

# Magnetic Core–Shell Nanostructured Palladium Catalysts for Green Oxidation of Benzyl Alcohol

Liping Kong<sup>1</sup> · Chengcheng Wang<sup>1</sup> · Feilong Gong<sup>2</sup> · Weidong Zhu<sup>1</sup> · Yijun Zhong<sup>1</sup> · Xiangrong Ye<sup>1</sup> · Feng Li<sup>3</sup>

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Abstract Multifunctional catalysts are highly attractive for green oxidation process integrating excellent conversion and selectivity with high separability and recyclability. In this regards, a facile method is developed to fabricate yolk-shell microspheres consisting of Fe<sub>3</sub>O<sub>4</sub> cores, mesoporous CeO<sub>2</sub> shells and loaded Pd nanoparticles. Microspheres with 2.6 % Pd loading exemplify excellent catalytic activity for solvent-free, selective oxidation of benzyl alcohol to benzaldehyde by molecular oxygen at 373 K and atmospheric pressure, resulting in 80.5 % conversion of benzyl alcohol with 94.8 % selectivity for benzaldehyde. The catalyst can be magnetically separated and recycled without significant loss of catalytic efficiency even after seven catalytic runs.

# **Graphical Abstract**



⊠ Xiangrong Ye yxr@zjnu.cn

- <sup>1</sup> College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, Zhejiang, China
- <sup>2</sup> College of Materials and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, Henan, China
- <sup>3</sup> American Advanced Nanotechnology, Houston, TX 77459, USA

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# **1** Introduction

Catalytic partial oxidation of benzyl alcohol is one of the main routes to benzaldehyde, an indispensable bulk intermediate for perfumes, pharmaceuticals, dyestuffs and agrochemicals. In a typical homogeneous catalytic process, costly and hazardous organic solvents are often heavily used [1-3]. Therefore, a green reaction with water as byproduct, e.g., solvent-free, liquid-phase oxidation of benzyl alcohol to benzaldehyde by molecular oxygen over supported noble metal catalysts, has triggered enormous interests [4, 5], and the mostly used catalysts consist of Pd or Au [6, 7] as primary active component, the performance of which highly depends on its chemical status and the support materials [8, 9]. Particularly, Pd or Au nanoparticles highly dispersed on reductive (CeO<sub>2</sub> [10], TiO<sub>2</sub> [11], etc.) supports show significantly promoted activity compared to those on non-reductive (C, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) substrates because of the synergistic metal-support interaction [12]. It has been reported that, due to the reversible valence exchange of Ce<sup>4+</sup>/Ce<sup>3+</sup> and high oxygen transport capability [13], CeO<sub>2</sub> can supply reactive oxygen in the form of surface superoxide and peroxide at one-electron defect site to the supported active species of metal for oxidation [14]. With surface oxygen vacancies, typical reductive support material such as CeO<sub>2</sub> serves as catalyst promoter to activate the  $O_2$  molecules through support or metal-support interface [15]. Synergistic metal-support interaction has also been reported for visible-light-driven oxidation of benzyl alcohol by O2 at room temperature and ambient pressure using Pd core@ CeO2 shell nanocomposite as photocatalyst. Under visible light irradiation, electron-hole pairs are produced by CeO<sub>2</sub> shell, and the generated electrons are trapped by the Pd cores and the adsorbed benzyl alcohol interacts with holes to form the corresponding radical cation. Further reaction with dioxygen or superoxide radical species will lead to the formation of the corresponding aldehydes [16]. Nevertheless, further studies are inexorable integrating CeO<sub>2</sub> shell with other materials to develop advanced, multifunctional heterogeneous catalysts, e.g., magnetically responsive catalyst as addressed bellow.

