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# Insights into the Mechanism of n-Hexane Reforming over a Single Site Platinum Catalyst

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**ABSTRACT:** We demonstrated the single site catalyst Pt<sub>1</sub>/CeO<sub>2</sub> greatly enhanced the selectivity of cyclization and aromatization in the n-hexane reforming reaction. Specifically, the selectivity of single site Pt<sub>1</sub>/CeO<sub>2</sub> towards both cyclization and aromatization is above 86 % at 350 °C. The turnover frequency (TOF) of Pt<sub>1</sub>/CeO<sub>2</sub> is 58.8 h<sup>-1</sup> at 400 °C, which is close to Pt cluster/CeO<sub>2</sub> (61.4 h<sup>-1</sup>), and much higher than Pt nanoparticle/CeO<sub>2</sub> with Pt size of 2.5 nm and 7 nm. Combined with the catalytic results of cyclopentane (MCP) reforming, the dehydrocyclization and further aromatization of n-hexane was attributed to the prominent adsorption of ring intermediate products on the single site Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. On the other side, with the multiple Pt adjacent active sites, the cluster and nanoparticle Pt/CeO<sub>2</sub> samples favor the C-C bond cracking reaction. Ultimately, this in-depth study unravels the principles of hydrocarbons activation with different Pt size and represents a key step towards the rational design of new heterogeneous catalysts.

Supported metal nanoparticles play a central role in various chemical transformations enabled by heterogeneous catalysis. Recently, the discovery of single site catalysts (SSCs), where single metal sites are anchored on a support via the interaction with neighboring atoms (e.g. N or O), has opened up a new research frontier in the catalysis field.<sup>[1-4]</sup> Many catalytic reactions have been explored, such as methane selectively oxidation to methanol and acetic acid using Rh SSCs,<sup>[5]</sup> CO oxidation and hydrogen generation from methanol using Pt SSCs,<sup>[6-8]</sup> etc. The reduction of particle size to single-atom level always achieves the maximum utilization of expensive noble metals, along with enhancement of activity, stability or selectivity.<sup>[9-10]</sup> However, typically in most application of SSCs, the scientists always focused on some small molecule reactant due to the lack of an ensemble of active metal atoms adjacent to the noble metal single atom.<sup>[11-12]</sup> Hence, investigating the reaction mechanism of a large probe molecule on SSCs and designing a novel catalytic material are the goal of our studies to accelerate the development of next generation SSCs.<sup>[4-9]</sup>

Catalytic reforming of linear hydrocarbons is one of the petroleum refining processes for upgrading light hydrocarbon feedstocks,<sup>[13]</sup> involving dehydrocyclization, isomerization, and dehydrogenation.<sup>[14-16]</sup> The hydrocarbon stream needs to be heated due to difficulty for C-H activation in reforming reactions. Pt and Pd nanoparticles dispersed on acidic supports such as silica, alumina, and zeolites are commonly used catalysts.<sup>[15-17]</sup> Previously, with n-hexane as a probe reactant, the reforming mechanism on Pt nanoparticles has been systematically studied in our group. The size effect and support effect have been illustrated clearly for pursuing a high selectivity of isomerization and dehydrogenation.<sup>[15-16]</sup> Recently, a significantly improvement on the activity and selectivity of hydrocarbons reforming reactions have been made by studies of single Pt and pseudo single Pt catalysts.<sup>[18-19]</sup> These works inspired us to further study the catalytic performance of Pt SSC, Pt cluster and Pt nanoparticle catalysts in n-hexane reforming, and clarify the reforming mechanism on these materials.

In this work, we successfully synthesized isolated Pt single atoms on CeO<sub>2</sub> catalyst (Pt<sub>1</sub>/CeO<sub>2</sub>), which obviously changes the product distribution of n-hexane reforming compared to Pt cluster and Pt nanoparticle catalysts (2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub>). Specifically, Pt<sub>1</sub>/CeO<sub>2</sub> displays a significantly higher selectivity of both dehydrocyclization and aromatization in n-hexane reforming. Key to this high selectivity is that the cracking reaction were inhibited due to the absence of multiple Pt reaction sites on single site Pt catalyst. And the cyclization and aromatization of hydrocarbons was attributed to prominent adsorption of intermediate products with a ring on the single site Pt<sub>1</sub>/CeO<sub>2</sub> catalysts.

