, respectively. This was solely due to the imidazole ring vibration. The peaks around 714 and 1160 cm⁻¹ were associated with the vibration peak of the long-chain alkyl-CH₂ and the stretching vibration peak of the tertiary amine N-C respectively. And the characteristic peaks around 1456 and 3031 cm⁻¹ were attributed to the vibration peak of the



Fig. 2. Zeta potential of the PILM prepared sample.



Fig. 3. FTIR spectra of (a) IL, (b) PILM, (c) PILM/Pd, (d) PILM/Pd/CeO2.

aromatic skeleton and the stretching vibration peak of -C-H on the imidazole ring respectively. The FTIR indicated the successful anchoring of 1-vinylimidazole on the crosslinked copolymer microspheres.

Fig. 4 showed the X-ray diffraction (XRD) spectra of as-prepared samples. It helped to characterize the crystal structure of the samples. Fig. 4(a) showed a peak around 20.7°, which was attributed to the diffraction of amorphous nature of PILM and also was seen in the same position in Fig. 4(b) and (c). The XRD spectra of PILM/Pd was shown in Fig. 4(b). The peaks at 2θ of 40.0°, 46.53°, 67.92 characteristic peaks of the Pd species, which were assigned to (111), (200), and (220) crystalline plane diffraction peaks of Pd nanoparticles, respectively. However, no diffraction peaks were observed at the same positions in Fig. 4(c), which were ascribed to the good dispersion of Pd nanoparticles and low loading amount beyond the detection limit [34–36]. Moreover, the peaks at 2θ of 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7°, and 79.1° (Fig. 4(c)) corresponded to the plane diffraction patterns of the fluorite CeO₂.

The surface morphological structures of PILM, PILM/Pd and PILM/Pd/CeO₂ were characterized by SEM. The Fig. 5(a) showed that the synthesized PILM was microspheres with the diameter size in the range of $1-2\,\mu\text{m}$ and was uniform in size and

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Fig. 4. XRD spectra of (a)PILM, (b) PILM/Pd, (c) PILM/Pd/CeO_{2.}

dispersion. The same morphology was seen in Fig. 5(b) and 5(c). CeO_2 particles had been synthesized and evenly distributed on the surface of PILM/Pd microspheres (Fig. 5(c)). As shown in the elemental analysis mapping images of the Fig. 6(e,f), It observed that C, O, Pd and Ce elements were relatively homogeneously distributed, which illustrated the existence of Pd nanoparticles and CeO_2 particles on the surface of PILM. The element content table was also seen in Fig. 6(a,f).

The structures of the as-sample were further studied by TEM. The Pd nanoparticles were tightly bound to the surface of PILM (Fig. 7(a)), which was attributed to the electrostatic interaction between imidazolium cations and metal nanoparticles. Moreover, it was noted that Pd nanoparticles were uniformly distributed on the surface of the PILM and were not significantly aggregated. The existence of Pd nanoparticles was not be found due to high electron density of polycrystalline CeO₂.The Fig. 7(b) showed that a layer of CeO₂ shell structure was distributed on the surface of the microspheres, which further confirmed the core-shell structured of PILM/Pd/CeO₂. The HRTEM was applied to figure out the state palladium species. As shown in Fig. 7(c), it could be found that the interplanar spacing of Pd nanoparticles was equivalent to Pd (111).

The X-ray photoelectron spectra (XPS) of obtained samples were shown in Fig. 8, which aimed to analysis the chemical status of samples. The Pd 3d spectrum showed two peaks at 335.8 eV and 341.4 eV (Fig. 8(a)), respectively, which could be attributed to Pd(0) species. Obviously, eight peaks appeared in the Ce 3d spectrum shown in Fig. 8, which were denoted by U, U', V, V' and *. The reason for its formation were be attributed to Ce 3d5/2 and Ce $3d_{3/2}$. And the peaks labeled as U, V and * were assigned to Ce^{4+} . The V'/U' doublet was attributed to the existence of Ce^{3+} , indicating that oxygen vacancies existed in CeO2, which was beneficial for the chemical adsorption of oxygen and the spark of molecular oxygen, thereby promoting the oxidation of benzyl alcohol. As seen in Fig. 8. (c), the N 1s spectrum displayed two peaks around 399.9 and 401.2 eV, which corresponded to C-N of the quaternized N in the imidazole rings [37]. In addition, the O 1s spectrum was also shown in Fig. 8. (d), the peak at 529.8 eV could be attributed to lattice oxygen, and the peak appearing in the range of 531 to 532.8 eV was considered as a defect in CeO₂ or an adsorbed oxygen species. These results also implied the high oxygen storage capacity of CeO₂. XPS also showed that the imidazole ring was not damaged during the preparation, even in ultrasound.

