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### C-3 alkylation of oxindoles with alcohols by Pt/CeO<sub>2</sub> catalyst in additive-free conditions

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**Abstract:** In a series of transition metal-loaded CeO<sub>2</sub> catalysts and Pt-loaded catalysts on various supports, Pt-loaded CeO<sub>2</sub> shows the highest activity for the selective C-3 alkylation of oxindole with octanol. The catalyst is effective for alkylation of oxindole and N-substituted oxindole with a series of substituted benzyl, linear, hetero-aryl alcohols under additive-free conditions and is recyclable. Our results demonstrate the first additive-free catalytic system for this reaction. Mechanistic studies show that this system is driven by the borrowing-hydrogen pathway. Structure-activity relationship studies show that co-presence of surface Pt<sup>0</sup> species on Pt metal clusters and basic support is indispensable for this catalytic system.

### Introduction

Oxindole and their derivatives, particularly C-3 functionalized oxindoles, are important intermediate in pharmaceutical industry due to their biological activity. These include the antiinflammatory Tenidap<sup>1</sup> and anti-cancer kinase inhibitor Sunitinib.<sup>2</sup> The conventional C-3 alkylation of oxindoles with alkyl halides has serious drawbacks such as poor regioselectivity, the formation of dialkylated products, formation of salt wastes and use of hazardous reagents. Recently, much attention has been focused on the use of alcohols as economic and environmentally benign alkylating reagents in indirect C-C bond formation reactions<sup>3-10</sup> so-called borrowing-hydrogen<sup>3</sup> (or hydrogen-autotransfer<sup>4</sup>) methodology, where alcohol is initially dehydrogenated, then undergoes a functionalization reaction, and finally, re-hydrogenated. Wenkert has first described the C-3 alkylation of oxindole with alcohols in the presence of excess amount of Raney nickel.<sup>11</sup> Simig and co-workers reported the C-3 alkylation of oxindole with alcohols at 150-220 °C with relatively less amount of Raney Ni, but the system was still non-catalytic; substrate/catalyst molar ratio was 10:17.<sup>12</sup> Recently, Madsen and a co-worker<sup>13</sup> and Grigg et al.<sup>14</sup> independently reported the first catalytic C-3 alkylation of oxindole with alcohols at 110 °C by homogeneous catalysts (2 mol% RuCl<sub>3</sub>/PPh<sub>3</sub><sup>13</sup>; 2.5 mol% [IrCp\*Cl<sub>2</sub>]<sub>2</sub><sup>14</sup>) in the presence of strong base (10-20 mol% of KOH or NaOH). Liu et al.<sup>15</sup> developed a support-immobilized Ir complex as reusable catalysts for this reaction. However, the system has drawbacks such as narrow scope and needs of sub-stoichiometric amount of strong base (KOH) and an organic ligand. As a part of our continuing interest in the heterogeneous catalysis for hydrogen-transfer

reactions<sup>16-19</sup> (such as Pt-catalyzed C-3 alkylation of indoles with alcohols<sup>19</sup>), we report herein the first additive-free catalytic system for C-3 selective alkylation of indole with alcohols by Pt-loaded CeO<sub>2</sub> as a reusable heterogeneous catalyst.

### Experimental Section

*General:* Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) were used without further purifications. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA<sup>+</sup>-5 (Frontier Laboratories Ltd.) using nitrogen as the carrier gas.

*Catalyst:* CeO<sub>2</sub> (JRC-CEO-1, 157 m<sup>2</sup> g<sup>-1</sup>), MgO (JRC-MGO-3), TiO<sub>2</sub> (JRC-TIO-4) and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (JRC-SAL-2) were supplied from Catalysis Society of Japan. ZrO<sub>2</sub> was prepared by hydrolysis of zirconium oxynitrate 2-hydrate by an aqueous NH<sub>4</sub>OH solution, followed by filtration, washing with distilled water, drying at 100 °C for 12 h, and by calcination at 500 °C for 3 h.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by calcination of  $\gamma$ -AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. Precursor of 1 wt% Pt/CeO<sub>2</sub> catalyst was prepared by an impregnation method; a mixture of CeO<sub>2</sub> and an aqueous HNO<sub>3</sub> solution of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was evaporated at 50 °C, followed by drying at 90 °C for 12 h. A pre-reduced catalyst (named Pt/CeO<sub>2</sub>) was prepared by pre-reduction of the precursor in a pyrex tube under a flow of H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>) at 500 °C for 0.5 h. Platinum oxides-loaded CeO<sub>2</sub> (PtOx/CeO<sub>2</sub>), as a comparative catalyst, was prepared calcination of the precursor at 300 °C for 3 h. By using various supports, several pre-reduced Pt catalysts were prepared by the same method as Pt/CeO<sub>2</sub>. CeO<sub>2</sub>-supported metal catalysts, M/CeO<sub>2</sub> (M = Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir) with metal loading of 1 wt% were prepared by impregnation method in the similar manner as Pt/CeO<sub>2</sub> using aqueous solution of metal nitrates (for Co, Ni, Cu, Ag), RuCl<sub>3</sub>, IrCl<sub>3</sub>, or aqueous HNO<sub>3</sub> solution of Rh(NO<sub>3</sub>)<sub>3</sub> or Pd(NO<sub>3</sub>)<sub>2</sub>.

