

Preliminary Study of Pd/CeO₂ Derived from Cerium Complexes as Solid Support Catalysts for Hydrogenation Reaction in a Micro-reactor

W. Wattanathana, A. Lakkham, N. Koonsaeng, A. Laobuthee and C. Veranitisagul*

Abstract— This work was studied on the Pd/CeO₂ used as solid support for hydrogenation reaction in micro-reactor. A simple cerium complex for CeO₂ was prepared from cerium nitrate and triethanolamine in 1-propanol. The feasible structures of cerium complexes as four-coordinate and five-coordinate TEA-Ce complexes were determined by MS and FTIR. By calcining the TEA-Ce complexes at 600°C for 2 h, the single phase of CeO₂ identified by XRD was obtained.

Pd/CeO₂, the hydrogenation catalyst support, was prepared by doping palladium nitrate into the cerium complex before calcining at 600°C for 2 h and investigated by XRD and SEM. The Pd-doped CeO₂ was preliminarily studied for catalytic hydrogenation of 4-cyanobenzaldehyde in a continuous-flow micro-reactor. Among all Pd/CeO₂ prepared, 10% Pd doped CeO₂ exhibited the greatest performance towards hydrogenation of 4-cyanobenzaldehyde in terms of the amount of hydrogenated products as 4-cyanobenzyl alcohol, 4-hydroxymethylbenzylamine, and 4-hydroxymethyltoluene.

Keywords— Ceria, cerium complex, hydrogenation, micro-reactor

1. INTRODUCTION

Cerium(IV) oxide (ceria or CeO₂) has been considered as materials for applications of automotive exhaust catalyst [1], polishing material [2], reforming reaction catalyst [3], and electrochemical device [4]. The success of the material applications depended on the routes of powder synthesis, many synthetic routes were, therefore, proposed in the relevant literatures, such as solid-solid reaction [5] co-precipitation of hydroxides [6] sol-gel method [7]. However, The obtained ceramic powders lack of homogeneity and purity, complicated procedure, or high processing temperature leading to high cost were found from these synthetic routes. Laobuthee *et al.* [8]-[14] successfully prepared various high purity and homogeneous ceramic powders from the metal complexes decomposition method, a very simple, low cost, and straightforward process. Based upon the basis of this process, CeO₂ was successfully prepared [14].

Nowadays, hydrogenation reactions show important roles in pharmaceutical, chemical and petroleum industries. Yoswathananont *et al.* reported an efficient hydrogenation reaction in a tube reactor [15]. In this flow system, a substrate solution was running through narrow channels formed in the Pd/C packed column with provided various advantages, such as, reducing in mass transfer between phases, no need for separation of products from catalyst, and providing an efficient hydrogenation reaction.

In this work, our group proposed an idea to prepare Pd-doped CeO₂ prepared from mixtures of cerium complex with palladium nitrate salt for using as hydrogenation catalyst in flow system micro-reactor.

2. EXPERIMENTAL

2.1 Materials

Cerium(III) nitrate hexahydrate [Ce(NO₃)₃·6H₂O, 99.5% purity] was supplied from Acros Organics Co. Inc. (USA). Palladium nitrate hydrate [Pd(NO₃)₂·xH₂O] and 4-cyanobenzaldehyde were purchased from Aldrich Chemical Co. Inc (USA). Triethanolamine [TEA, N(CH₂CH₂OH)₃, 98% purity] and 1-propanol were obtained from Carlo Erba (Barcelona).

2.2 Instrumentals

The cerium complex was characterized by ESI-MS (Bruker Esquire mass spectrometer). Methanol was used as a solvent to prepare a cerium complex solution for mass analysis. The mass range of a complex was set from m/z 100 to 1000.

Fourier Transform infrared spectra were obtained by a Perkin-Elmer 2000-FTIR. Potassium bromide (KBr) as a matrix was mixed with a solid sample (0.3-0.5 wt %) by an agate mortar and pestle to prepare a pellet specimen for identifying the cerium complex functional group.

The decomposition of the cerium complex was studied by thermogravimetric analysis (TGA, a Perkin-Elmer TGA 7). Each sample (10 mg) was heated by heating rate 5°C/min in N₂ (20 psi) from 50-1000°C. The TGA balance flow meter was set at 20 psi N₂, while the purge flow meter was adjusted at 20 psi of synthetic air.

The powder product obtained after calcining a cerium complex was spread on glass microscope slides and then characterized by XRD (X'PertPRO MPD diffractometer) using nickel-filtered CuK_α radiation. Diffraction patterns were recorded over a range of 2θ angles from 5 to 90° and identified using the Joint Committee on Powder Diffraction Standards (JCPDS) file No. 34-0394.

