Chinese Journal of Catalysis 36 (2015) 1623–1630

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue for Excellent Research Work in Recognition of Scientists Who Are in Catalysis Field in China)

An investigation of the effects of CeO_2 crystal planes on the aerobic oxidative synthesis of imines from alcohols and amines

Zhixin Zhang [a,b], Yehong Wang [b], Min Wang [b], Jianmin Lü [b], Lihua Li [b], Zhe Zhang [b], Mingrun Li [b], Jingyang Jiang [a,#], Feng Wang [b,*]

[a] *State Key Laboratory of Fine Chemicals, College of Chemistry, Faculty of Chemical Environmental and Biological Science and Technology, Dalian University of Technology, Dalian 116024, Liaoning, China*

[b] *State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

ARTICLE INFO

Article history:
Received 27 March 2015
Accepted 19 April 2015
Published 20 September 2015

Keywords:
Ceria
Crystal plane effect
Oxidative coupling
Imine
Defect site

ABSTRACT

We herein report the effects of CeO_2 crystal planes on the oxidative coupling of alcohols and amines to form imines. CeO_2 exhibits significant catalytic activity under mild reaction conditions (60 °C) during the synthesis of 13 different imines, giving >89% conversions and >90% selectivities. The crystal planes of CeO_2 greatly affect the catalytic performance. Among the crystal planes investigated (the (110), (100) and (111) planes), the (110) plane shows the strongest redox ability and thus the best catalytic activity, generating a 97% yield of the imine at 60 °C in 2 h, because it contains the highest concentration of oxygen vacancies.

1. Introduction

The effect of the crystal planes of metal oxides on their catalytic performance is well known and has generated a significant number of research studies [1–5]. CeO_2 is a particularly promising metal oxide because it readily forms oxygen vacancies and potentially has a wide range of applications, including as an active species, a promoter and a heterogeneous catalyst [6–9]. The crystal plane effect in CeO_2 primarily originates from differences in oxygen vacancies and has been widely studied with regard to gas phase reactions occurring at high temperatures (>200 °C) and involving small molecules such as CO_x, H_2O, H_2, CH_4 and NO_x [5, 10–14]. It has been reported that the oxygen vacancies in this material are mobile at high temperatures [15], which makes it challenging to study the crystal plane effect at elevated temperatures. Therefore, an alternative means of assessing this effect is required, and one such method involves the study of liquid phase organic reactions at low temperatures. In previous research, we have studied the acid properties of the different crystal planes of CeO_2 during hydrolysis reactions [16]. However, the redox properties of the various crystal planes during reactions involving large molecules at low temperatures have not yet been examined.

Imines represent an important class of N-based reaction intermediates and are widely used in the synthesis of various biological, agricultural and pharmaceutical compounds [17,18].

---

* Corresponding author. Tel/Fax: +86-411-84379762; E-mail: wangfeng@dicp.ac.cn
# Corresponding author. Tel/Fax: +86-411-84986033; E-mail: jyjiang@dlut.edu.cn

This work was supported by the National Natural Science Foundation of China (21403216, 21303189, 21422308), and Hundred Person Project of the Chinese Academy of Sciences.

DOI: 10.1016/S1872-2067(15)60869-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 9, September 2015

Traditionally, imines are synthesized by the condensation reactions of aldehydes or ketones with amines in the presence of an acid catalyst. More recently, new methodologies allowing the green synthesis of imines have been developed, such as the oxidative dehydrogenation of amines [19], the hydroamination of alkynes with amines [20] and the dehydrogenative or oxidative coupling of alcohols and amines [21–40]. The dehydrogenation or oxidative coupling method is one of the most promising approaches, because alcohols are both readily available and inexpensive, and because only hydrogen or water may be produced as by-products. CeO_2 has been reported to act as an efficient catalyst for this reaction at room temperature [41]. The high activity of CeO_2 for this reaction is derived from the reactive oxygen species in its oxygen vacancies [1], although the redox properties of the various crystal planes of CeO_2 remain unclear.

Herein, we report the crystal plane effects in CeO_2 for the oxidative coupling of alcohols and amines. The results demonstrate that CeO_2(110) possesses a greater concentration of oxygen vacancies than either CeO_2(111) or CeO_2(100), thus the highest activity was observed over CeO_2(110). These findings provide insights that should assist in the tuning of the low-temperature redox properties of CeO_2-based catalysts.

2. Experimental

2.1. Chemicals and Reagents

All chemicals were of analytical purity and were used as-received without further purification. $Ce(NO_3)_3·6H_2O$ was purchased from Aladdin Chemicals. MgO, Y_2O_3, Nb_2O_5, Al_2O_3, ZrO_2, SiO_2, TiO_2, Cr_2O_3, CrO_3, Fe_2O_3, CuO, ZnO, MoO_3, WO_3 and V_2O_5 were obtained from commercial sources and the majority were purchased from the Aladdin Chemicals.