Conventional filtration-based recovery of expensive Pd or Au catalyst from the liquid reaction system is quite time and energy consuming [17, 18]. Hybridization of magnetically responsive phase with the catalyst support offers a solution to efficient recovery of catalyst from the reaction system under a magnetic field, and re-dispersion of the recovered catalyst for new run of reaction upon removal of the applied magnetic field [19, 20]. Although magnetically responsive catalyst has been intensively investigated [21, 22], there is dearth of work dedicated to its combination with reductive support for the selective oxidation of benzyl alcohol. From both the magnetic and catalytic point of view, Fe<sub>3</sub>O<sub>4</sub>@mesoporous CeO<sub>2</sub> (Fe<sub>3</sub> O<sub>4</sub>@mCeO<sub>2</sub>) core-shell nanostructured composite could be a satisfactory support to realize convenient catalyst recycling in addition to excellent conversion and selectivity. The Fe<sub>3</sub>O<sub>4</sub> core enables magnetically driven separation and recycle of catalyst. The CeO<sub>2</sub> shell not only protects the Fe<sub>3</sub>O<sub>4</sub> core from external harsh conditions and provides extra adsorption sites for nanocatalyst loading besides the interior space, but also promotes the performance of the loaded nanocatalyst in catalyzing liquid-phase oxidation of benzyl alcohol. In the present work, a layer-by-layer assembly method has been developed to fabricate Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> core-shell nanostructured catalyst. Mesoporous CeO2 shell was chemically deposited onto the surface of Fe<sub>3</sub>O<sub>4</sub> magnetic cores, followed by one pot loading of Pd nanoparticles using NaBH<sub>4</sub> as reductant. The composition and structure of the resultant catalysts were examined by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray photoelectron spectroscopy (XPS) characterization, and their catalytic performance as well as separability and recyclability were probed in solvent-free, aerobic oxidation of benzyl alcohol to explore the correlation with composition and structure for future development of multifunctional heterogeneous nanocatalyst.

# 2 Experimental

## 2.1 Preparation of Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>

The magnetite microspheres were prepared according to the method described below. Typically, 1.35 g of FeCl<sub>3</sub>·  $6H_2O$ , 1.0 g of polyethylene glycol and 3.6 g of NaAc were dissolved in 40 mL of ethylene glycol with stirring applied for 30 min to form a clear solution. The solution was then transferred into a 50 ml Teflon-lined stainless steel autoclave and heated at 200 °C for 8 h. The resultant precipitate was collected by magnetic separation and then washed with ethanol and deionized water for several times.

The mCeO<sub>2</sub> outer layer was deposited onto  $Fe_3O_4$  cores through chemical precipitation to form Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocomposite. 0.7 g of polyethylene glycol monododecyl ether (Brij) and 0.05 g of cetyltrimethylammonium bromide (CTAB) were blended in mixed-liquor of 20 mL water and 20 mL ethanol to form solution A. 0.1 g of Fe<sub>3</sub>O<sub>4</sub> particles were ultrasonicated in 0.1 M nitric acid solution for 15 min in order to obtain hydroxyl-rich surface, and then dispersed in solution A.  $(NH_4)_2Ce(NO_3)_6$ was dissolved in 20 mL of H<sub>2</sub>O to form a yellow solution B, which was added dropwise to solution A and kept at room temperature under vigorous stirring for 2 h. The mixture was then titrated with ammonium hydroxide until pH 9.0, and stirred at room temperature for 5 h. Afterwards, the particles were separated from the mixture by a magnet, washed, dried, and then re-dispersed in 100 mL of ethanol and refluxed at 95 °C for 24 h to remove the CTAB and Brij template. The ethanol extraction was repeated twice and the resultant powder was washed with water and dried at 60 °C overnight.

Pd nanoparticles were loaded onto  $Fe_3O_4@mCeO_2$ nanocomposite through sol-immobilization. A certain amount of H<sub>2</sub>PdCl<sub>6</sub>·6H<sub>2</sub>O and 0.05 mL of 1 wt% polyvinyl alcohol (PVA) solution were diluted in 40 mL of water. After 30 min of stirring, 0.29 mL of 0.1 M NaBH<sub>4</sub> solution was added to form a dark brown mixture. 0.1 g of Fe<sub>3-</sub>  $O_4@mCeO_2$  was then ultrasonically dispersed in the mixture under vigorous agitation. After 3 h, particles were collected by a magnet, and washed with deionized water and absolute alcohol to remove the surface adsorbed PVA. Finally, the particle samples were dried in vacuum at 60 °C for 8 h.