Scanning Electron Microscope (SEM, a JEOL JSM-6510 scanning microscope) operating at an acceleration

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voltage of 5 kV, a work distance of 10 mm and magnification values in 5,000x was used to identify the microstructure of powder samples. Samples were mounted on stubs using a liquid carbon paste and then sputter coated with Pt to avoid particle charging.

2.3 Procedure

2.3.1 Preparation of CeO₂ from cerium complex

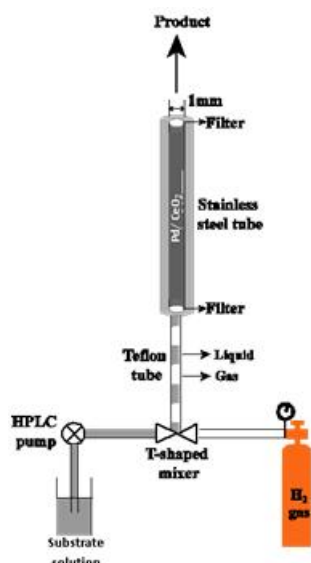
The mixture of cerium nitrate hexahydrate [Ce(NO₃)₃·6H₂O (10.86 g, 25 mmol)], triethanolamine (TEA, 3.4 ml, 25 mmol) and 200 ml of 1-propanol as a solvent, was added into a round bottomed flask and then heated for 2 h to complete the reaction. The homogeneous product was characterized by ESI-MS, FTIR, and TGA.

Cerium complex was calcined in the horizontal tube furnace at 600°C for 2 h. The powder product was ground in an alumina mortar and characterized by XRD and SEM.

2.3.2 Study on Pd/CeO₂ as solid support catalysts in hydrogenation reaction

Palladium nitrate hydrate [Pd(NO₃)₂·xH₂O, 0.1728, 0.2880 and 0.5760 g] was mixed with cerium complex (8.333 g) to prepare CeO₂ doped 3%, 5% and 10% by mol of palladium. The doped cerium complex was calcined in a furnace at 600°C for 2 h. The powder products were characterized by XRD and SEM.

Each of the Pd/CeO₂ powders was packed in a stainless steel tube (25 cm in length, 1.0 mm and 6.3 mm as inner and outer diameters, respectively) with two filters at both ends to hold the catalyst in the column, was performed in a high pressure flow system operating via a continuous-flow micro-reactor with the residence time of 2 min 50 s (Scheme 1). 4-Cyanobenzaldehyde in methanol as a substrate solution was mixed with hydrogen gas at the T-shaped mixer. The flow rate of the substrate solution controlled by HPLC pump was 0.038 mL/min while the hydrogen gas was set around 2.0 MPa. To observe the gas-liquid flow, a transparent teflon tube was connected between the T-shaped mixer and the tube column. The product solution eluted at the end of the column was characterized by ¹H-NMR.



Scheme 1

3. RESULTS AND DISCUSSION

3.1 Cerium complex preparation

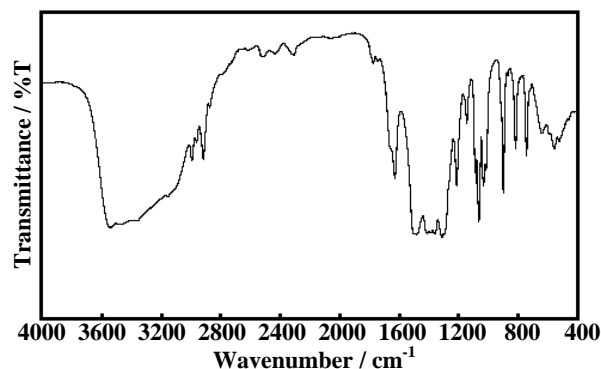


Figure 1. FTIR Spectrum of Cerium Complex

By FTIR, the yellowish powder obtained from the complete reaction of Ce(NO₃)₃ and TEA in 2 h was studied. FTIR spectrum (Figure 1) revealed characteristic groups in the cerium complex. The broad peak centered at 3402 cm⁻¹ was assigned to the O-H stretching due to moisture absorption and/or triethanolamine residue from the reaction. The peaks at 2988 and 2915 cm⁻¹ were assigned to asymmetric and symmetric modes of methylene (-CH₂-) stretching, respectively. The peak at 1627 cm⁻¹ was assigned to O-H bending overtone. The C-H bending bands were shown in the region of 1450-1200 cm⁻¹. The N-O stretching of nitrate group showed absorption bands in region of 1550-1250 cm⁻¹. The Ce-O-C bending resonated at 1082 cm⁻¹. Moreover, the band at 554 cm⁻¹ was assigned to Ce-O stretching.