2.2. Synthesis of CeO_2

CeO_2 was synthesized by a conventional precipitation method [16]. In this process, $Ce(NO_3)_3·6H_2O$ (5.0 g) was dissolved in 100 mL of deionized water and the pH of the solution was adjusted to 11.0 by the addition of NH_4OH (3.4 mol/L) at room temperature with magnetic stirring. The resulting precipitate was filtrated and washed with deionized water, dried in an oven overnight at 120 °C, then calcined at 500 °C for 4 h.

2.3. Synthesis of different CeO_2 morphologies

$Ce(NO_3)_3·6H_2O$ was used as the cerium source for the synthesis of different CeO_2 morphologies. The preparation method was similar to the hydrothermal process reported by Yan's group [42]. Briefly, $Ce(NO_3)_3·6H_2O$ (0.868 g) and the requisite amount of NaOH (0.016–15 g) were dissolved in 5 and 35 mL of deionized water, respectively, after which these two solutions were mixed in a Teflon bottle with stirring at room temperature. The mixture was stirred for an additional 30 min, promoting the formation of a milky slurry. The Teflon bottle was subsequently inserted into a tightly sealed stainless steel vessel autoclave and the autoclave was transferred into an oven and subjected to hydrothermal treatment at 100–180 °C for 24 h. After cooling, the precipitate was separated by centrifugation and washed repeatedly with deionized water and ethanol, followed by drying in an oven overnight at 60 °C.

2.4. General procedure for the synthesis of imines from alcohols and amines

In a typical reaction, the catalyst was weighed into a screw-capped glass pressure vessel containing a stir bar. The required amounts of alcohol (0.5 mmol) and amine (0.6 mmol), pre-dissolved in solvent (2 mL), were added and the vessel was filled with oxygen, sealed, and heated to the desired temperature in an oil bath with stirring. The products of the reaction were analyzed by gas chromatography (GC, Agilent 7890A) and GC-mass spectrometry (MS, Agilent 7890A/5975C).

2.5. Characterization

Powder X-ray diffraction (XRD) patterns were acquired using a PANalytical X-Pert diffractometer, applying Cu-Kα radiation at 40 kV and 40 mA. Continuous scans were collected over the 2θ range of 5° to 80°. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEOL-2100F electron microscope operating at 200 kV. Raman spectra were recorded on a micro-Raman spectrometer (Renishaw) equipped with a CCD detector, using a He/Ne laser with a wavelength of 532 nm.

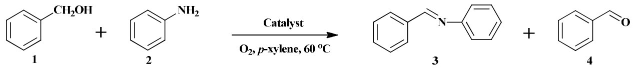
***Feng Wang** (Dalian Institute of Chemical Physics, Chinese Academy of Science) **received the Catalysis Rising Star Award in 2012**, which was presented by the Catalysis Society of China. Professor Feng Wang received his Ph.D. degree in Physical Chemistry from Dalian Institute of Chemical Physics, Chinese Academy of Sciences, in 2005, and he joined the same institute and was promoted to full professor in 2011. He did postdoctoral research on heterogeneous catalysis at University of California at Berkeley and Catalysis Research Center of Hokkaido University. Currently, he is the associate director of the Biomass and Bio-energy Division of the Dalian National Laboratory for Clean Energy (DNL). His research interests include (1) Heterogeneous C-O band transformation catalysis; (2) synthesis of nanostructured metal and metal oxide catalyst; (3) in situ characterization technique for liquid phase reaction; (4) catalytic biomass conversion to valuable chemicals. He has published 50 peer-reviewed papers with over 800 citations.*

3. Results and discussion

3.1. Catalyst screening tests and optimization of reaction conditions

Initially, the synthesis of an imine from benzyl alcohol and aniline was conducted over various solid metal oxides at 60 °C for 12 h (Table 1). The reaction was found not to occur in the absence of the catalyst (Table 1, entry 1). Other metal oxides either showed low benzyl alcohol conversions (Al_2O_3, V_2O_5, MgO, Fe_2O_3, Y_2O_3, Nb_2O_5, ZnO and ZrO_2; Table 1, entries 3–10) or poor imine selectivities (SiO_2, TiO_2, Cr_2O_3, CrO_3, CuO, MoO_3 and WO_3; Table 1, entries 11–17). In contrast, CeO_2 exhibited the best performance, giving >99% conversion of benzyl alcohol and 94% selectivity for the imine (**3**) (Table 1, entry 2). The solvent also had a remarkable effect on the reaction (Table 1, entries 18–23), such that the low polarity solvent *p*-xylene showed better performance (Table 1, entry 2). More polar solvents, such as acetonitrile, 2-propanol, methanol, dioxane, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), gave lower conversions. The reaction did not progress beyond 9% conversion in Ar atmosphere, indicating that the presence of oxygen is necessary to obtain suitable yields (Table 1, entry 24). Following removal of the CeO_2 from the reaction mixture by hot filtration, no further conversion of benzyl alcohol was observed (Fig. 1), demonstrating the heterogeneous nature of the catalyst.