*XANES/EXAFS:* X-ray absorption near-edge structures (XANES) and X-ray absorption fine structure (EXAFS) at Pt L<sub>3</sub>-edge were measured at the BL14B2 in the SPring-8 (Proposal No. 2012A1734). The storage ring was operated at 8 GeV. A Si(111) single crystal was used to obtain a monochromatic X-ray beam. The spectra of Pt/CeO<sub>2</sub> and PtOx/CeO<sub>2</sub> were obtained in the fluorescent mode using a Lytle detector, and that of Pt foil was obtained in a transmittance mode. The Pt/CeO<sub>2</sub> catalyst pre-reduced in a flow of 100% H<sub>2</sub> (20 cm<sup>3</sup> min<sup>-1</sup>) for 0.5 h at 500 °C was cooled to room temperature in the flow of H<sub>2</sub> and was sealed in cells made of polyethylene under N<sub>2</sub>, and then the EXAFS spectrum was taken at room temperature. The spectra of Pt foil and PtOx/CeO<sub>2</sub> were recorded without the pre-reduction treatment. The EXAFS analysis was performed using the REX version 2.5 program (RIGAKU). The parameters for the Pt–O and Pt–Pt shells were provided by the FEFF6.

*In situ IR :* In situ IR (infrared) spectra were recorded at 40 °C using a JASCO FT/IR-4200 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 40 mg of self-supporting wafer ( $\phi$  = 2 cm) and mounted into the quartz IR cell with CaF<sub>2</sub> windows. Spectra were measured accumulating 30 scans at a resolution of 4 cm<sup>-1</sup>. A reference spectrum of the catalyst wafer in He taken at measurement temperature was subtracted from each spectrum. Prior to the experiment the disk of Pt/CeO<sub>2</sub> was heated in H<sub>2</sub> flow (20 cm<sup>3</sup> min<sup>-1</sup>) at 500 °C for 0.5 h, followed by cooling to 40 °C and purging with He. Then, the catalyst

was exposed to a flow of CO(5%)/He ( $20 \text{ cm}^3 \text{ min}^{-1}$ ) for 180 s, followed by purging with He ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) for 600 s.

*Typical procedures of catalytic test:* Pt/CeO<sub>2</sub> was used as a standard catalyst. After the pre-reduction at 500 °C, we carried out catalytic tests using a batch-type reactor without exposing the catalyst to air as follows. Typically, the mixture of oxindole (1.0 mmol) and 1-octanol (1.1 mmol) in mesitylene (1.5 g) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube) through a septum inlet, followed by filling N<sub>2</sub>. Then, the resulting mixture was magnetically stirred for 24 h under reflux condition; the bath temperature was 170 °C and reaction temperature was ca 165 °C. After cooling the mixture, followed by removal of the catalyst, the mixture was purified with column chromatography and analyzed by <sup>1</sup>H NMR and GCMS. For the screening and catalyst recycle studies, conversion of indole and yield of C-3 alkylated product were determined by GC using *n*-dodecane as an internal standard.

## Results and discussion

We chose the alkylation of oxindole (1 mmol) with 1-octanol (1.1 mmol) as a model reaction for optimization of catalysts and conditions. Table 1 summarizes the results of the initial catalyst screening test under the same reaction conditions (reflux in mesitylene under N<sub>2</sub> for 24 h) using 1 mol% of transition metal-loaded CeO<sub>2</sub>. The Ru and Ir-loaded CeO<sub>2</sub> and CeO<sub>2</sub> itself were completely inactive. Co, Ni, Cu, Rh, Re, Ir, and Au catalysts showed low yield of the C-3 alkylated oxindole (2-16%). In contrast, Pt-loaded CeO<sub>2</sub> (Pt/CeO<sub>2</sub>) showed 99% yield of the C-3 alkylated oxindole. Then, we studied the support effect on the activity of Pt-loaded catalysts. Pt/MgO and Pt/CeO<sub>2</sub> gave higher yield (99%) than the other catalysts. Especially, Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> gave low yields (12, 17%). Combined with a well known classification on acid-base character of metal oxides,<sup>20</sup> it is suggested that the basic oxides (MgO and CeO<sub>2</sub>) are more effective than acidic oxides (Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>). On the basis of the fact that Pt/CeO<sub>2</sub> showed higher yield (96%) after 6 h than Pt/MgO (73%), we adopted Pt/CeO<sub>2</sub> as the standard catalyst.