The possible structures of the product were identified using electrospray ionization (ESI) techniques. The major peaks was appeared at m/z = 286 and 349. The structures of product were proposed in Figure 2.

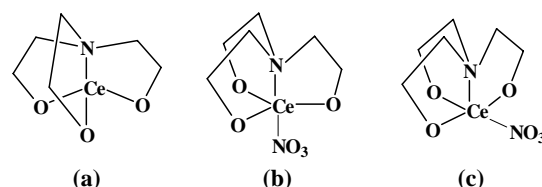


Figure 2. The Possible Structures of Cerium Complex:
(a) Corresponding to m/z = 286,
(b) and (c) Corresponding to m/z = 349

To obtain CeO₂, TGA was used to clarify the appropriate calcination temperature for the cerium complex. Thermogram (Figure 3) shows three regions of mass loss. The first mass loss involved the decomposition of the organic ligand occurs between 100° and 250°C. In this step, volatiles and char were generated. The obtained char was continuously oxidized by heating from 250° to 500°C as shown in the region of second mass loss. The TGA result indicated that the appropriate temperature for calcination was 600°C. Hence, cerium complex was then calcined at 600°C for 2 h to obtain a yellowish color of CeO₂.

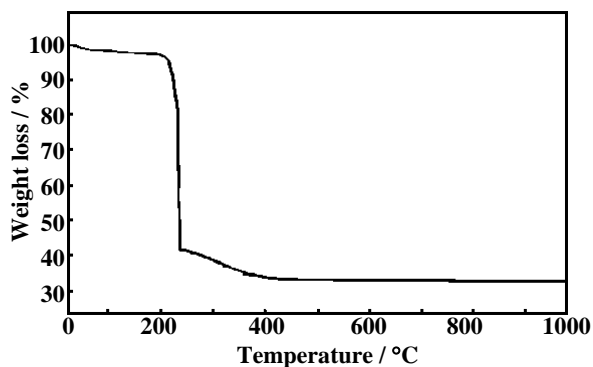
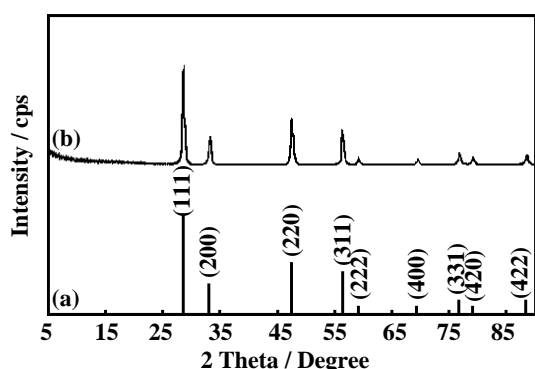


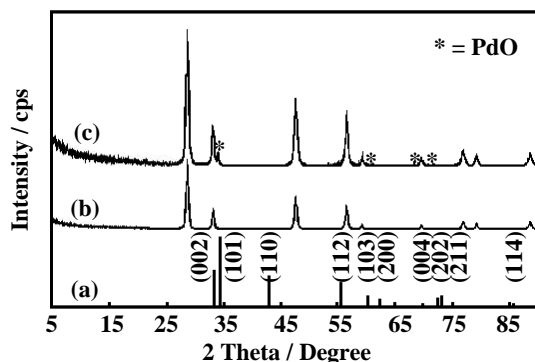
Figure 3. Thermogram of Cerium Complex

X-ray powder diffraction pattern (Figure 4) of the calcined product showed nine major peaks of CeO₂ with *hkl* reflections at (111), (200), (220), (311), (222), (400), (331), (420), and (422) which are located at 2θ are 28.555, 33.082, 47.479, 56.335, 59.087, 69.402, 76.700, 79.070, and 88.412, respectively. All peak positions were identified by comparing with JCPDS file No. 34-0394, indicating the phase purity of CeO₂.