Table 1
The oxidative coupling imine formation reaction over various oxides.[a]



Entry	Catalyst	Solvent	Conversion of **1**[b] (%)	Selectivity (%) **3**	Selectivity (%) **4**
1	—	*p*-Xylene	0	—	—
2	CeO_2	*p*-Xylene	>99	94	6
3	Al_2O_3	*p*-Xylene	27	97	3
4	V_2O_5	*p*-Xylene	9	93	7
5	MgO	*p*-Xylene	8	51	49
6	Fe_2O_3	*p*-Xylene	7	97	8
7	Y_2O_3	*p*-Xylene	4	63	37
8	Nb_2O_5	*p*-Xylene	3	85	15
9	ZnO	*p*-Xylene	2	73	27
10	ZrO_2	*p*-Xylene	2	77	23
11	SiO_2	*p*-Xylene	< 1	—	>99
12	TiO_2	*p*-Xylene	< 1	—	>99
13	Cr_2O_3	*p*-Xylene	< 1	—	>99
14	CrO_3	*p*-Xylene	1	—	>99
15	CuO	*p*-Xylene	< 1	—	>99
16	MoO_3	*p*-Xylene	< 1	—	>99
17	WO_3	*p*-Xylene	< 1	—	>99
18	CeO_2	Acetonitrile	72	94	6
19	CeO_2	2-Propanol	41	>99	0
20	CeO_2	Methanol	11	>99	0
21	CeO_2	Dioxane	4	>99	0
22	CeO_2	DMF	0	—	—
23	CeO_2	DMSO	0	—	—
24[c]	CeO_2	*p*-Xylene	9	>99	—

[a] Reaction conditions: solvent (2 mL), catalyst (100 mg), **1** (0.5 mmol), **2** (0.6 mmol), 60 °C, 12 h, O_2. [b] The conversions, based on benzyl alcohol consumption, were determined by GC and the products were identified by GC-MS. [c] Under Ar.

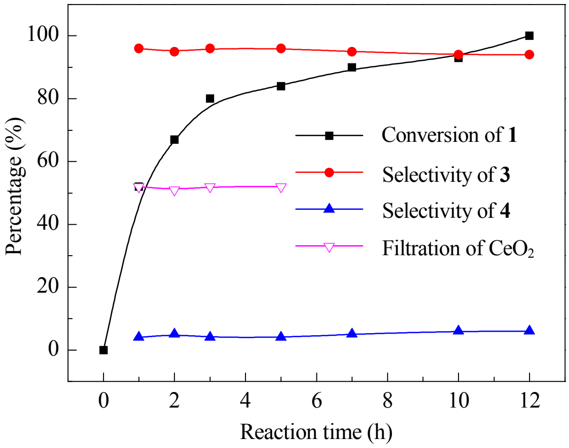


Fig. 1. Reaction profiles and hot filtration tests for the synthesis of an imine from benzyl alcohol and aniline over CeO_2. Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 °C, O_2.

A remarkable deactivation of the CeO_2 was observed during attempts to recycle the catalyst. Following one reaction, the catalyst was filtered from the reaction mixture, washed with ethanol three times, dried and then used for the next cycle. In the subsequent trial, the yield of imine decreased to 35%. In addition, a significant change in the color of the catalyst was observed, from pale yellow to greyish yellow. The catalytic activity could, however, be recovered by calcination of the used catalyst in air (Fig. 2). Therefore, the deactivation of the catalyst may be attributed to poisoning of the active sites by the adsorption of organic species.

3.2. Oxidative coupling with various amines and alcohols

After screening for the most suitable catalyst and optimizing the reaction conditions, we focused on the scope of substrates and the functional group tolerance (Table 2). Various alcohols and amines underwent oxidative coupling smoothly to afford