#### 2.2 Reaction Process

The catalytic performance of the materials was tested in the selective oxidation of benzyl alcohol to benzaldehyde at



normal pressure. Briefly, the oxidation was carried out in a three-neck flask connected to O2. Added to the reactor was 5 mL of benzyl alcohol and Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> catalyst with the molar ratio of substrate to metal at about 2500. Before the reaction, the device was purged for half an hour with  $O_2$  to get rid of the air. Magnetic stirring (1000 rpm) was initiated when the reaction mixture was heated up to the desired temperature. After the reaction, the catalyst was separated via magnetic field, and the liquid mixture accompanied by N,N-dimethylformamide as an internal standard was analyzed by a gas chromatograph (Agilent 6820) equipped with an FID detector and a capillary column (DB-5, 30 m  $\times$  0.45 mm  $\times$  0.42  $\mu$ m). In order to test the catalytic reusability, the catalyst collected through magnetic separation was washed with ethanol and dried in a vacuum oven at 333 K for 8 h. The recovered catalyst was then used in the next run of reaction.

## **3** Results and Discussion

The preparation of  $Pd/Fe_3O_4@mCeO_2$  core-shell structured nanocatalyst mainly included three steps (Scheme 1), and Fig. 1 represents the XRD patterns of the products at different synthetic steps. As shown in Fig. 1a, the XRD pattern of the magnetic core matches well with the standard



Fig. 1 X-ray diffractograms of (a)  $Fe_3O_4$ , (b)  $Fe_3O_4@mCeO_2$  and (c) 2.6 wt% Pd/Fe\_3O\_4@mCeO\_2

card (JCPDS No. 72-2303) of  $Fe_3O_4$  with cubic spinel structure. After being coated with CeO<sub>2</sub>, the intensity of  $Fe_3O_4$  phase decreased, and some new diffraction peaks appeared at 28.6°, 33.1°, 47.6°, 56.5°, and 59.3°, which can be assigned to CeO<sub>2</sub> phase. In the case of Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>, a weak diffraction peak corresponding to the (111) reflection of the Pd crystal was observed, conforming the successful loading of highly dispersed Pd nanoparticles.

Figure 2 displays the N<sub>2</sub> adsorption-desorption isotherms and BJH measurements of the pure CeO<sub>2</sub> materials, Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> spheres and 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocatalyst, and some results are summarized in Table 1. The adsorption-desorption isotherm of CeO<sub>2</sub> was type IVlike with an apparent H2 hysteresis loop at relatively high  $P/P_0$  signifying the presence of mesopores, and the Brunauer-Emmett-Teller (BET) surface area for CeO2 was 195.41 m<sup>2</sup> g<sup>-1</sup>. For Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> spheres, a type IV-like isotherm combined with an H3 hysteresis loop was observed, also indicating the presence of mesoporous structure. The BET surface area of the Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocomposite was 125.57 m<sup>2</sup> g<sup>-1</sup> with an average pore size of 5.07 nm. The surface area and average pore size both reduced for 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>, implying the loading of Pd into mesoporous structure.

The SEM images of the representative products from each synthetic step are exhibited in Fig. 3. The  $Fe_3O_4$ magnetic cores clearly display a spherical shape as shown in Fig. 3a,b. After CeO<sub>2</sub> coating, the size of core-shell spheres increased and the surface became rougher. No obvious aggregation occurred after Pd loading. As verified by the TEM images in Fig. 4, the as-prepared Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> microsphere is composed of a magnetite core and a mesoporous  $CeO_2$  shell (ca. 20 nm) with a relatively rough surface. HR-TEM image in Fig. 4d further indicated that the shell is porous and consists of a large number of assembled ultrafine nanocrystallites with an average size of approximately 5 nm. The lattice fringe with d-spacing of 0.32 nm can be readily indexed to the (111) lattice planes of CeO<sub>2</sub>, being consistent with the XRD results. After solimmobilization, Pd NPs with average diameter of about 4 nm are remarkably well-dispersed on the surface of the Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> microspheres without obvious aggregation, and the lattice fringes are clearly visible with spacing of about 0.23 nm which corresponds to that of the (111) lattice planes of Pd.



