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### Authors

Chen, Lu-Ning  
Hou, Kai-Peng  
Liu, Yi-Sheng  
[et al.](#)

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# Efficient Hydrogen Production from Methanol Using A Single-Site Pt<sub>1</sub>/CeO<sub>2</sub> Catalyst

Lu-Ning Chen,<sup>1,2</sup> Kai-Peng Hou,<sup>1,3</sup> Yi-Sheng Liu,<sup>5</sup> Zhi-Yuan Qi,<sup>1</sup> Qi Zheng,<sup>1</sup> Yi-Hsien Lu,<sup>1</sup> Jia-Yu Chen,<sup>2</sup> Jeng-Lung Chen,<sup>6</sup> Chih-Wen Pao,<sup>6</sup> Shuo-Bo Wang,<sup>1</sup> Yao-Bin Li,<sup>7</sup> Shao-Hua Xie,<sup>8</sup> Fu-Dong Liu,<sup>8</sup> David Prendergast,<sup>4</sup> Leonard E. Klebanoff,<sup>9</sup> Vitalie Stavila,<sup>9</sup> Mark D. Allendorf,<sup>9</sup> Jinghua Guo,<sup>5</sup> Lan-Sun Zheng,<sup>2</sup> Ji Su,<sup>\*,1,4</sup> Gabor A. Somorjai<sup>\*,1,3</sup>

<sup>1</sup> Materials Sciences Division, <sup>4</sup> Molecular Foundry, Material Science Division, <sup>5</sup> Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States.

<sup>2</sup> State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

<sup>3</sup> Department of Chemistry, University of California-Berkeley, Berkeley, California 94720, United States.

<sup>6</sup> National Synchrotron Radiation Research Center, Science-Based Industrial Park Hsinchu 30076, Taiwan.

<sup>7</sup> Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.

<sup>8</sup> Department of Civil, Environmental, and Construction Engineering, Catalysis Cluster for Renewable Energy and Chemical Transformations (REACT), Nano-Science Technology Center (NSTC), University of Central Florida, Orlando, Florida, 32916, United States.

<sup>9</sup> Sandia National Laboratories, Livermore, CA 94551, United States.

## Supporting Information Placeholder

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**ABSTRACT:** Hydrogen is regarded as an attractive alternative energy carrier due to its high gravimetric energy density and only water production upon combustion. However, due to its low volumetric energy density, there are still some challenges in practical hydrogen storage and transportation. In the last decade, using chemical bonds of liquid organic molecules as hydrogen carriers to generate hydrogen in situ provided a feasible method to potentially solve this problem. Research efforts on liquid organic hydrogen carriers (LOHCs) seek practical carrier systems and advanced catalytic materials that have the potential to reduce costs, increase reaction rate, and provide a more efficient catalytic hydrogen generation/storage process. In this work, we used methanol as a hydrogen carrier to release hydrogen in situ with the single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst. Moreover, in this reaction, compared with traditional nanoparticle catalysts, the single site catalyst displays excellent hydrogen generation efficiency, 40 times higher than 2.5 nm Pt/CeO<sub>2</sub> sample, and 800 times higher compared to 7.0 nm Pt/CeO<sub>2</sub> sample. This in-depth study highlights the benefits of single-site catalysts and paves the way for further rational design of highly efficient catalysts for sustainable energy storage applications.

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In order to reduce atmospheric pollution and greenhouse gas emission, developing clean energy sources has attracted growing interest. Among them, hydrogen is desirable as an alternative clean fuel, because it can be converted efficiently to energy without producing toxic products or greenhouse gases.<sup>[1]</sup> Nowadays, hydrogen is widely used in different fields, especially in polymer electrolyte membrane fuel cells (PEMFCs) due to its high gravimetric energy density (120 MJ/kg).<sup>[2]</sup> In contrast to other hydrogen transportation and storage approaches, such as compressed gas, or solid-state storage in metal hydrides and metal-organic frameworks (MOFs),<sup>[3,4]</sup> the liquid organic hydrogen carriers (LOHCs) concept involves transportation of hydrogen in liquids, and generating hydrogen in situ by breaking chemical bonds, often times in the presence of a catalyst.<sup>[5,6]</sup> There are advantages to transporting and handling liquids, such as added safety, greater energy density, and possibility of utilizing the existing gasoline and oil infrastructure and reduced costs overall.