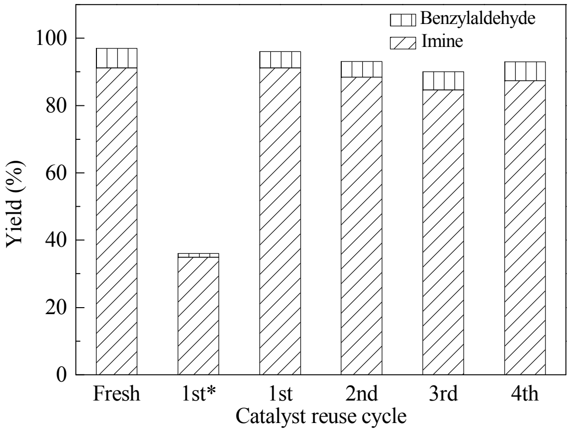
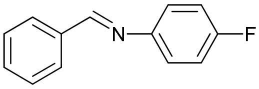
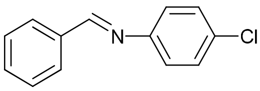
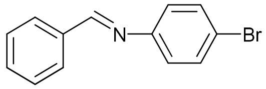
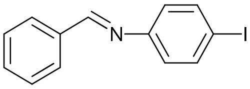
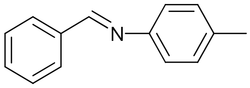
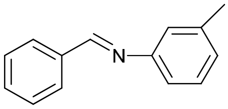
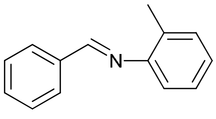
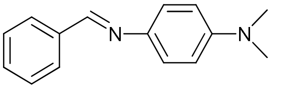
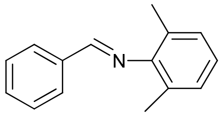
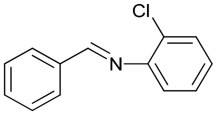
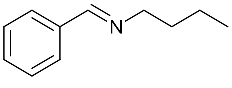
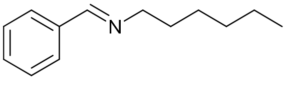
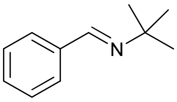
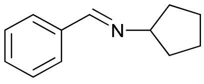
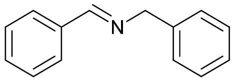
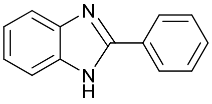
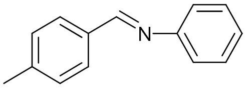
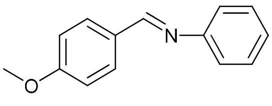
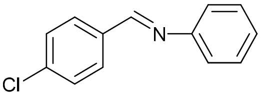
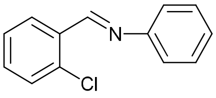
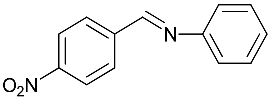
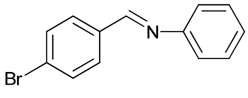
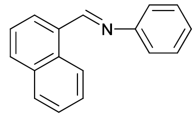
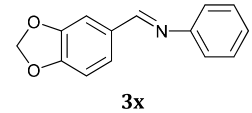


Fig. 2. Recycling of the catalyst during the synthesis of an imine from benzyl alcohol and aniline over CeO_2. Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 °C, 12 h, O_2. 1st* indicates the first run using recycled CeO_2 without calcination, while 1st indicates the first run after calcination.

the desired products with moderate to excellent yields. The scope of the amines to which the reaction could be applied was extended under the optimized reaction conditions when using benzyl alcohol (**3a**–**3p**). A wide range of aniline derivatives (**3a**–**3g**) gave the corresponding imines with excellent yields (>95% conversions and >96% selectivities). In the case of *N*,*N′*-dimethylbenzene-1,4-diamine (**3h**), however, the corresponding imine yield was 48% even at elevated temperature (120 °C). Moreover, 2,6-dimethyl-substituted (**3i**) and 2-chloro-substituted (**3j**) anilines gave low yields of imines, presumably because of steric hindrance. Different aliphatic amines were also examined in this catalytic system. The reactions of linear or branched alkyl amines, such as *n*-butyl amine (**3k**), *n*-hexyl amine (**3l**) and *tert*-butyl amine (**3m**), proceeded readily to afford the desired imines in moderate yields. Cyclopentyl amine (**3n**), benzylamine (3**o**) and *o*-phenylenediamine (**3p**) gave moderate yields at 120 °C. Next, a brief examination of various alcohols was conducted. Notably, aromatic alcohols with both electron-donating groups (*p*-CH_3 and *p*-OCH_3) and electron-withdrawing groups (*p*-Cl, *o*-Cl, *p*-Br and *p*-NO_2) could be converted into the corresponding imines with excellent yields (>89% conversions and >90% selectivities) (**3q**–**3v**). Additionally, the transformations of 1-naphthalenemethanol (**3w**) and piperonyl alcohol (**3x**) produced the corresponding imines with moderate conversions and selectivities greater than 90%.

Table 2
Scope of the oxidative coupling reaction of various amines with alcohols using CeO_2.[a]

$$\underset{\mathbf{1}}{R^1CH_2OH} + \underset{\mathbf{2}}{R^2NH_2} \xrightarrow[O_2,\ p\text{-xylene, } 60\ ^{\circ}C]{CeO_2} \underset{\mathbf{3}}{R^1CH{=}NR^2}$$

Product (**3**)	Conv. (%)	Sel. (%)	Product (**3**)	Conv. (%)	Sel. (%)	Product (**3**)	Conv. (%)	Sel. (%)
 **3a**	98	>99	 **3b**	96	97	 **3c**	95	97
 **3d**	>99	96	 **3e**	99	99	 **3f**	96	96
 **3g**	95	>99	 **3h**	48	>99[b]	 **3i**	67	45[b]
 **3j**	93	42[b]	 **3k**	44	80[b]	 **3l**	48	78[b]
 **3m**	49	>99	 **3n**	66	82[b]	 **3o**	58	99[b]
 **3p**	50	97[b]	 **3q**	92	>99	 **3r**	>99	90
 **3s**	>99	96	 **3t**	89	99	 **3u**	92	>99
 **3v**	>99	98	 **3w**	64	90	 **3x**	78	94

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 **°C**, for 12 h, O_2. The conversions based on alcohol consumption were determined by GC and GC-MS. [b] 120 °C.