To discuss the relationship between the structure of Pt species and catalytic activity, we carried out spectroscopic characterizations of these catalysts. Fig. 1A and 1B show XANES and EXAFS spectra of Pt/CeO<sub>2</sub>, platinum oxides-loaded CeO<sub>2</sub> (PtO<sub>x</sub>/CeO<sub>2</sub>) and a reference compound (Pt foil). The values of the coordination numbers for Pt-O and Pt-Pt shells as well as the distances derived from the EXAFS analysis are shown in Table 2. The XANES spectrum of PtO<sub>x</sub>/CeO<sub>2</sub> shows a strong white line peak at 11564 eV, which is generally observed for platinum oxides. The EXAFS of PtO<sub>x</sub>/CeO<sub>2</sub> consists of a Pt-O contribution (4.9 Pt-O bonds at the distance of 2.00 Å). The EXAFS result indicates that the dominant Pt species in PtO<sub>x</sub>/CeO<sub>2</sub> is cationic (oxidic) Pt species highly dispersed on the support, which is consistent with the XANES results. In contrast, the XANES spectrum of Pt/CeO<sub>2</sub> is nearly identical to that of Pt foil, which indicates that the electronic state of the Pt species in Pt/CeO<sub>2</sub> is metallic. The EXAFS of Pt/CeO<sub>2</sub> consists of a Pt-Pt contribution (7.7 Pt-Pt bonds at the distance of 2.73 Å). The Pt-Pt distance less than that of bulk Pt (2.76 Å) and the Pt-Pt coordination number lower than that of bulk Pt (12) are characteristic features of a few nm-sized Pt metal clusters.<sup>21</sup> As shown in Table 1, PtO<sub>x</sub>/CeO<sub>2</sub> was inactive for the reaction (entry 11), while Pt metal clusters on CeO<sub>2</sub> showed 99% yield. Combined with the structural results, it is concluded that oxidic Pt species are inactive and Pt metal clusters are active species.