The Pt<sub>1</sub>/CeO<sub>2</sub> catalyst was synthesized by a modified ascorbic acid-assisted reduction method, referred to previous literature.<sup>[8]</sup> As shown in Figure 1a, there was no obvious difference between the X-ray diffraction (XRD) patterns of CeO<sub>2</sub> supports before and after Pt loading, due to the low loading amount of Pt. It indicates the synthetic method has no significant effect on the CeO<sub>2</sub> support. To confirm the existence of Pt single sites, high resolution transmission electron microscopy (HRTEM) was applied. Both energy-

dispersive spectroscopy (EDS) mapping in Figure 1b and Cs-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) in Figure 1c showed that Pt atoms were homogeneously dispersed on CeO<sub>2</sub> nanorods. The Pt statement was further identified to single-site by XANES (Figure S4). Moreover, *in situ* diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO sorption on Pt<sub>1</sub>/CeO<sub>2</sub> catalyst reveals only one dominant vibrational mode at 2087 cm<sup>-1</sup> (Figure 1d), which can be assigned to the linearly adsorbed CO on Pt<sup>δ+</sup>. This result is consistent with the previously reported literature<sup>7</sup> and also proves the atomically dispersed Pt.

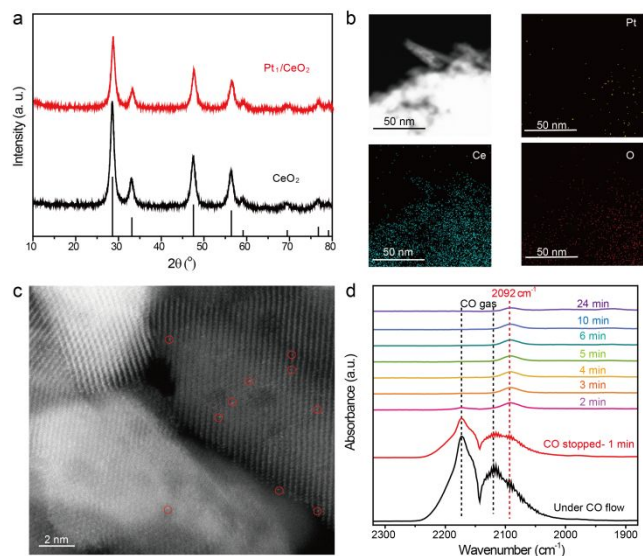


Figure 1. (a) XRD of Pt<sub>1</sub>/CeO<sub>2</sub> and pure CeO<sub>2</sub> support, respectively. (b) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and corresponding elemental mapping images of Pt<sub>1</sub>/CeO<sub>2</sub> (Pt: yellow; Ce: cyan; O: red). (c) Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) image of Pt<sub>1</sub>/CeO<sub>2</sub> catalyst, the red circled dots are single Pt sites. (d) *In situ* DRIFTS of CO adsorption and desorption on Pt<sub>1</sub>/CeO<sub>2</sub> catalysts.

n-Hexane reforming was chosen as the model reaction to explore the catalytic performance of Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. n-Hexane reforming was conducted over Pt<sub>1</sub>/CeO<sub>2</sub> at four different temperatures (350, 400, 450, 500 °C) (Figure 2a) and it shows distinct products distribution including cyclohexane, methyl-cyclopentane (MCP), benzene, isomers, and cracking products. Cyclization (cyclohexane and MCP) is the dominant reaction pathway at low temperature through activating C-H bond at primary and secondary carbon, which contributes the highest selectivity of 82 % at 350 °C. Benzene is the only aromatization product from the complete dehydrogenation of cyclohexane while no semi-dehydrogenation products were detected. Generally speaking, cracking, isomerization, and aromatization are favored at higher temperature over Pt<sub>1</sub>/CeO<sub>2</sub>. Conversely, the selectivity of cyclization products (i.e. cyclohexane and MCP) decreased at higher temperature. To clarify the size effect of Pt catalysts, Pt cluster and Pt nanoparticles were prepared and tested under the identical reaction conditions. Unlike single site