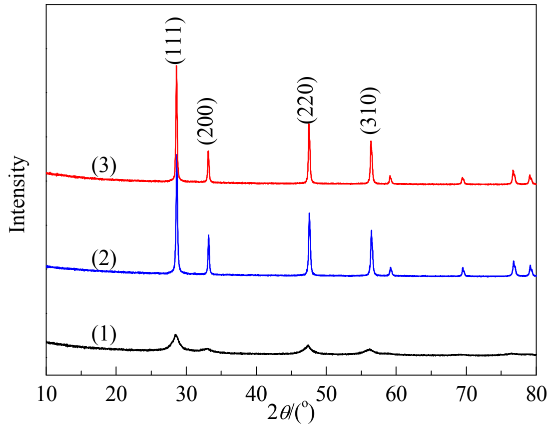


Fig. 3. XRD patterns of (1) CeO_2 nanorods, (2) CeO_2 nanocubes, and (3) CeO_2 nanooctahedra.

3.3. *Effect of the CeO_2 crystal planes*

The relationship between the catalytic activity and the shape (rod, cube or octahedron) and crystal plane of the nanostructured CeO_2 was investigated during the synthesis of an imine from benzyl alcohol and aniline. CeO_2 samples with different morphologies were synthesized according to a procedure previously reported in the literature [42]. The X-ray diffraction (XRD) patterns of the resulting materials (Fig. 3) confirm the formation of ceria based on the diffraction peaks observed at 2θ = 28.7°, 33.2°, 47.7° and 56.6° (JCPDS 65-2975), corresponding to the (111), (200), (220) and (311) planes of a CeO_2 fluorite-type structure, respectively, with no significant impurities observed. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images (Fig. 4) indicate that these samples had different exposed crystal planes: (110) and (100) for the rods, (100) for the cubes, and (111) for the octahedra. Furthermore, the CeO_2 rods consisted of 51% (110) planes and 49% (100) planes. These results are in good agreement with those of Yan's group [42] and other researchers [5, 10].

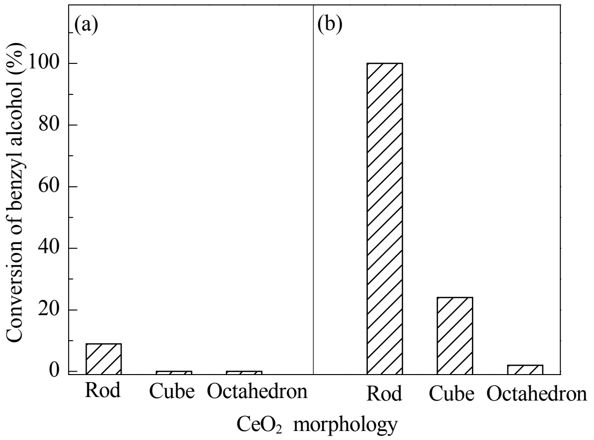


Fig. 5. (a) Benzyl alcohol oxidation and (b) the synthesis of an imine from benzyl alcohol and aniline over CeO_2 catalysts with differing morphologies. Reaction conditions: (a) **1** (0.5 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 °C, 12 h, O_2; (b) **1** (0.5 mmol), **2** (0.6 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 °C, 12 h, O_2.

Knowing that the synthesis of an imine from benzyl alcohol and aniline involves the oxidation of the alcohol to an aldehyde followed by the condensation of the aldehyde and aniline, we first investigated the alcohol oxidation activity over different CeO_2 samples (Fig. 5(a)). Without aniline, the alcohol oxidation can still takes place over CeO_2 nanorods, with 9% conversion of benzyl alcohol, while CeO_2 nanocubes and nanooctahedra are nearly inert. The addition of aniline increases the conversion for all three CeO_2 catalysts (Fig. 5(b)). In this case, the CeO_2 nanorods show the highest activity, with the conversion increasing from 9% to > 99%, whereas the CeO_2 nanocubes and nanooctahedra give 24% and 2% conversions, respectively. This is most likely because the removal of the benzaldehyde by