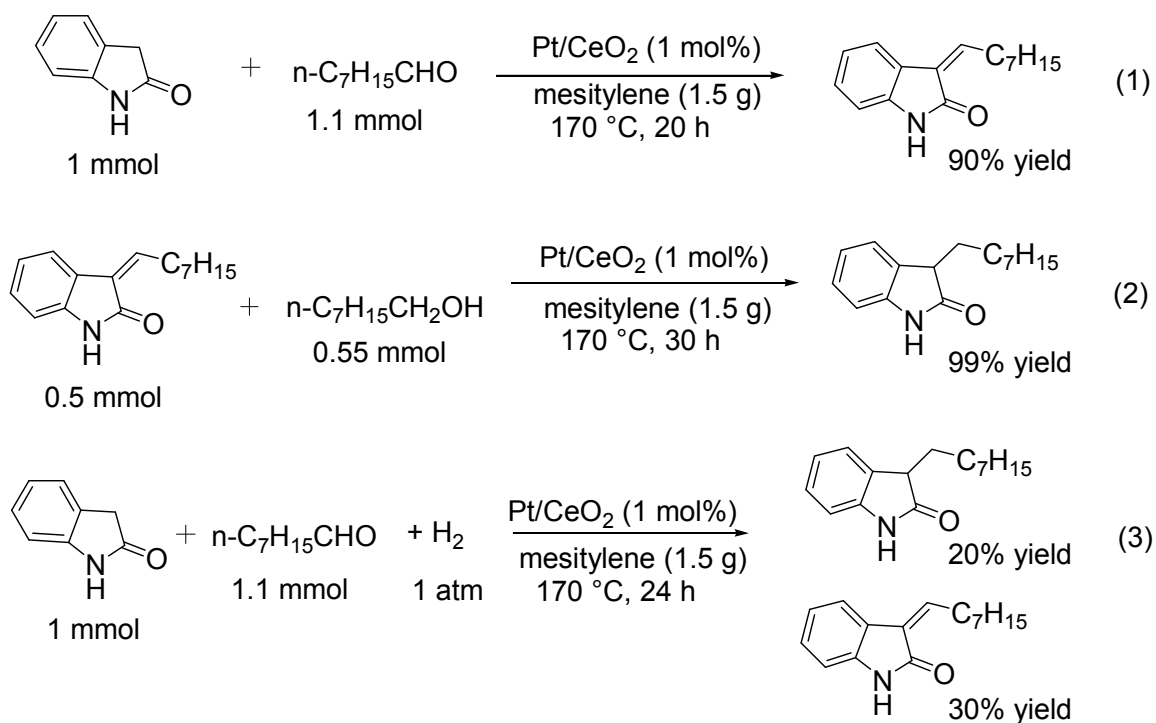
The catalyst named Pt/CeO<sub>2</sub>-air, prepared by exposing Pt/CeO<sub>2</sub> to the ambient conditions for 0.5 h, showed lower yield than as-reduced Pt/CeO<sub>2</sub>. This suggests that the metallic Pt<sup>0</sup> species on the surface of Pt nanoparticles are the active species and re-oxidation of them by O<sub>2</sub> under ambient conditions results in the catalyst deactivation. This hypothesis is confirmed by the following results. IR spectroscopy with CO as a probe molecule allows monitoring of the changes in the electronic states of Pt surface. As shown in Fig. 2, the IR spectra of CO adsorbed on Pt/CeO<sub>2</sub> showed a band at 2064 cm<sup>-1</sup> assignable to linearly coordinated CO on metallic Pt.<sup>18</sup> Upon exposure to air at room temperature for 0.5 h, the intensity of the band due to CO-Pt<sup>0</sup> decreased. Combined with the result of catalytic test, it is clarified that the surface metallic Pt<sup>0</sup> sites are the catalytically active species. Summarizing the above results, we conclude that co-presence of surface Pt<sup>0</sup> species on Pt metal clusters and basic support are indispensable elements in this catalytic system.

With the most effective catalyst, Pt/CeO<sub>2</sub>, we investigated general applicability of the present catalytic system. Table 3 shows the scope of C-3 alkylation of oxindole with different alcohols using 1 mol% of the catalyst. Various aliphatic primary alcohols including linear and branched aliphatic alcohols (entries 1-6) were tolerated, giving 100% conversion of oxindole and good to high yield of the corresponding C-3 alkylated oxindoles. The reactions of oxindole and benzylalcohols with an electron-donating or an electron-withdrawing substituent proceeded in moderate to excellent yield (entries 7-11). This method was also applicable for the alcohol with less stable substituent, *o*-substituted benzylic alcohol (entry 8). The catalyst was applicable to a heterocyclic alcohol containing nitrogen atoms (entry 12). The reactions of a *N*-alkylated oxindole with benzyl and aliphatic primary alcohols resulted in excellent yield (entries 13,14). Note that the turnover number (TON) for the alkylation of oxindole with benzylalcohol (entry 7) was 95, which is higher than those of in the previous homogeneous systems: TON of 45 for RuCl<sub>3</sub>/PPh<sub>3</sub>/KOH<sup>13</sup> and TON of 36 for [IrCp\*Cl<sub>2</sub>]<sub>2</sub>/KOH.<sup>14</sup>

The reaction of oxindole with 1-octanol was completely terminated by removal of the catalyst from the reaction mixture after 1.5 h; further heating of the filtrate for 24 h under the reflux condition did not increase the yield. ICP-AES analysis of the filtrate confirmed that the content of Pt in the solution was below the detection limit. These results confirm that the reaction is attributed to the heterogeneous catalysis of Pt/CeO<sub>2</sub>. Figure S1 shows the results of catalyst reuse. After the reaction of cycle 1 (entry 1, Table 2), the catalyst was separated from reaction mixture by centrifugation and was dried at 90 °C at 12 h and then reduced in H<sub>2</sub> at 500 °C for 0.5 h. The recovered catalyst showed nearly quantitative yield at least two times.