Fig. 2 N<sub>2</sub> adsorption-desorption isotherms and BJH measurements of a mCeO<sub>2</sub>, b Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> and c 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub>

Compound	Surface area $(m^2 g^{-1})$	Pore volume (cm <sup><math>3</math></sup> g <sup><math>-1</math></sup> )	Pore diameter (nm)	
CeO <sub>2</sub>	195.41	0.13	2.92	
Fe <sub>3</sub> O <sub>4</sub> @mCeO <sub>2</sub>	125.57	0.15	5.07	
2.6 wt % Pd/Fe $_3O_4$ @mCeO $_2$	108.18	0.09	3.87	

To investigate the composition and chemical state of especially the surface of the core-shell Pd/Fe<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub> material, XPS analysis was carried out and the results are shown in Fig. 5. Fe, Ce, O, Pd and C were detected distinctly in the survey scan XPS spectrum. The regional spectrum of Pd exhibits two peaks centered at 340.7 and 335.4 eV, which are assigned to  $3d_{3/2}$  and  $3d_{5/2}$  of Pd(0) [23], respectively. The spectrum for the O1 s ionization feature in Fig. 5d concluded two primary peaks, the one located at around 532.3 eV was denoted as oxygen coming from the H<sub>2</sub>O and CO<sub>2</sub> molecules chemisorbed on the surface, and the other at 530.5 eV was mainly ascribed to lattice oxygen (O<sub>lat</sub>) of Fe<sub>3</sub>O<sub>4</sub> and ceria support. Regarding the typical Ce3d spectrum shown in Fig. 5c,  $3d_{3/2}$  peaks at 917.5, 907.8 and 901.4 eV and 3d<sub>5/2</sub> peaks at 898.9, 888.2 and 883.2 eV correspond to  $Ce^{4+}$  [24] while  $3d_{3/2}$  at 904.3 eV and  $3d_{5/2}$  at 885.5 eV are characteristic of Ce<sup>3+</sup>. The coexistence of some  $Ce^{3+}$  with  $Ce^{4+}$  in the fresh Pd/ Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> catalyst might be resulted from the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> by ethanol during synthesis, and creates more oxygen defects in the CeO<sub>2</sub> supports which have been speculated to benefit the lattice oxygen transfer in the catalytic oxidation process [25–27].

Table 1BET surface area,pore volume and average poresize of mCeO2,  $Fe_3O_4@mCeO2$ and 2.6 wt% Pd/Fe\_3O\_4@mCeO2

Magnetic properties of pure  $Fe_3O_4$ ,  $Fe_3O_4@mCeO_2$  and  $Pd/Fe_3O_4@mCeO_2$  were investigated via a vibrating sample magnetometer at room temperature. The materials have magnetization saturation (Ms) values of 85.45, 27.56, 18.63 emu g<sup>-1</sup>, respectively. Due to the stepwise mCeO<sub>2</sub>

coating and then Pd loading,  $Fe_3O_4@mCeO_2$  and 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocomposites exhibit slightly but gradually decreased Ms values as compared with Fe<sub>3</sub>O<sub>4</sub>, which is attributed to the slight increase in both the mass and size of the resultant materials. However, 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> still can be separated from the reaction mixture under external magnetic field, as showed in Fig. 6 (inset).

Shown in Table 2 is the activity of Pd loaded by various magnetic supports on the oxidation of benzyl alcohol under identical condition. Pd loaded on  $CeO_2$  or  $TiO_2$  support exhibited higher activity than the counterpart on  $SiO_2$  or C. As has been widely reported [28, 29] and demonstrated by the above-mentioned XPS result,there usually exist numerous oxygen defects in  $CeO_2$  and  $TiO_2$ ,which not only enhance the synergistic interaction between the loaded metals and support, but also enable more efficient activation of  $O_2$  for oxidation of benzyl alcohol.