Pt<sub>1</sub>/CeO<sub>2</sub>, cracking is the dominant reaction over Pt clusters at all tested temperatures (Figure 2b-c, S13a) while 2.5 nm Pt/CeO<sub>2</sub> and 7.0 nm Pt/CeO<sub>2</sub> were almost inactive to n-hexane reforming until the temperature was over 450 °C, indicating the higher activity of Pt SSCs. To further evaluate the activity, the reaction conversion and total turnover frequency (TOF) of all tested catalysts were calculated and presented in Figure 2d. Pt<sub>1</sub>/CeO<sub>2</sub> exhibited a high TOF of 58.8 h<sup>-1</sup> at 400 °C and 75.7 h<sup>-1</sup> at 450 °C, which are comparable to Pt clusters and much higher than Pt NPs.

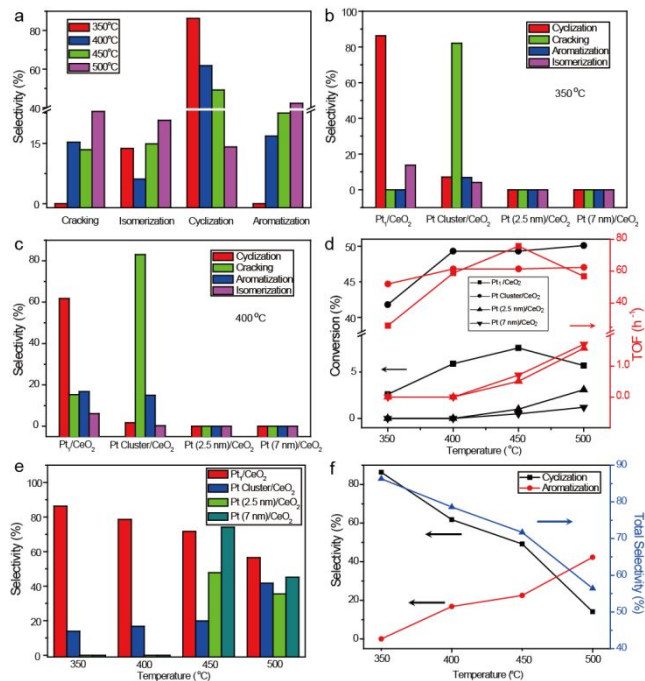


Figure 2. (a) Selectivity of n-hexane reforming over Pt<sub>1</sub>/CeO<sub>2</sub> at four tested temperatures (350, 400, 450, 500 °C). Selectivity of n-hexane reforming over different Pt catalysts at (b)350 °C and (c) 400 °C. (d) Total conversion and TOF of tested Pt catalysts at four reaction temperatures under ambient pressure. (e) Cyclization selectivity of n-hexane reforming using Pt catalysts with different sizes. (f) Cyclization, aromatization selectivity and total selectivity of both reactions using Pt<sub>1</sub>/CeO<sub>2</sub> catalyst.

The cyclization selectivity of Pt<sub>1</sub>/CeO<sub>2</sub>, Pt clusters and Pt nanoparticles were further compared in Figure 2e. At lower temperature (350 and 400 °C), Pt<sub>1</sub>/CeO<sub>2</sub> had a 5-fold enhanced cyclization selectivity compared to Pt cluster, while 2.5 and 7.0 nm Pt nanoparticles showed no selectivity towards cyclization products until the temperature was elevated to 450 and 500 °C. But for Pt<sub>1</sub>/CeO<sub>2</sub>, cyclization products decreased within the increasing reaction temperature, due to the further dehydrogenation of formed cyclohexane to benzene (Figure 2f). The total selectivity of cyclic products from cyclization and aromatization over Pt<sub>1</sub>/CeO<sub>2</sub> was lowered as the temperature increases. To investigate the temperature-dependent selectivity of Pt<sub>1</sub>/CeO<sub>2</sub>, HRTEM was first applied to examine the thermal stability of used Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. Pt could remain as single atoms up to 400 °C, while Pt clusters appeared after reaction at 450 °C (Figure S13b). Moreover, for catalyst after n-hexane