As proposed in the previous papers on the C-3 alkylation of oxindole with alcohols,<sup>13,14</sup> the present reaction can proceed through the hydrogen-borrowing pathway, which is evidenced by the following results. The reaction of *n*-octanal and indole with Pt/CeO<sub>2</sub> under N<sub>2</sub> resulted in the formation of the aldol condensation product, alkenyl-oxindole, in a quantitative yield (eq. 1). The same reaction was catalyzed by CeO<sub>2</sub> with higher reaction rate than Pt/CeO<sub>2</sub> (result not shown). Considering that solid base catalysts catalyze the aldol condensation reaction,<sup>17</sup> the result indicates that basic site of the CeO<sub>2</sub> support can be the active site for the aldol condensation of aldehyde and oxindole. Then, the aldol condensation product was isolated and underwent the transfer hydrogenation with 1-octanol (1.1 equiv) as a hydrogen donor in the presence of Pt/CeO<sub>2</sub> under N<sub>2</sub>. As shown in eq. 2, the C=C bond in the aldol condensation product was hydrogenated

to give the C-3 alkylated oxindole in a quantitative yield. Molecular hydrogen, which can be produced during the alkylation of oxindole with alcohols, might hydrogenate the alkenyl-oxindole, but the following result excludes this possibility. The reaction of *n*-octanal and indole with Pt/CeO<sub>2</sub> under 1 atm H<sub>2</sub> resulted in only 20% yield of the hydrogenated product accompanying alkenyl-oxindole in 30% yield (eq. 3). Based on the above results, we propose the mechanism for Pt/CeO<sub>2</sub>-catalyzed alkylation of oxindole in Fig. 2. The reaction begins with the dehydrogenation of alcohol to carbonyl compound accompanied by the generation of Pt-H species. Then, CeO<sub>2</sub>-catalysed aldol condensation between aldehyde and oxindole occurs to give the aldol condensation product, alkenyl-oxindole. Finally, hydrogen transfer from Pt-H species to the C=C bond of the alkenyl-oxindole gives the alkylated oxindole.



## Conclusions

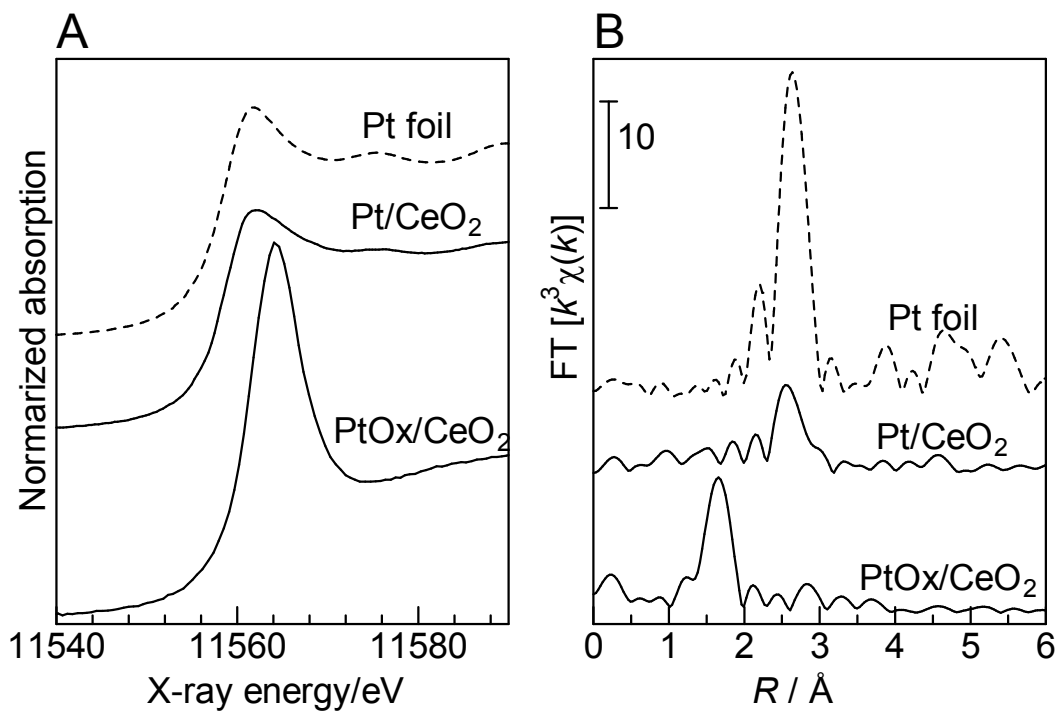
We have developed the first additive-free method for catalytic C3 alkylation of oxindole with various alcohols by Pt-loaded CeO<sub>2</sub> catalyst driven by the borrowing-hydrogen pathway. Considering the fact that the previous catalytic systems need sub-stoichiometric amount of strong base and expensive organic ligands, our method provides the most environmentally benign catalytic system for C-3-alkylated oxindoles from oxindoles and alcohols because of the following advantages: (1) no needs of basic co-catalyst and organic ligands, (2) easy catalyst/product separation, (3) catalyst reuse, (4) wide scope including aliphatic alcohols and *N*-substituted oxindole, and (5) high TON. Structure-activity relationship studies show that both surface Pt<sup>0</sup> species on Pt metal clusters and basic support are indispensable elements in this catalytic system.