Table 3 summarizes the influence of Pd content on benzyl alcohol oxidation catalyzed by Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>. At a same reaction temperature of 373 K, the conversion of benzyl alcohol dramatically increased from 25.5 to 88.4 % along with the increase of Pd loading from 0.3 to 4.3 %, whilst the selectivity towards benzaldehyde slightly increased and reached a value more than 94.5 %. For Pd/ Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> with 2.6 % of Pd loading, the turnover frequency (TOF), an indicator of the average reaction rate over the catalyst, showed a maximal value of 443.5 h<sup>-1</sup>



Fig. 3 SEM images of a,b Fe<sub>3</sub>O<sub>4</sub>, c,d Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> and e,f 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>

along with relatively high benzyl alcohol conversion around 80.5 % and benzaldehyde selectivity around 94.8 %. Such a high performance might be resulted from the collaborative effect between the  $CeO_2$  and Pd particles.

The influence of temperature on benzyl alcohol oxidation is shown in Table 4. At an elevated temperature of 413 K, the reaction rate was significantly enhanced, leading to a very high TOF value of 501.3 h<sup>-1</sup>. Also the conversion of benzyl alcohol increased to 88.2 %. These results indicate that high temperature is beneficial to oxidation reaction, one of possible reasons being that the small amount of water produced in the reaction process could be more easily removed from the activate sites of catalyst at high temperature. However, the selectivity to benzaldehyde almost unchanged. If the reaction was carried out at a temperature lower than 373 K, a sharp decline of benzyl alcohol conversion occurred. At 333 K, the conversion was 10.1 % only. In the reaction process, the surface of Pd catalyst might be deactivated due to the oxidation by the activated oxygen to form PdO. The reduction of PdO back to Pd by the substrate alcohol could recover the active sites of Pd to keep the reaction proceed continuously. However, such reduction would be slow at a temperature as low as 333 K, resulting in a low conversion of benzyl alcohol. When the reaction temperature increased to 353 K, the conversion of benzyl alcohol increased significantly to 58.9 %.

The catalytic activity of Pd/Fe<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub> on oxidation of benzyl alcohols with different substituent groups was also evaluated and the results are compared in Table 5. The conversion of alcohol decreases according to the descending order of substituent groups:  $-C(CH_3)_3 >$  $-OCH_3 > -CH_3 > -Cl > -NO_2$ . Most likely, the electron



Fig. 4 TEM and HR-TEM images of a,b Fe<sub>3</sub>O<sub>4</sub>, c,d Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> and e,f 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>

cloud density of benzene ring increases with the electron donating ability of substituent group, leading to easier oxidation of aromatic alcohol to aromatic aldehyde.

Figure 7 describes the results of catalytic stability test of the fabricated 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocomposite.

After seven cycles, the conversion of benzyl alcohol decrease to 74.5 %, and the selectivity for benzyl aldehyde reduce to 89.8 %. ICP analysis indicated a negligible loss of palladium from catalyst to the reaction system, less than 1 ppm.



Fig. 5 XPS spectra of the 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> microspheres catalyst: a full spectrum, b Pd 3d, c Ce 3d and d O 1s



**Fig. 6** Magnetization curves of samples measured at 298 K: (*a*) Fe<sub>3</sub>O<sub>4</sub>, (*b*) Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>, (*c*) 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub>. Photographs (*inset*) of 2.6 wt% Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> dispersed in or collected from aqueous solution with or without external magnetic field

<b>Table 2</b> Support chect on oxidation of beinzyl alcon	Fable 2	Support e	effect or	n oxidation	of	benzyl	alcoho
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Pd/support	Conversion (%)	Selectivity (%) Benzyldehyde	TOF(h <sup>-1</sup> ) <sup>a</sup>
Pd/Fe <sub>3</sub> O <sub>4</sub>	60.0	70.1	303.5
Pd/Fe <sub>3</sub> O <sub>4</sub> @C	72.0	83.5	353.3
Pd/Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub>	74.5	93.2	369.7
Pd/Fe <sub>3</sub> O <sub>4</sub> @CeO <sub>2</sub>	80.5	94.8	443.5
Pd/Fe <sub>3</sub> O <sub>4</sub> @TiO <sub>2</sub>	80.1	93.1	428.9

Reaction condition: benzyl alcohol (5 ml),  $O_2$  (20 ml/min), w=2.6 %, molar ratio of substrate:metal at about 2500, t=7 h, T=373 K