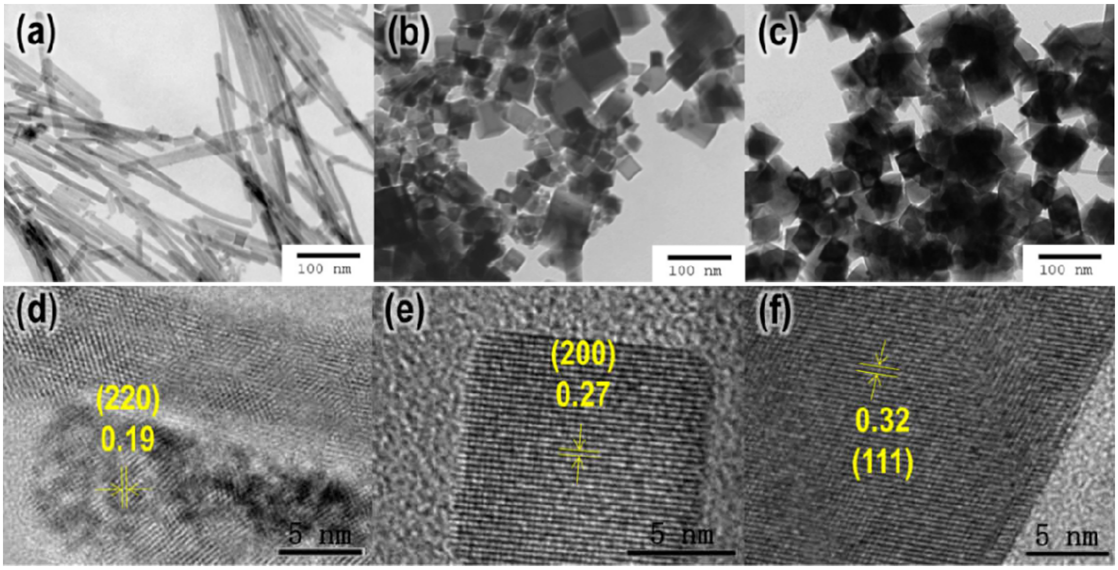


Fig. 4. TEM images of CeO_2 (a) nanorods, (b) nanocubes and (c) nanooctahedra and HRTEM images of CeO_2 (d) nanorods, (e) nanocubes and (f) nanooctahedra.

reaction with aniline promotes the alcohol oxidation reaction. These results indicate the different redox properties of the different crystal planes.

Subsequently, the catalytic performance during the oxidative coupling of benzyl alcohol and aniline was assessed using shorter reaction time spans (Table 3). Under these conditions, CeO_2 cubes and octahedra give low imine yields of 5.7% and 3.8%, respectively (Table 3, entries 2 and 3), although the CeO_2 rods generate a remarkably high yield of 97% at 60 °C in 2 h (Table 3, entry 1). The imine generation rate over the (110) planes was calculated to be 4.618 mmol/(g·h), a value that is approximately 32 and 49 times faster than the rates obtained from the cubic (100) (0.143 mmol/(g·h)) and octahedral forms (111) (0.095 mmol/(g·h)), respectively.

The above results motivated us to conduct more in-depth investigations of the crystal plane structures. The redox sites of CeO_2, which are correlated to the concentrations of oxygen vacancies, may play an important role in promoting the reaction. The oxygen vacancies were thus characterized by Raman spectroscopy (Fig. 6). Two bands are observed in the spectra of these samples; the intense band at 462 cm^{-1} is associated with the Raman-active F_{2g} vibrational mode of the CeO_2 fluorite-type structure [43], whereas the weak band at 595 cm^{-1} is attributed to Frenkel-type oxygen vacancies [44]. Because Raman spectroscopy using a 532 nm laser provides only surface information for CeO_2 [45], the oxygen vacancy sites detected by Raman spectroscopy are primarily those on the CeO_2 surface, and so the ratios of the integrated peak areas (A_{595}/A_{462}) were subsequently calculated to quantify the relative surface concentrations of oxygen vacancies. [46] The A_{595}/A_{462} value for the nanorods is 0.077, while the nanocube and nanooctahedron samples generated ratios that were negligibly low. In the case of a perfect sample of CeO_2 nanorods, the surface oxygen concentration should be 9.5×10^{19}/g, a value that is three and seven times greater than those of the cube and octahedron forms, respectively [47], meaning that the probability of oxygen vacancies appearing on the surfaces of the CeO_2 nanorods is higher than for the other two morphologies. Theoretical studies have shown that the oxygen vacancy formation energy of different CeO_2 surfaces follows the order (110) < (100) < (111) [12,48], hence oxygen vacancies are more readily formed on the CeO_2(110) planes. Our previous work [2] has also proven that CeO_2(110) possesses the highest concentration of oxygen vacancies, followed by CeO_2(100) and CeO_2(111), and this explains why the catalytic activity of CeO_2(100) is superior to that of CeO_2(100) and CeO_2(111). This phenomenon demonstrates that the oxygen vacancies of CeO_2 are capable of functioning as redox sites and hence act as active sites for this reaction.