### Acknowledgment

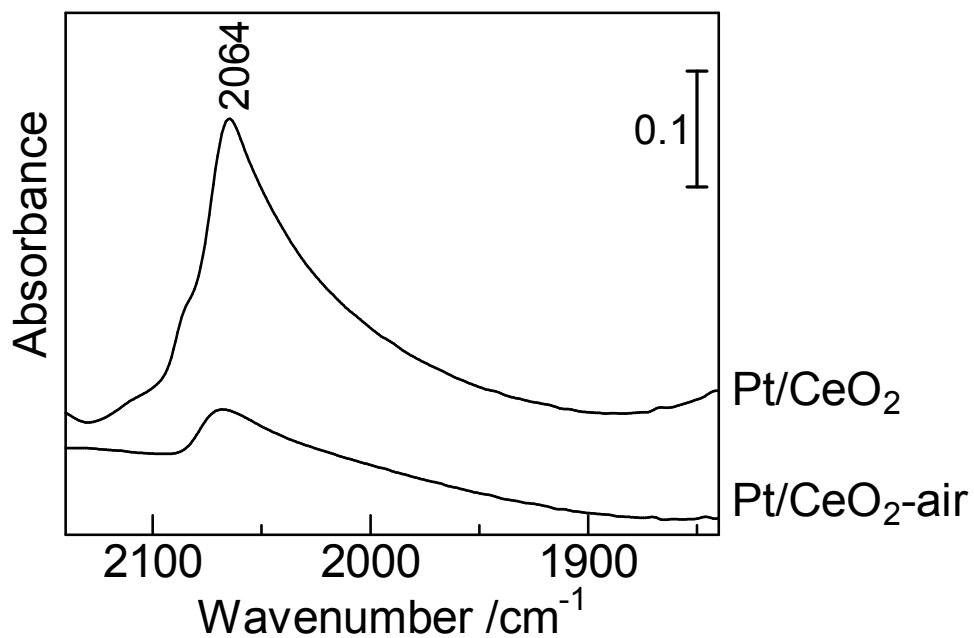
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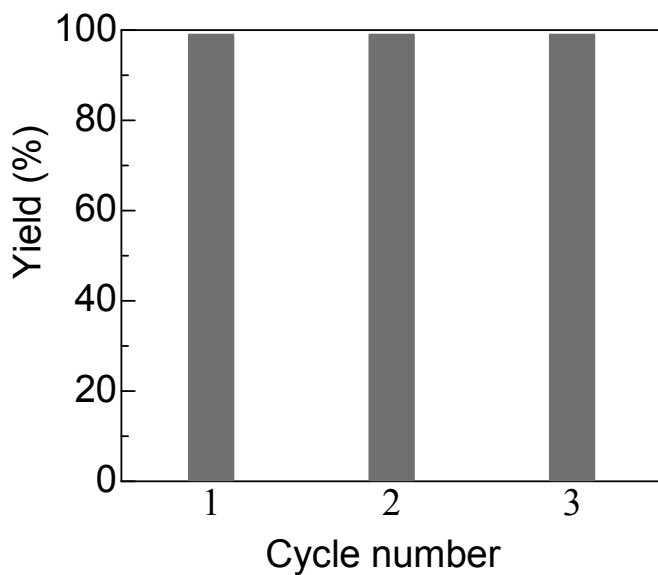