<sup>a</sup> TOFs were calculated on the basis of practical loading of Pd

It is widely accepted that oxidative dehydrogenation is responsible for the mechanism of alcohol oxidation shown in Fig. 8, although the precise pathway is still under debate because the nature and concentration of adsorbed species

Actual content (%) <sup>a</sup>	Conversion (%)	Selectivity (%)	TOF $(h^{-1})^b$			
		Benzaldehyde	Toluene	Benzoic acid	Benzyl benzoate	
0.3	25.5	88.3	8.6	2.1	1.0	348.4
0.8	40.5	89.5	8.3	1.3	0.9	358.5
1.5	55.3	90.1	7.8	1.3	0.8	308.3
2.6	80.5	94.8	3.4	0.9	0.9	443.5
3.4	87.8	94.6	3.9	1.1	0.4	289.2
4.3	88.4	93.2	4.4	1.4	1.0	258.1

Reaction condition: benzyl alcohol (5 ml),  $O_2$  (20 ml/min), m = 0.05 g, t = 7 h, T = 373 K

<sup>a</sup> Determined by ICP-AES

<sup>b</sup> TOFs were calculated on the basis of practical loading of Pd

<b>Table 4</b> The influence of   temperature to oxidation of	Temperature	Conversion	Selectivity				TOF $(h^{-1})^a$
benzyl alcohol			Benzaldehyde	Toluene	Benzoic acid	Benzyl benzoate	
	333	10.1	89.8	5.9	2.1	2.2	35.2
	353	58.9	91.2	5.8	1.4	1.6	253.7
	373	80.5	94.8	3.4	0.9	0.9	443.5
	403	87.5	94.5	3.0	1.1	1.4	454.8
	413	88.2	93.9	3.2	0.8	2.1	501.3

Reaction condition: benzyl alcohol (5 ml),  $O_2$  (20 ml/min), w=2.6 %, molar ratio of substrate:metal at about 2500,  $t=7\ h$ 

<sup>a</sup> TOFs were calculated on the basis of practical loading of Pd

# Table 5 Catalytic activity of Pd/Fe<sub>3</sub>O<sub>4</sub>@CeO<sub>2</sub> on oxidation of different alcohols



Reaction condition: benzyl alcohol (5 ml), O<sub>2</sub> (20 ml/min), w = 2.6 %, molar ratio of substrate:metal at about 2500, t = 7 h



C.Conversion of benzyr abconc

S: Selectivity for benzaldehyde





Fig. 8 The mechanism of benzyl alcohol oxidation

are unknown [30]. The reaction process mainly includes two steps: the dehydrogenation of alcohol molecule on the active sites of metal particles and the removal of the generated hydrogen from the metal particles to liberate the active sites [31]. The reaction will be suppressed or prohibited due to the coverage of active sites by the adsorbed hydrogen, if there is no "activated" oxygen or other abstractors for hydrogen cleaning. For the Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> catalyst prepared in this work, the CeO<sub>2</sub> shell rich in oxygen defects could activate oxygen molecules to scavenge hydrogen from the metal surface, and simultaneously serve as reservoir for temporary hydrogen storage [32], leading to a faster recovery of the active sites of metal particles and hence a high performance of the Pd/Fe<sub>3</sub> O<sub>4</sub>@mCeO<sub>2</sub> catalyst.

## 4 Conclusion

For low cost, environmentally friendly and selective oxidation of benzyl alcohol to benzaldehyde, a layer-by-layer strategy has been established to prepare core–shell structured multifunctional Pd/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> nanocatalyst uniquely integrating excellent conversion and selectivity with efficient separability and recyclability. The Fe<sub>3</sub>O<sub>4</sub> core allows for magnetically driven separation and recycle of catalyst, and the defect-rich CeO<sub>2</sub> shell enables promoted catalytic performance of the loaded Pd nanoparticles. Being superior to other reported heterogeneous nanocatalysts, the synthesized Pd(2.6 %)/Fe<sub>3</sub>O<sub>4</sub>@mCeO<sub>2</sub> composite results in 80.5 % benzyl alcohol conversion and 94.8 % selectivity for benzaldehyde in a short reaction period of 7 h at 100 °C, and no significant loss of efficiency was observed after seven catalytic runs.

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