reforming at 500 °C, even some Pt nanoparticles (< 3 nm) could be observed. Therefore, the decreased cyclization selectivity and the drop in TOF at 500 °C could be explained by the appearance of Pt clusters/nanoparticles as a result of the instability of Pt SSCs above 450 °C. X-ray photoelectron spectroscopy (XPS) spectrum of used Pt<sub>1</sub>/CeO<sub>2</sub> after 450 °C reaction (Figure S17) revealed a lower shift of Pt binding energy compared to as-synthesized catalyst (Figure S9) and used catalyst after 400 °C reaction (Figure S16), which also suggests the Pt aggregation. Combined with catalytic results, a conclusion could be obtained that single-site Pt catalysts showed unique selectivity of dehydrocyclization of n-hexane.

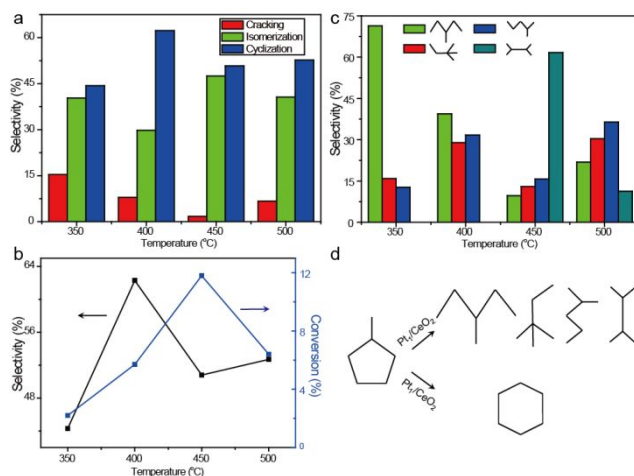


Figure 3. (a) Selectivity of Pt<sub>1</sub>/CeO<sub>2</sub> for methylcyclopentane (MCP) reforming at 350, 400, 450, 500 °C. The rearrangement of MCP to cyclohexane was regarded as cyclization. (b) Selectivity of ring-expansion reaction and total conversion of MCP reforming by Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. (c) Related selectivity of different isomers in MCP reforming using Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. (d) Schematic presentation of possible products of MCP reforming by Pt<sub>1</sub>/CeO<sub>2</sub>.

To further understand the mechanism of n-hexane reforming, MCP, as one reforming product in n-hexane reforming reaction, was also employed to evaluate the catalytic performance of different Pt catalysts. The selectivity of cyclization (i.e. ring expansion reaction), cracking, and isomerization over Pt<sub>1</sub>/CeO<sub>2</sub> at different reaction temperatures (350, 400, 450, 500 °C) were summarized in Figure 3a. Cyclohexane and hydrogenation isomers (Figure 3a) are the main products in MCP reforming at all temperatures, while only a small amount of cracking products was obtained. When compared with n-hexane reforming, a much higher conversion of MCP (Figure 3b) was obtained. This phenomenon proved that with the stronger adsorption of MCP, the produced cyclohexane is favored to be replaced by the following MCP molecules. We inferred this higher conversion also came from the activation of tertiary carbon atoms through C-H bond breaking, which is much easier to activate than terminal C-H in n-hexane. Therefore, the formation of the cyclic compounds is the key step in reforming of C<sub>6</sub> hydrocarbons on Pt<sub>1</sub>/CeO<sub>2</sub>. Because of the existence of a ring in MCP, continuous dehydrogenation reaction can proceed smoothly with less influence for the further isomerization by breaking C-C bond. Figure 3c

showed the further analysis on selectivity of different isomers in MCP reforming. No preferential isomer product was observed at 400 and 500 °C. The different isomerism selectivity at 350 °C and 450 °C were produced for the continuous dehydrogenation on the ring and the activation of C-C bond in MCP respectively. At low temperature (350 °C), continuous dehydrogenation in a five-member ring leads to open loop isomerization and at high temperature (450 °C), C-C bond will be activated to drive the isomerization process for the formation of Pt cluster. Dealing with much higher temperature, the higher energy leads to all the C-C bond could be broken and the random distribution of all the isomerization products. Figure 3d shows the detailed products appearing in the MCP reforming using single-site Pt<sub>1</sub>/CeO<sub>2</sub> catalysts.