**Fig. 1** Pt L<sub>3</sub>-edge XANES spectra (A) and EXAFS Fourier transforms (B).

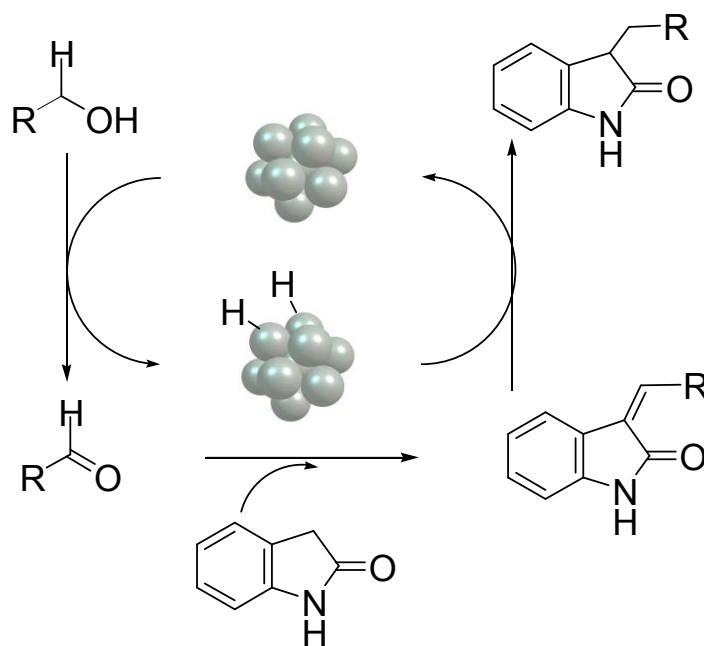


**Fig. 2** IR spectra of CO adsorbed on Pt/CeO<sub>2</sub> (after H<sub>2</sub>-reduction at 500 °C for 0.5 h) and Pt/CeO<sub>2</sub>-air (after re-oxidation of Pt/CeO<sub>2</sub> under air at room temperature for 0.5 h) at 40 °C.

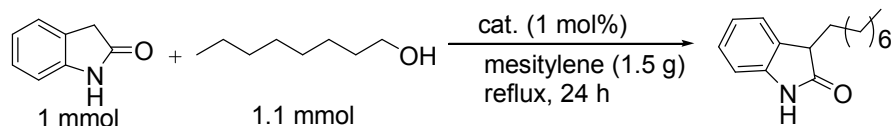




**Fig. 3** Catalyst reuse for alkylation of oxindole by 1-octanol with by Pt/CeO<sub>2</sub>. Conditions are the same as those in Table 3 (entry 1).



**Fig. 4** Possible mechanism for C-3 alkylation of oxindole with alcohols by Pt/CeO<sub>2</sub>.

**Table 1.** Alkylation of oxindole by 1-octanol with 1 wt% metal (M)-loaded CeO<sub>2</sub> catalysts.

entry	catalyst	conv.(%)	yield (%)
1	Co/CeO <sub>2</sub>	13	8
2	Ni/CeO <sub>2</sub>	20	2
3	Cu/CeO <sub>2</sub>	30	21
4	Ru/CeO <sub>2</sub>	0	0
5	Rh/CeO <sub>2</sub>	8	5
6	Pd/CeO <sub>2</sub>	88	40
7	Ag/CeO <sub>2</sub>	14	10
8	Ir/CeO <sub>2</sub>	0	0
9	Pt/CeO <sub>2</sub>	99	99
10 <sup>a</sup>	Pt/CeO <sub>2</sub> -air	99	75
11 <sup>b</sup>	PtOx/CeO <sub>2</sub>	10	0
12 <sup>c</sup>	CeO <sub>2</sub>	10	0
13	Pt/MgO	99	99
14	Pt/TiO <sub>2</sub>	99	94
15	Pt/ZrO <sub>2</sub>	99	71
16	Pt/Al <sub>2</sub> O <sub>3</sub>	99	27
17	Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	84	12

<sup>a</sup> Pre-reduced Pt/CeO<sub>2</sub> was exposed to air at room temperature for 0.5 h.

<sup>b</sup> Tested without pre-reduction.

<sup>c</sup> Catalyst amount was 50 mg.

**Table 2.** Curve-fitting analysis of Pt L<sub>3</sub>-edge EXAFS.

Sample	Shell	N <sup>a</sup>	R / Å <sup>b</sup>	σ / Å <sup>c</sup>	R <sub>f</sub> / % <sup>d</sup>
PtOx/CeO <sub>2</sub>	O	4.9	2.00	0.044	3.5
Pt/CeO <sub>2</sub>	Pt	7.7	2.73	0.084	2.3
Pt foil	Pt	(12)	(2.76)	-	-