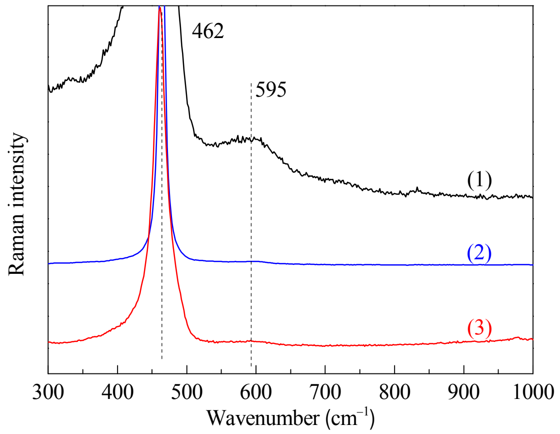


Fig. 6. Raman spectra of (1) CeO_2 nanorods, (2) CeO_2 nanocubes and (3) CeO_2 nanooctahedra.

Table 3
Synthesis of an imine from benzyl alcohol and aniline over different CeO_2 crystal planes. [a]

Entry	Shape	Crystal plane [b]	T [c]	Imine yield [d] (%)
1	rod	(110)/(100)= 2/1	9.5	97 (4.618+0.143) [e,f]
2	cube	(100)	2.9	5.7 (0.143)
3	octahedron	(111)	1.4	3.8 (0.095)

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), CeO_2 (100 mg), *p*-xylene (2 mL), 60 °C, for 2 h, O_2. [b] The theoretical exposed crystalline planes and their ratio were obtained from the literature [42]. [c] Total number of surface oxygen atoms ($\times10^{19}$/g). [d] Yield = conversion × selectivity, the conversions are based on benzyl alcohol consumption as determined by GC. [e] Data in parentheses indicate the moles of product per reaction time (h) per gram of CeO_2 (units: mmol/(g·h)). [f] These values indicate the results for the (110) and (100) planes.

4. Conclusions

In summary, we have successfully synthesized various imines by the aerobic oxidative coupling of alcohols and amines using pure CeO_2 as a non-noble metal heterogeneous catalyst under oxygen. In the absence of a base or additives, a diverse range of substituted imines can be obtained with moderate to excellent yields. We have demonstrated that the CeO_2(110) crystal planes are more active than the (100) and (111) planes during the synthesis of an imine from benzyl alcohol and aniline, because these planes possess the greatest concentration of oxygen vacancies. The data obtained in this work suggests that the redox properties of CeO_2 are crucial for this reaction.

References

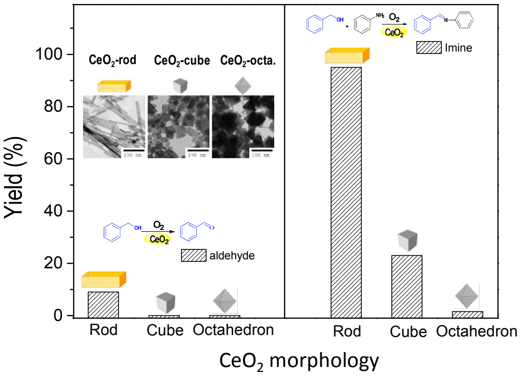
[1] Wang M, Wang F. *Chin J Catal*, 2014, 35: 453
[2] Wang M, Wang F, Ma J P, Li M R, Zhang Z, Wang Y H, Zhang X C, Xu J. *Chem Commun*, 2014, 50: 292
[3] Li Y, Shen W J. *Sci Chin Chem*, 2012, 55: 2485
[4] Li Y, Shen W J. *Chem Soc Rev*, 2014, 43: 1543
[5] Ta N, Liu J Y, Shen W J. *Chin J Catal*, 2013, 34: 838
[6] Trovarelli A. *Catal Rev - Sci Eng*, 1996, 38: 439
[7] Vivier L, Duprez D. *ChemSusChem*, 2010, 3: 654
[8] Sun C W, Li H, Chen L Q. *Energy Environ Sci*, 2012, 5: 8475
[9] Senanayake S D, Stacchiola D, Rodriguez J A. *Acc Chem Res*, 2013, 46: 1702
[10] He J L, Xu T, Wang Z H, Zhang Q H, Deng W P, Wang Y. *Angew Chem Int Ed*, 2012, 51: 2438
[11] Huang X S, Sun H, Wang L C, Liu Y M, Fan K N, Cao Y. *Appl Catal B*, 2009, 90: 224
[12] Si R, Flytzani-Stephanopoulos M. *Angew Chem Int Ed*, 2008, 47: 2884
[13] Ta N, Liu J Y, Chenna S, Crozier P A, Li Y, Chen A L, Shen W J. *J Am*

Graphical Abstract

Chin. J. Catal., 2015, 36: 1623–1630 doi: 10.1016/S1872-2067(15)60869-5

An investigation of the effects of CeO_2 crystal planes on the aerobic oxidative synthesis of imines from alcohols and amines

Zhixin Zhang, Yehong Wang, Min Wang, Jianmin Lü, Lihua Li, Zhe Zhang, Mingrun Li, Jingyang Jiang*, Feng Wang*
Dalian University of Technology;
Dalian Institute of Chemical Physics, Chinese Academy of Sciences



The crystal planes of CeO_2 affect its catalytic performance during the oxidative coupling of alcohols and amines to imines. The (110) plane, having the highest concentration of oxygen vacancies, exhibits the most pronounced redox ability.

