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Project Title: Investigation of Forming Pd Single Atoms on CePdO_x Surfaces via Controlled Modification Procedures

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Ceria is a well-known oxygen storage catalyst widely used for the exhaust system of automobiles to remove pollutants, reforming processes for hydrogen production, and water gas shift reactions [1-3]. The success of ceria-based materials is mainly ascribed to the unique combination of high oxide-ion diffusivity with the redox cycle of Ce³⁺ and Ce⁴⁺ states [3]. Recently, ceria has been shown to catalyze the partial hydrogenation of propyne with a high selectivity [4-6]. Although it required high temperature and slow space velocity, ceria offers a unique opportunity to design and develop a stable and easy regeneration catalyst system to effectively address the selectivity issue of selective hydrogenation reactions, including gas-phase hydrogenation of acetylene in ethylene for polyethylene industry [5,6] and selective hydrogenation of alkynes to alkenes in liquid phase.

As reported in the 1st year, semi-hydrogenation of alkynes to alkenes is an important transformation that is followed by both large industrial process and the smaller scale of fine chemical and pharmaceutical industries. In the 2nd year of the project, the investigation focuses on the uses of supported palladium-ceria for liquid-phase semi-hydrogenation of ethyl phenylpropionate (EPP).

The batch semi-hydrogenation reaction products are isolated and analyzed for the calculation of conversion and selectivity of reactions to measure the efficiency of catalysts under different reaction conditions, such as variables of reaction time, catalyst loading, Pd loading, Ce loading, reduction procedure, etc. The addition of ceria to palladium as a promoter for enhancing the selectivity of the catalyst has also been evaluated. The results show that support material, reduction temperatures and ceria promoter did play important roles. The results of alumina and active carbon supported Pd and/or Pd-ceria catalysts are summarized below:

The activity and selectivity of various catalysts are summarized in Table 1, including Al₂O₃ and activated carbon (AC) supported Pd catalysts and Ce modified Pd on active carbon. As shown in Table 1, the AC supported Pd is not as active as Al₂O₃ supported Pd. 0.05% Pd/γ-Al₂O₃ is more active than 1% Pd/AC even with much less Pd loading. However, AC supported Pd appears to be a bit more selective and more stable in terms of catalyst leaching. Al₂O₃ appears to break down during the reaction and is difficult to recycle.

Table 1. Conversion and selectivity of hydrogenation of EPP over ceria promoted Pd catalysts.

Catalyst	Reaction time (min)	EPP Conversion (%)	Selectivity, cis-ethyl cinnamate (%)	Selectivity, trans-ethyl cinnamate (%)	Selectivity, ethyl hydrocinnamate (%)
0.05% Pd/γ-Al ₂ O ₃	60	85.8	84.2	5.2	10.6
0.05% Pd/AC	60	0.0	0.0	0.0	0.0
0.1% Pd/AC	60	0.0	0.0	0.0	0.0
1% Pd/AC	60	46.2	91.2	2.8	6.0
1% Pd/AC	120	100	73.2	5.6	21.2
1% Pd-0.2% Ce/AC	120	99.8	80.5	6.7	12.8
1% Pd-0.5% Ce/AC	120	100	82.6	5.4	12.0
0.5% Pd/AC	120	100	84.9	4.5	10.6
0.5% Pd-0.5% Ce/AC	120	87.6	91.6	1.1	7.3
0.5% Pd-1% Ce/AC	120	50.0	92.4	2.7	4.9

Reaction conditions: reduction at 300°C (1h) followed by reaction in 5 ml of methanol at 25°C using 40 mg of catalysts and 100 mg ethyl phenylpropionate.

Among ceria promoted Pd/AC, 0.5% Pd-0.5% Ce/AC shows the best combination of activity and selectivity to cis-ethyl cinnamate. With higher Pd loading, the selectivity decreases while conversion increases. On the other hand, with higher ceria loading, the activity of the catalysts decreases with increasing selectivity. We, therefore, focused on the investigation of treatment effects, including reduction temperatures of 300°C to 600°C to form PdCeO_x, on the 0.5% Pd-0.5% Ce/AC catalyst. The results of EPP conversion and the selectivity and yield of cis ethyl cinnamate are summarized in Table 2. The selectivity is typically high when the conversion is low. But, it decreases quickly when the conversion is approaching 100%. The activity order is 400°C ~ 500°C > 300°C > 600°C while the selectivity order is 600°C > 500°C ~ 300°C > 400°C. Overall, with 500°C reduction, its yield of cis ethyl cinnamate, as shown in Figure 1, is the highest of 90.9% at 30-min. But, it decreases with time quickly to 40.0% at 60-min and 8.0% at 120-min. The yield of 300°C reduced one is the 2nd highest. It starts with 63.9% at 30-min then increases to 84.2% at 60-min followed by decreasing. But, the decrease appears to be slow, with 56.8% at 120-min. Both 400°C

Table 2. Reduction temperature effect on 0.5% Pd-0.5% Ce/AC catalyst.

Reduction temperature (°C)	Reaction time (min)	Conversion (%)	Selectivity, cis-ethyl cinnamate (%)	Yield, cis-ethyl cinnamate (%)
300	30	63.9	100	63.9
	60	100	84.2	84.2
	90	100	65.4	65.4
	120	100	56.8	56.8
400	30	100	80.0	80.0
	60	100	21.4	21.4
	90	100	0.0	0.0
	120	100	0.0	0.0
500	30	100	90.9	90.9
	60	100	40.0	40.0
	90	100	16.5	16.5
	120	100	8.0	8.0
600	30	10.7	100	10.7
	60	16.0	100	16.0
	90	22.1	100	22.1
	120	28.3	100	28.3

Reaction conditions: 40 mg of catalysts and 100 mg ethyl phenylpropiolate in 5 ml of methanol at 25°C.

and 600°C ones are with low yields due to extreme high and low activities. It is interesting that the reduction temperature has a very critical impact on the performance of the catalyst, likely due to the properties of the formed PdCeOx after reduction. The detailed surface and bulk properties of PdCeOx will be investigated with in-situ FTIR, pulse chemisorption and temperature programmed techniques.

Impact of the Research: This project has provided significant amount of support for PI to mentor and train two undergraduate students and two Master students during the project year. Both master students finished their MS degrees, one in Spring 2019 and is working in industry and the other in Summer 2019 working on her PhD in Chemistry. One of the two undergraduates successful finished his BS degree in Spring 2019 and is working in industry. The other undergraduate is scheduled to finish his BS degree in Fall 2019.

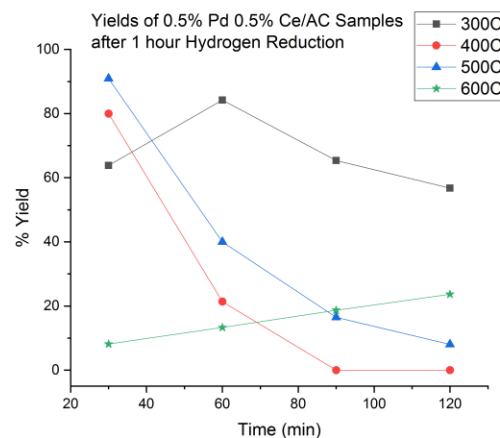


Figure 1. Yield of cis-ethyl cinnamate as a function of time over 0.5% Pd-0.5% Ce/AC reduced at various temperatures (1h).

Reference:

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