For practical applications, a key factor is to look for an appropriate liquid organic molecule as hydrogen carrier.<sup>[7]</sup> Compared to other liquid organic molecules, methanol is a suitable molecule with high hydrogen gravimetric density. Moreover, methanol is relatively inexpensive and can be manufactured from a variety of sources which can be transformed from some harmful gas or greenhouse gases like CO, CO<sub>2</sub> and CH<sub>4</sub>.<sup>[8,9]</sup> In

addition, seeking an efficient catalyst to in situ generate large quantity of hydrogen in a short time is another significant factor. In catalytic hydrogen production, the traditional support metal catalysts typically need high temperature and high metal loadings to achieve a relatively good catalytic performance.<sup>[10]</sup> As previously studied, the size of metal particles is critically important in determining the performance of metal supported catalysts in many catalytic reactions.<sup>[11,12]</sup> Moreover, the ultimate small-size limit for particles is the single-site catalyst with isolated single metal sites dispersed on solid supports. With maximum atom-utilization efficiency (100 %), high specific activity and unique properties can be realized, single-site catalysts are emerging as a new frontier in catalytic science.<sup>[13-17]</sup>

Herein, we successfully synthesized single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst with single Pt sites anchored on porous CeO<sub>2</sub> supported by a modified ascorbic acid (AA)-assisted reduction route.<sup>[18-19]</sup> In the catalytic hydrogen production from methanol, compared with traditional Pt nanoparticles catalysts (2.5 nm Pt/CeO<sub>2</sub>, 7.0 nm Pt/CeO<sub>2</sub>), this single-site catalyst performed high activity at relative low temperature with low Pt loading. Additionally, this single-site catalyst can be applied to other alcohol catalytic hydrogen production.

In our study, porous CeO<sub>2</sub> nanorods (Figure S1) were chosen as the support to anchor Pt single atoms by AA-assisted reduction route, named Pt<sub>1</sub>/CeO<sub>2</sub>. Meanwhile, we also synthesized Pt nanoparticles with different sizes and loadings on CeO<sub>2</sub> by pre-synthesizing Pt nanoparticles and mixing them with CeO<sub>2</sub>, and the capping agent on Pt surface was further removed by UV-ozone treatment.<sup>[20,21]</sup> The loading amounts of Pt are both were about 1% wt. For convenience, the Pt nanoparticles loaded on CeO<sub>2</sub> are named 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>, whose sizes are determined by TEM measurement (Figure S2).

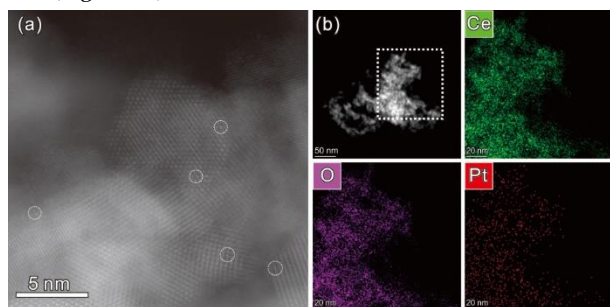


Figure 1. (a) Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst, the brighter dots cycled are Pt single sites, (b) HAADF-STEM and corresponding elemental mappings images of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst.

The loading status of Pt loading on CeO<sub>2</sub> catalysts were compared by powder X-ray diffraction (XRD) and transmission electron microscope (TEM). From the XRD data, there are no diffraction peaks observable from metallic Pt for all the three catalysts due to the low Pt content and small Pt particle sizes (Figure S3). In the bright-field TEM images of 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>, the Pt nanoparticles are uniformly dispersed on CeO<sub>2</sub> nanorods (Figure S4b, c). However, for Pt<sub>1</sub>/CeO<sub>2</sub> catalyst there is no apparent difference compared to original CeO<sub>2</sub> nanorods (Figure S1a), with no metallic clusters or particles being observed (Figure S4a). Moreover, from corresponding elemental mapping, the Pt signals are

uniformly distributed overall CeO<sub>2</sub> nanorods (Figure 1b). In order to further confirmed the actual Pt loading information on CeO<sub>2</sub>, the HAADF-STEM measurement was applied. As shown in Figure 1a, the Pt catalytic sites were atomically dispersed throughout the porous CeO<sub>2</sub>, and the actual Pt content was 0.15%.