Chem Soc, 2012, 134: 20585
[14] Xie X W, Li Y, Liu Z Q, Haruta M, Shen W J. *Nature*, 2009, 458: 746
[15] Namai Y, Fukui K-i, Iwasawa Y. *J Phys Chem B*, 2003, 107: 11666
[16] Wang Y H, Wang F, Song Q, Xin Q, Xu S T, Xu J. *J Am Chem Soc*, 2013, 135: 1506
[17] Gawronski J, Wascinska N, Gajewy J. *Chem Rev*, 2008, 108: 5227
[18] Zhang Z, Wang F, Wang M, Xu S T, Chen H J, Zhang C F, Xu J. *Green Chem*, 2014, 16: 2523
[19] Grirrane A, Corma A, Garcia H. *J Catal*, 2009, 264: 138
[20] Smolensky E, Kapon M, Eisen M S. *Organometallics*, 2007, 26: 4510
[21] Tang L, Sun H Y, Li Y F, Zha Z G, Wang Z Y. *Green Chem*, 2012, 14: 3423
[22] Kim J W, He J L, Yamaguchi K, Mizuno N. *Chem Lett*, 2009, 38: 920
[23] Cano R, Ramon D J, Yus M. *J Org Chem*, 2011, 76: 5547
[24] Esteruelas M A, Honczek N, Olivan M, Onate E, Valencia M. *Organometallics*, 2011, 30: 2468
[25] Kwon M S, Kim S, Park S, Bosco W, Chidrala R K, Park J. *J Org Chem*, 2009, 74: 2877
[26] Soule J F, Miyamura H, Kobayashi S. *Chem Commun*, 2013, 49: 355
[27] Blackburn L, Taylor R J K. *Org Lett*, 2001, 3: 1637
[28] He W, Wang L D, Sun C L, Wu K K, He S B, Chen J P, Wu P, Yu Z K. *Chem Eur J*, 2011, 17: 13308
[29] Shiraishi Y, Ikeda M, Tsukamoto D, Tanaka S, Hirai T. *Chem Commun*, 2011, 47: 4811
[30] Liu P, Li C, Hensen E J M. *Chem Eur J*, 2012, 18: 12122
[31] Chen B, Li J, Dai W, Wang L Y, Gao S. *Green Chem*, 2014, 16: 3328
[32] Kegnaes S, Mielby J, Mentzel U V, Christensen C H, Riisager A. *Green Chem*, 2010, 12: 1437
[33] Pérez J M, Cano R, Yus M, Ramón D J. *Eur J Org Chem*, 2012, 2012: 4548
[34] Sithambaram S, Kumar R, Son Y C, Suib S L. *J Catal*, 2008, 253: 269
[35] Sun H, Su F Z, Ni J, Cao Y, He H Y, Fan K N. *Angew Chem Int Ed*, 2009, 48: 4390
[36] Li H X, Wang X T, Wen M W, Wang Z X. *Eur J Inorg Chem*, 2012, 2012: 5011
[37] Gnanaprakasam B, Zhang J, Milstein D. *Angew Chem Int Ed*, 2010, 49: 1468
[38] Kang Q, Zhang Y G. *Green Chem*, 2012, 14: 1016
[39] Rigoli J W, Moyer S A, Pearce S D, Schomaker J M. *Org Biomol Chem*, 2012, 10: 1746
[40] Xu J, Zhuang R Q, Bao L L, Tang G, Zhao Y F. *Green Chem*, 2012, 14: 2384
[41] Tamura M, Tomishige K. *Angew Chem Int Ed*, 2015, 54: 864
[42] Mai H X, Sun L D, Zhang Y W, Si R, Feng W, Zhang H P, Liu H C, Yan C H. *J Phys Chem B*, 2005, 109: 24380
[43] Shyu J Z, Weber W H, Gandhi H S. *J Phys Chem*, 1988, 92: 4964
[44] Popovic Z V, Dohcevic-Mitrovic Z, Konstantinovic M J, Scepanovic M. *J Raman Spectrosc*, 2007, 38: 750
[45] Pu Z Y, Lu J Q, Luo M F, Me Y L. *J Phys Chem C*, 2007, 111: 18695
[46] Li L, Chen F, Lu J Q, Luo M F. *J Phys Chem A*, 2011, 115: 7972
[47] Wang Y H, Wang F, Zhang C F, Zhang J, Li M R, Xu J. *Chem Commun*, 2014, 50: 2438
[48] Sayle T X T, Parker S C, Sayle D C. *Phys Chem Chem Phys*, 2005, 7: 2936

Page numbers refer to the contents in the print version, which include both the English version and extended Chinese abstract of the paper. The online version only has the English version. The pages with the extended Chinese abstract are only available in the print version.