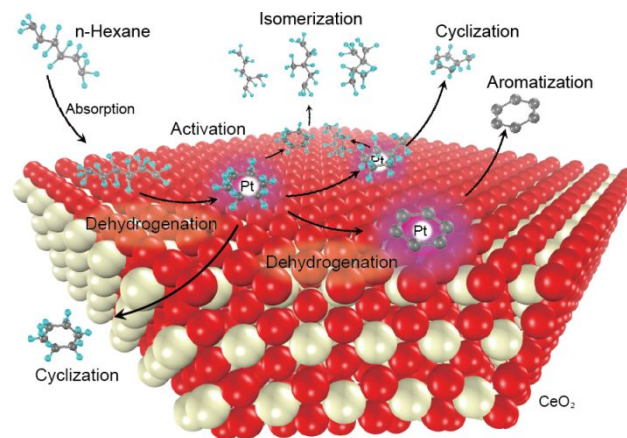


Figure 4. Scheme of cyclization mechanism of n-hexane reforming without cracking reaction localized on Pt<sub>1</sub>/CeO<sub>2</sub>.

Reforming products of n-hexane and MCP by Pt<sub>1</sub>/CeO<sub>2</sub> were further compared, as summarized in Table S1. For both n-hexane and MCP reforming at lower temperature, the main products are cyclic compounds with five and six member rings. Therefore, the reforming mechanism of n-hexane was proposed in Figure 4. n-Hexane was first adsorbed on CeO<sub>2</sub> supports and then transferred to the Pt single sites to activate the terminal C-H. XPS spectrum in Figure S17 indicates the valence of Pt will slightly decrease in the catalysts due to the reduction ability of n-hexane (Figure S9). The activated n-hexane can go through different reforming pathways by forming hydrocarbons with stable five- or six-member rings, which both adsorb more strongly on Pt<sub>1</sub>/CeO<sub>2</sub> surface than n-hexane. The six-member ring intermediate (i.e. cyclohexane) could be further dehydrogenated to form aromatic products, while the five-member ring (i.e. MCP) could undergo the ring expansion to six-member ring, isomerism or crack directly. To confirm this cyclization mechanism for alkane reforming, butane was also employed. No activity was obtained at the conduct temperatures because butane could not form a cyclic compound and its terminal C-H is also hard to activate at low temperatures. This process further proves the specific selectivity of Pt SSC for C-H activation of C<sub>6</sub> hydrocarbons.

In Summary, the mechanism of n-hexane reforming was investigated over a series of CeO<sub>2</sub> supported Pt catalysts

including Pt single sites, Pt clusters and Pt nanoparticles. Notably, Pt<sub>1</sub>/CeO<sub>2</sub> SSC changed the products distribution of n-hexane reforming and displayed a significantly higher selectivity for both dehydrocyclization and aromatization. Specifically, the total selectivity of dehydrocyclization and aromatization of single site Pt<sub>1</sub>/CeO<sub>2</sub> is > 86 % at 350 °C, with TOF of 58.8 h<sup>-1</sup> at 400 °C. When catalytic results of MCP reforming were combined, we proved this high selectivity was attributed to the inhibited cracking reaction over Pt<sub>1</sub>/CeO<sub>2</sub> surface due to the absence of multiple adjacent Pt active sites. And the cyclization and aromatization of hydrocarbons was attributed to the prominent adsorption of intermediate products with a ring on the single site Pt<sub>1</sub>/CeO<sub>2</sub> catalysts. Ultimately, this in-depth study highlights the benefits of SSCs and paves the way for further rational design of highly efficient catalysts.

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### Author Contributions

All authors have given approval to the final version of the manuscript.

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### Notes

The authors declare no competing financial interests.

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