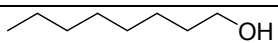
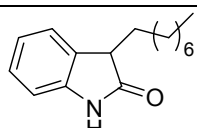
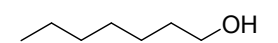
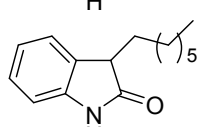
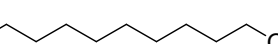
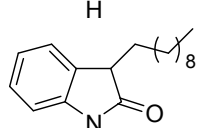
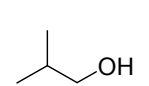
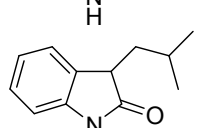
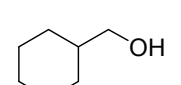
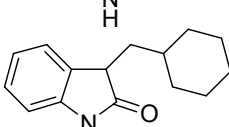
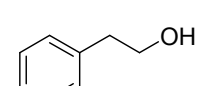
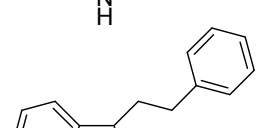
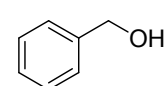
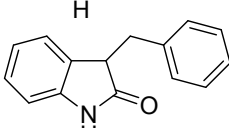
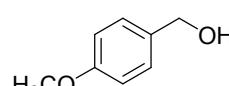
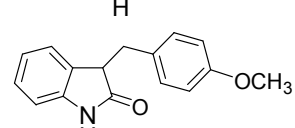
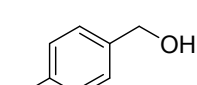
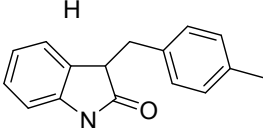
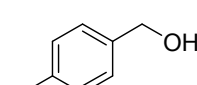
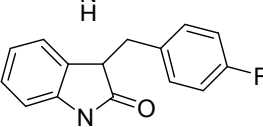
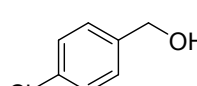
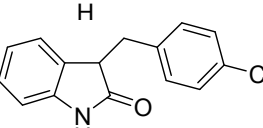
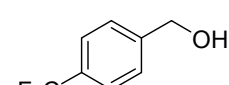
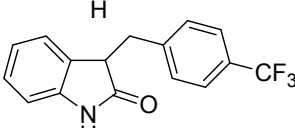
<sup>a</sup> Coordination numbers.

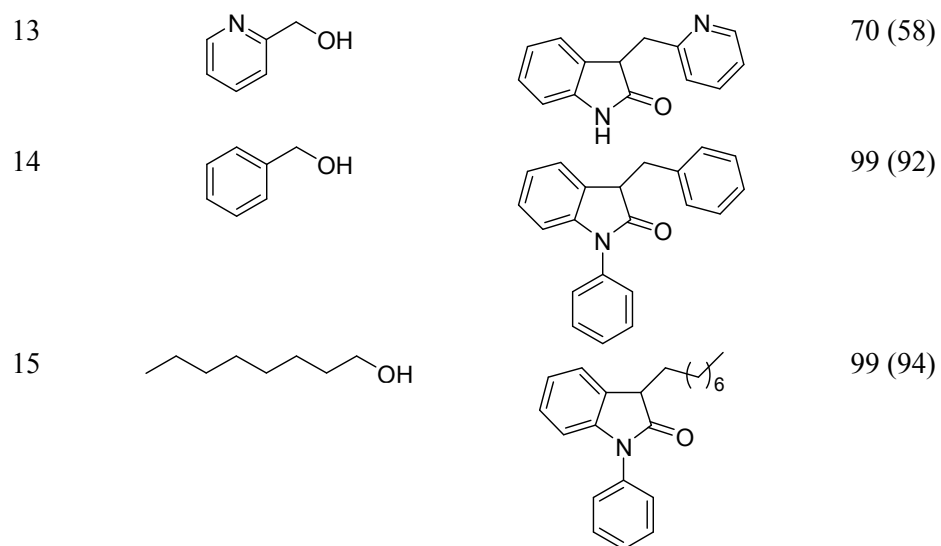
<sup>b</sup> Bond distance.

<sup>c</sup> Debye-Waller factor.

<sup>d</sup> Residual factor.

**Table 3.** Alkylation of oxindole with different alcohols using Pt/CeO<sub>2</sub>.<sup>a</sup>

entry	alcohols	products	yield (%) <sup>b</sup>
1			99 (95)
2			99 (90)
3			90 (82)
4			90 (79)
5			99 (92)
6			99 (90)
7			99 (95)
8 <sup>c</sup>			79
9			60 (54)
10			99 (89)
11			99 (92)
12			99 (85)



<sup>a</sup> 0.01 mmol Pt, 1 mmol oxindole, 1.1 mmol alcohol, 1.5 g mesitylene, 170 °C, 24 h, in N<sub>2</sub>.

<sup>b</sup> GC yield. Isolated yield is in the parentheses.

<sup>c</sup> 1 mmol oxindole, 1.5 mmol alcohol, 1.5 g mesitylene, 155°C, 24 h

**For Table of contents**

Pt-loaded CeO<sub>2</sub> acted as an effective and recyclable catalyst for alkylation of oxindoles with alcohols under additive-free conditions.