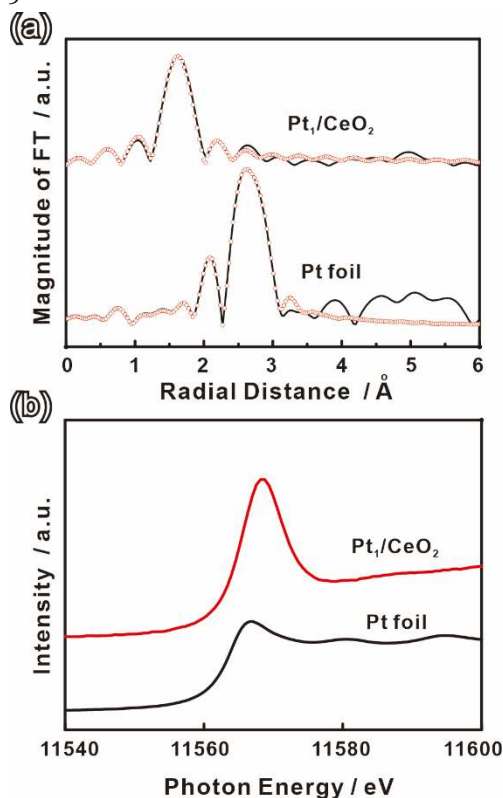


Figure 2. (a)  $k^3$ -weighted Fourier transform EXAFS spectra and (b) normalized XANES spectra of Pt<sub>1</sub>/CeO<sub>2</sub> and bulk Pt foil at the Pt L<sub>3</sub>-edge. The red hollow points are fitting results.

Extended X-ray absorption fine structure (EXAFS) spectra were acquired to provide the valence and coordinated structure of single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst. Compared with bulk Pt foil there is no nearest neighbor Pt-Pt bond observed in the single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst, while the notable peak observed between 1 to 2 Å is attributed to contribution of Pt-O bond (Figure 2). The Pt dispersion states for the three samples are further verified by in situ DRIFTS of CO absorption and desorption (Figure S5). For the single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst, three bands are observed, of which the bands at 2171 and 2117 cm<sup>-1</sup> are attributed to the CO gas, while that at 2090 cm<sup>-1</sup> are attributed to the linearly (on-top) bonded CO on Pt ionic species.<sup>[13, 18]</sup> However, for 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub> there is another band on at 2050 cm<sup>-1</sup> due to the linear absorbance of CO on the small sized Pt nanoparticles on CeO<sub>2</sub>.<sup>[13,22]</sup>

In the direct methanol catalytic hydrogen production, compared with traditional Pt nanoparticles (2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>), the single-site Pt loaded on CeO<sub>2</sub> (Pt<sub>1</sub>/CeO<sub>2</sub>) displayed excellent catalytic performance (Figure 3a). At the temperature below 150 °C, both the Pt single-site and Pt nanoparticle catalysts have no obviously catalytic activity. As the temperature was increased to above 150 °C, both the formation of hydrogen and carbon monoxide were detected. Further increasing the reaction temperature, more methanol was converted to hydrogen and carbon monoxide. Moreover, due to the size effect, the single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst performed

with higher activity for hydrogen production from methanol than the 7.0 nm Pt/CeO<sub>2</sub> and 2.5 nm Pt/CeO<sub>2</sub> counterparts. The turnover frequency (TOF) of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst is much higher than traditional Pt nanoparticle, up to 12500 h<sup>-1</sup> at 300 °C, which is 40 times that of 2.5 nm Pt/CeO<sub>2</sub> and almost 800 times that of 7.0 nm Pt/CeO<sub>2</sub>. Furthermore, the single-site Pt<sub>1</sub>/CeO<sub>2</sub> sample is highly stable: after reaction at 300 °C for 120 hours, the catalyst keeps more than 90% of its best activity (Figure 3b). The decrease of activity at initial times is due to the loss of unstable absorb Pt sites on CeO<sub>2</sub> surface. The Pt content of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst decreased to 0.13% after the first 10 hours of reaction and thereafter remains almost the same after 120 hours reaction. After long-time reaction, there is still no Pt-Pt bond detected by EXAFS (Figure S6) indicating there is no agglomeration happened even after long-time reaction at 300 °C.