3.2. Selective oxidation of benzyl alcohol

The catalytic activity of the prepared catalysts in the oxidation of benzyl alcohol was also investigated. The effects of the base to alcohol ratio, reaction temperature and O_2 flow rate on the yield and conversion rate were studied to optimize the reaction conditions.

3.2.1. Effect of different reaction parameters on the catalytic activity of PILM/Pd/CeO $_2$

3.2.1.1. Effect of the base to alcohol ratio. The base selected in the this reaction was K₂CO₃, and the alkali content significantly affected its oxidation. Therefore, five molar ratios (0.1, 0.2, 0.5, 1 and 2) of [K₂CO₃]:[alcohol] were selected to explore its effect on yield and conversion. The alkoxy intermediate was formed by the alcohol deprotonation at the first stage in the reaction, while the existence of an alkaline medium facilitated the intermediate production. The selectivity at 0.1, 0.2, 0.5 and 2 equivalents of K₂CO₃ was between 95% and 98% (Fig. 9). However, its selectivity was significantly reduced when molar ratios of [K₂CO₃]: [alcohol] was 1. This because the addition of K₂CO₃ allowed the system to form a carbonate/bicarbonate buffer. The buffer solution system was destroyed when the [K₂CO₃]: [alcohol] molar ratio was 1.When the The small or large amount of K₂CO₃ had little effect on and even decreased the selectivity. By comparison, the selectivity maximized to 98% and its conversion reached 48% when the of [K₂CO₃]: [alcohol] molar ratio was 0.2. Thus, the optimal [K₂CO₃]: [alcohol] molar ratio was selected to be 0.2.

3.2.1.2. Effect of reaction temperature. The reaction temperature played an important role in the oxidation of benzyl alcohol. As



Fig. 5. SEM images of (a) PILM, (b) PILM/Pd, (c) PILM/Pd/CeO₂.

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Fig. 6. (a), (b), (c), (d), (e) and (f) the corresponding elemental mapping images of PILM/Pd/CeO₂ sample in SEM.



Fig. 7. (a) TEM images of PILM/Pd, (b)the size distribution of Pd nanoparticles in PILM/Pd, (c) SEM images of PILM/Pd/CeO2, (d) HRTEM images of PILM/Pd/CeO2.

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Fig. 8. XPS spectra of (a) Pd 3d, (b) Ce 3d, (c) N 1s and (d) O 1s in PILM/Pd/CeO₂ sample.

shown in Fig. 10, as the reaction temperature changed, its selectivity tended to and was up to 98%. However, it was worth noting that the conversion rate changed significantly when the reaction temperature varied. The conversion rate gradually rose and reached 48% at 160 °C with the temperature rise from 100 to 160 °C. This reason was that the increase in reaction temperature that facilitated intermolecular collisions and activated molecules, thereby reducing mass transfer limitations between molecules. When the reaction temperature exceeded 160 °C, the conversion rate slightly decreased. The reason was that with further temperature rise, the solubility of O_2 was lowered, resulting in a decrease in the conversion of benzyl alcohol. Therefore, 160 °C was the more suitable reaction temperature.

3.2.1.3. Effect of O_2 flow rate. It could be observed from Fig. 11 that the conversion rate gradually decreased when the O_2 flow rate increased and exceeded 60 ml/min. It was speculated that the increase in the O_2 flow rate promoted the production of the by-product benzoic acid, which was adsorbed on the surface of the

catalyst, causing catalyst poisoning and reducing conversion. Benzoic acid was converted to benzyl benzoate at elevated reaction temperatures. As the reaction temperature changed, its selectivity tended to balance. It could be seen from Fig. 11 that the optimum O_2 flow rate was 60 ml/min.

3.3. Reusability of catalysts

The recyclability of the catalysts was investigated through the oxidation reaction of benzyl alcohol under the optimal reaction conditions. After each cycle, the reaction system was centrifuged, while the lower solid was removed and washed several times with ethanol and deionized wate. Then the recycled catalyst was used in the next cycle. It could be observed from Fig. 12 that after 5 cycles of experiments, the recycled catalysts yet displayed high selectivity and conversion rate indicating the catalysts assynthesized were reusable and highly stable for oxidation of benzyl alcohol.



Fig. 9. Aqueous oxidation of benzyl alcohol catalyzed by catalyst with the reaction parameters of different [K₂CO₃]:[alcohol]. Reaction conditions: benzyl alcohol (2.08 g, 20 mmol), catalyst (25 mg), O₂ (60 ml/min), H₂O (20 ml), 160 °C, 6 h.



Fig. 10. Aqueous oxidation of benzyl alcohol catalyzed by catalyst with the reaction parameters of different reaction temperature. Reaction conditions: benzyl alcohol (2.08 g, 20 mmol), catalyst (25 mg), O₂ (60 ml/min), H₂O (20 ml), [K₂CO₃]: [alcohol] = 0.2, 6 h.