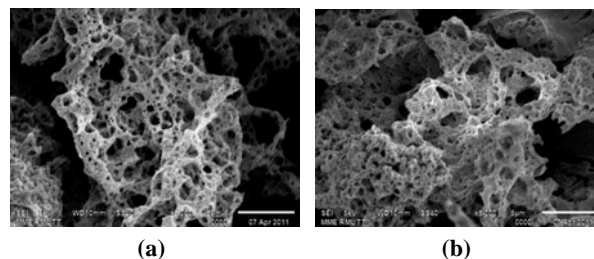
Figure 4. (a) CeO₂ Reference (JCPDS No 34-0394)
(b) XRD Pattern of Prepared CeO₂

3.2 Study on Pd/CeO₂ as solid support catalysts in hydrogenation reaction

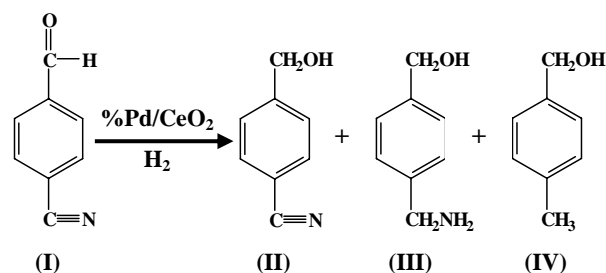
The obtained Pd doped cerium complexes are black-yellow color powders while the cerium complex was a yellow powder. The Pd doped cerium complexes were calcined with the same condition as an undoped cerium complex (600°C for 2 h) to obtain the brown powder products. To confirm the successfully doping of palladium on CeO₂, XRD and SEM were employed.

Figure 5. (a) PdO Reference (JCPDS No 88-2434)
(b) XRD Pattern of Prepared CeO₂ and
(c) XRD Pattern of 10% Pd-doped CeO₂

By comparing XRD patterns of single phase CeO₂ and Pd-doped CeO₂ (Figure 5), it was found that no difference in CeO₂ matrix phase, however, there are some addition peaks generated in Pd-doped CeO₂ implying the presence of palladium (II) oxide.

Figure 6. SEM Micrographs of (a) CeO₂ and
(b) 10%Pd/CeO₂

SEM micrographs of CeO₂ and 10%Pd doped CeO₂ were shown in Figure 6. The CeO₂ and 10%Pd/CeO₂ exhibit the foam-like structures containing various sizes of porosity. In this work, all of the samples; 0%, 3%, 5%, and 10% Pd/CeO₂, were preliminarily applied as catalysts for hydrogenation of 4-cyanobenzaldehyde. The obtained products from hydrogenation were shown in Scheme 2 while the amount of products quantitatively analyzed by ¹H-NMR was presents in Table 1.



Scheme 2

Table 1 Catalytic Activity of Pd/CeO₂ to Hydrogenation Reaction

% Pd in CeO ₂	Compound (%)			
	(I)	(II)	(III)	(IV)
0%	0	0	0	0
3%	0	3.6	81	15.4
5%	0	0	88.7	11.3
10%	0	0	84	16

Aldehyde and cyanide functional groups consisting in 4-cyanobenzaldehyde (I) were hydrogenated by Pd/CeO₂ to obtain 4-cyanobenzyl alcohol (II), 4-hydroxybenzylamine (III), and 4-hydroxybenzyltoluene (IV) (Table 1). No starting material remained in this condition. As comparing the results with that of 5% NiAl₂O₄ and 5% Pd/C studied previously by Ummartyothin *et al.*[11] and Yoswathananont *et al.* [15], respectively, the same products (II and III) were obtained but the product (IV) was only obtained in this work. The results indicated that Pd/CeO₂, especially 10%Pd/CeO₂, shows the most efficiency to use as a catalyst for hydrogenation of 4-cyanobenzaldehyde.

4. CONCLUSION

The cerium complex decomposition which retains the advantages of purity, homogeneity, low processing temperatures is an inexpensive, straightforward alternative to prepare CeO₂. A pure and homogeneous CeO₂ powder was obtained by calcining the cerium complex at 600°C for 2 h.

The doping palladium on CeO₂ was successfully prepared by calcining the mixture of cerium complex with palladium nitrate at 600°C for 2 h. Among all prepared Pd/CeO₂, 10% Pd/CeO₂ showed the greatest performance towards hydrogenation reaction of 4-cyanobenzaldehyde in terms of the highest 4-hydroxymethyltoluene. In addition, the catalytic efficiency of the prepared Pd/CeO₂ for hydrogenation reaction in the continuous-flow micro-reactor was higher than Pd/C and Pd/NiAl₂O₄.

ACKNOWLEDGMENT

This work was supported by Junior Science Talent Project (JSTP-50-19R) and National Science and Technology Development Agency (NSTDA) and the Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (ADB-MUA). The authors would like to thank Dr. Nungruethai Yoswathananont and Prof. Masaaki Sato from Department of Chemistry, Faculty of Science, Osaka Prefecture University, Osaka, Japan for helping in the study on the hydrogenation by using a continuous-flow micro-reactor.

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