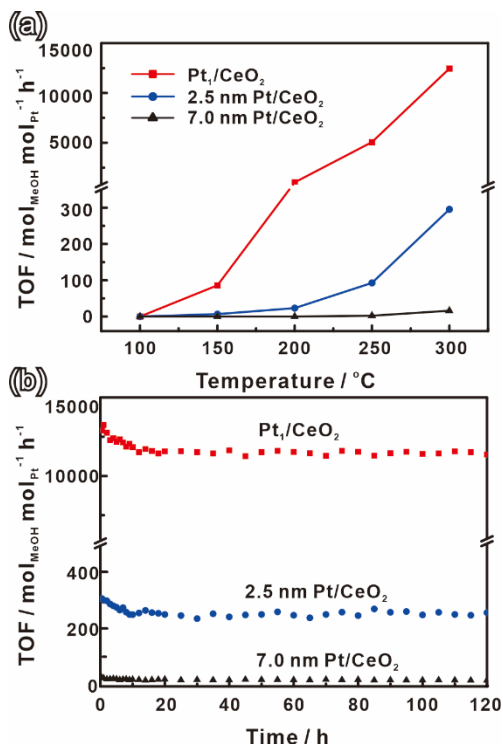


Figure 3. (a) Turnover frequency (TOF) of hydrogen production from methanol in terms of methanol conversion per Pt site of Pt<sub>1</sub>/CeO<sub>2</sub>, 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>, at different temperatures. (b) the stability Pt<sub>1</sub>/CeO<sub>2</sub>, 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub> at reaction condition at 300 °C.

The dehydrogenation mechanism of methanol on the Pt surface have been experimentally examined using advanced techniques such as: TPD, EELS, IR, UPS, and AES. The dehydrogenation mechanism has also been examined via DFT theoretical simulation.<sup>[10,23-25]</sup> These results indicate that, at low temperature, methanol molecularly adsorbs at the surface of Pt and then decomposes to form methoxy species by breaking the O-H bond. Then successively, the three C-H bonds will be broken up and generate the final products CO<sub>ads</sub> and H<sub>ads</sub>. Importantly, both experimental and computational results demonstrated that smaller Pt nanoparticle size favor the methanol dehydrogenation due to the energy barriers of both O-H and C-H bond cleavage, much lower on the defects and steps of the Pt surface.

We also measured the catalytic hydrogen production performance of single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst as a function of the

methanol feeding rate (Figure S7). At lower methanol feeding rate, the conversion of methanol is higher. When the feeding rate is 0.01 ml/min, methanol can totally convert to hydrogen, which proves that this catalyst can be applied in practical applications. As the feeding rate of methanol is increased, the TOF increases as well. The TOF is almost 15000 h<sup>-1</sup> at the feeding rate of 0.1 ml/min, illustrating the high catalytic activity of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst. We as well synthesized a series of Pt<sub>1</sub>/CeO<sub>2</sub> catalysts with different Pt content by controlling the feeding amount of Pt precursor (Figure S8a). And all the Pt/CeO<sub>2</sub> catalysts performed high activity in methanol dehydrogenation. However, the TOF decrease of Pt/CeO<sub>2</sub>-0.3% and 0.45%, due to Pt agglomeration at higher content (Figure S8b). No hydrogenation formation was detected with pure CeO<sub>2</sub> nanorods without Pt loading, indicating that the active site is Pt instead of CeO<sub>2</sub>.

Single-site catalysts are typically systems where the activity of a central metal atom/atoms relies on interactions with heteroatomic ligands (such as N or O bridge) that anchor it to metal atoms of the substrate. The electronic structure and reactivity of Pt are very sensitive to support. In our study, the Pt element valence states was proven to be another factor influencing its catalytic activity. The Pt and Ce valence states of Pt<sub>1</sub>/CeO<sub>2</sub>, 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub> are further confirmed by XPS analysis (Figure S9). Importantly, for the Pt 4f XPS spectra, the binding energies of Pt 4f<sub>2/7</sub> and 4f<sub>2/5</sub> in Pt<sub>1</sub>/CeO<sub>2</sub> are close to Pt<sup>2+</sup> species, indicating that Pt single-site supported on CeO<sub>2</sub> are oxidized owing to the electron transfer Pt to CeO<sub>2</sub>.<sup>[26]</sup> Interestingly, the Pt species of 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub> are mainly metallic Pt. The previous reports have certified that the Pt-CO bonding energy of CO absorption on positive Pt species is lower than on metallic Pt.<sup>[19,27]</sup> Thus, for the methanol dehydrogenation process, as the CO<sub>ads</sub> species forms, it is much easier to desorb CO from positive Pt sites in Pt<sub>1</sub>/CeO<sub>2</sub> than the metallic Pt sites of other two catalysts (Figure S10). Therefore, the size effect and valence states of Pt may explain the relative catalytic activity of these catalyst samples, with activity ordered as: single-site Pt<sub>1</sub>/CeO<sub>2</sub> >> 2.5 nm Pt/CeO<sub>2</sub> > 7.0 nm Pt/CeO<sub>2</sub>.