The prepared catalysts were compared with other precious metal catalysts. From Table 1, due to the different reaction conditions and metal supports, the catalysts prepared can not be accurately compared with the various catalysts in the literature. However, it is worth noting that the catalysts prepared had high selectivity and good conversion. At the same time, the prepared catalyst not only has high selectivity, but also has a reasonable TOF values. Moreover, compared with various catalysts in the literature, the core-shell catalyst prepared could significantly reduce the loss of Pd metal nanoparticles.

3.4. Reaction mechanism

Based on the above experimental results, a reasonable reaction mechanism was proposed. CeO_2 had high oxygen spillover ability owing to the coexistence of Ce^{4+} and Ce^{3+} . Ce^{4+} was reduced to Ce^{3+} and lattice oxygen atoms were transferred to benzyl alcohol to form carbon cationic intermediates. Then, the carbon cationic

intermediates removed alcohol H and bonded with Pd nanoparticles via O atoms. With the presence of O_2 , the Ce^{3+} was oxidized to Ce⁴⁺, thus supplying lattice oxygen from oxygen supply. It was the synergistic effect of CeO₂ and Pd that facilitated the continuous oxidation of benzyl alcohol [45]. As shown in Fig. 13, the deprotonation process of benzyl alcohol was first carried out, and the addition of basic K₂CO₃ promoted the de-peripherization of the alcohol by accelerating the removal of H atom from benzyl alcohol, forming a Pd-alcohol intermediate, which was co-adsorbed on the Pd nanoparticles. At the same time, O₂ and H₂O formed an interaction, and molecular oxygen extracted hydrogen from H₂O to form a hydrogen peroxy (OOH*) intermediate, which was enhanced by activation and further decomposed into OH* and O*. The Pd-alcoholate intermediate reacted with the OOH*, the O* and the OH* to form benzaldehyde. In addition, the benzaldehyde produced was further oxidized to form benzoic acid, and under the conditions of high temperature and basicity, it was easy to form a only by-product benzyl benzoate with unreacted benzyl alcohol.

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Fig. 11. Aqueous oxidation of benzyl alcohol catalyzed by catalyst with the reaction parameters of different O2 flow rate. Reaction conditions : benzyl alcohol (2.08 g, 20 mmol), catalyst (25 mg), H_2O (20 ml), $[K_2CO_3]$: [alcohol] = 0.2,160 °C, 6 h.



Fig. 12. Aqueous oxidation of benzyl alcohol catalyzed by catalyst with the 5 cycles of experiment. Reaction conditions : benzyl alcohol (2.08 g, 20 mmol), catalyst (25 mg), H₂O (20 ml), [K₂CO₃]: [alcohol] = 0.2, 160 °C, 6 h, O₂ (60 ml/min).

Table 1	
Oxidation of benzyl alcohol to major product benzaldehyde under different noble metal ca	atalyst.

Catalyst	Amount (mg)	Conversion ^a (%)	Selectivity ^b (%)	TOF^{c} (h^{-1})	Refs
4Pd/CN	25	33.00	100.00	672.00	[38]
Au/HMS	200	42.90	95.00	98.00	[39]
Pd/CMK-3	10	55.00	80.00	234.00	[40]
Au-Pd/TiO ₂	400	71.70	95.80	589.00	[41]
Pd/AC	-	18.00	91.00	30.00	[42]
Au-Pd/C	300	47.20	84.80	525.25	[43]
Pt/CNT-plasma	12	13.20	88.70	1234.90	[44]
PILM/Pd/CeO2	25	48.00	98.00	633.30	this work

^a Conversion of benzyl alcohol under the oxidation of benzyl alcohol.

^b Selectivity to benzaldehyde in the oxidation of benzyl alcohol.

^c TOF is defined as turnover frequency, moles of substrate converted per mole metal ion per hour.



Fig. 13. Speculation of reaction mechanism of benzyl alcohol oxidation on PILM/Pd/CeO₂ catalyst.

However, this mechanism was unfeasible if no catalyst was added. [46–50].

4. Conclusion

New polymeric ionic liquid microspheres (PILM) as the catalyst carrier were synthesized. One-step exchange of the imidazolium cation in the PILM with the anion $PtCl_4^{2-}$ of the metal precursor was operated, followed by reduction of the metal ion to produce a PILM/Pd product. Then, CeO₂ was loaded on the outer layer, which strongly interacted with Pd nanoparticles, and finally formed the core-shell PILM/Pd/CeO₂ catalysts. The catalytic performances of the synthesized catalysts were evaluated by an oxidation reaction of benzyl alcohol. The PILM/Pd/CeO₂ was an effective and reusable heterogeneous catalyst and had a promising application prospect. Nevertheless, synthetic PILM for loading other metals or alloys should be further studied.

Declaration of Competing Interest

The authors declare that no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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