The single-site Pt<sub>1</sub>/CeO<sub>2</sub> also performed excellent catalytic activity in hydrogen production from other alcohols, namely ethanol, 1-propanol, isopropanol, 1-butanol, and benzyl alcohol (Figure 4). The proposed mechanism of the alcohol dehydrogenation process includes several steps. First, the alcohol molecules adsorb on Pt sites and form R<sub>1</sub>R<sub>2</sub>CHO<sub>ads</sub> by breaking O-H bond, then dehydrogenation into R<sub>1</sub>R<sub>2</sub>CO<sub>ads</sub>. As for methanol, after formaldehyde (CH<sub>2</sub>O) intermediate is formed, it will further dehydrogenate to yield formyl (CHO) and carbon monoxide (CO).<sup>[10,24,25]</sup> Hence, compared to other alcohols, all the hydrogen in methanol can be released to generate two molecules of H<sub>2</sub> and leave CO behind. For other longer chain alcohols, after aldehydes or ketones formed, more energy is needed for additional dehydrogenation steps. Moreover, for primary alcohols, the activity of substrates is decreased with the growth of carbon chain, and after transformation to corresponding aldehydes, some C-C bonds will be cleaved to form CO and alkanes. Besides, the hydrogen production from benzyl alcohol and isopropanol is higher, owing to their first dehydrogenated products are more stable.

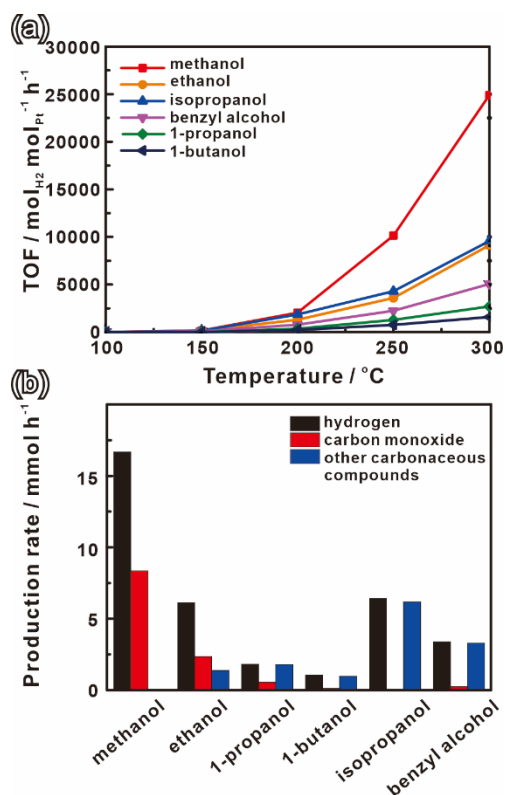


Figure 4. (a) Turnover frequency (TOF) of hydrogen production from different alcohol in terms of hydrogen production per Pt site of Pt<sub>1</sub>/CeO<sub>2</sub> at different temperature. (b) Products diffusion of different alcohol at 300 °C by Pt<sub>1</sub>/CeO<sub>2</sub> catalyst.

In summary, a well-defined single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalyst was developed and its catalytic performance was evaluated for hydrogen generation from methanol. Importantly, compared to the Pt/CeO<sub>2</sub> nanoparticle catalysts (2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>), the single-site catalyst Pt<sub>1</sub>/CeO<sub>2</sub>, exhibited reaction rates that are 40 and 800 times higher, respectively. Moreover, beside the methanol, this single-site catalyst performed high efficiency in other liquid alcohol hydrogen production. Ultimately, this in-depth study highlights the benefits of single-site catalyst and paves the way for further rational design of highly efficient catalysts for hydrogen production.

## ASSOCIATED CONTENT

### Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Experimental details, characterization data and partial catalytic data, including the synthesis of catalysts, the characterization of CeO<sub>2</sub> support and catalysts, the characterization of catalyst after reaction, and the catalytic result of some control tests.

## AUTHOR INFORMATION

### Corresponding Author

[jisu@lbl.gov](mailto:jisu@lbl.gov)

[somorjai@berkeley.edu](mailto:somorjai@berkeley.edu)

### Notes

The authors declare no competing financial interests.

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