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METHANE LIQUEFACTION: Selective Conversion of Methane to Cyclohexane via Efficient Surface-Hydrogen-Transfer Catalyzed by GaN-Supported Platinum Clusters

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Abstract

Non-oxidative liquefaction of methane at room temperature and ambient pressure has long been a *scientific “holy grail”* of chemical research. In this report, we exploit an unprecedented catalytic transformation of methane exclusively to cyclohexane through effective surface-hydrogen-transfer (SHT) at the heterojunctions boundary consisting of electron-rich platinum cluster (Pt) loaded on methane-activating gallium nitride (GaN) host. The experimental analysis demonstrates that interface-induced overall reaction starts with methane aromatization to benzene initiated by the Ga-N pairs, followed by hydrogenation of benzene to cyclohexane via hydrogen transfer. The in-situ activated hydrogen at electron-rich metal Pt cluster plays a key role for the hydrogenation and enables an outstanding selectivity (as high as 89 %) towards cyclohexane, which is well-delivered even after 5 recycling runs.

Main text:

The direct and selective liquefaction of methane serving as a pivotal technology has been termed one of the “holy grails” in the scientific community.¹⁻² The commonly available industrial liquefaction approach relies on high-pressure and/or low-temperature tank for ease of storage and transportation that requires harsh operating process and large energy input (Figure 1a).³⁻⁴ To date, another successful application in industrial-scale methane liquefaction is to produce liquid hydrocarbons based on well-known two-step transformation involving the water-gas shift and the Fischer-Tropsch (F-T) processes (Figure 1b).⁵⁻⁷ In the view of economical cost, directly converting methane as building block feedstock into value-added liquid chemicals has received considerable attention for on-site transformation of methane of remote oil-rig.⁸⁻¹⁰ In this context, tremendous effort has been devoted to exploit new reactivities of partial oxidation, oxidative condensation, and non-oxidative aromatization for the direct methane liquefaction into liquid fuels including methanol,¹¹⁻¹³ formic acid,¹⁴⁻¹⁵ acetic acid,¹⁶⁻¹⁸ even aromatics¹⁹⁻²¹ (Figure 1c-d). However, unlocking novel and challenging transformation of methane to generate commodity chemicals is still rare and calls for new scientific routes.

Figure 1 | Methods for methane liquefaction. (a) High pressure tank for methane storage. (b) Typical two-steps process in large-scale industrial catalysis. (c) Oxidative conversion of methane into primary fuels and (d) non-oxidative conversion into aromatics. This work: A new methane liquefaction for cyclohexane synthesis over Pt/GaN catalyst via in situ surface-hydrogen-transfer (SHT).

On the other hand, cyclohexane as an important solvent and raw material has found its extensive applications in the plastic industry,²² bulk chemicals synthesis,²³ and liquid organic hydrogen storage,²⁴

affording huge market potential. In particular, taking an example of Nylon production, the annual consumption of cyclohexane around the world is more than million-tons-scales.²⁵ Currently, the hydrogenation of benzene represents a mainstream methodology for cyclohexane production at the industrial-scale level.²⁶⁻²⁷ Such a method is subjected to the over-dependence on the depleting petroleum resource, high environmental footprints, and elevated greenhouse gas emissions.²⁸⁻²⁹ An efficient catalytic system has not yet been discovered to generate cyclohexane via one-step gas-to-liquid process from methane, a naturally abundant resource yet an environmentally concerning greenhouse gas. Therefore, rationally constructing and unlocking selective methane chemical liquefaction using advanced catalyst technology is of fundamental significance for the straightforward, economical, and sustainable production of cyclohexane.

The key challenge of converting methane into cyclohexane lies in the high dissociation energy of C-H bonds (104 kcal/mol) and the difficulty of preventing over-oxidation.³⁰⁻³¹ Our previous studies found that gallium nitride surface, even for commercial ones with rich gallium-nitrogen pair sites, is active for both strong C-H bond activation and subsequent aromatization to generate benzene in high yield as well as release detectable hydrogen gas.³²⁻³³ To further obtain the desired cyclohexane, introduction of metal nanoparticles onto methane-active GaN support will, in principle, be powerful enough to trigger the subsequent benzene hydrogenation, which has been validated in the Pt/TiO₂ example for catalyzing a reversible hydrogen storage-release process.³⁴ In the last decade, metal-semiconductor heterojunctions, particularly with well-defined interface engineering, can couple and even maximize catalytic functions of metal and the support concurrently through a joint boundary.³⁵⁻³⁷ Such a conceptual “Two-in-One” protocol undoubtedly offers a facile toolbox for a vast array of various transformations that need multiple-function sites. For the present case, it is anticipated that rationally designed and fabricated metal-GaN interface in which methane-activation and hydrogenation areas are integrated simultaneously represents a promising solution for the challenging methane liquefaction process via cyclohexane.

Herein, we document an unprecedented and one-step methane conversion into cyclohexane based on robust platinum-metal clusters deposited on gallium nitride (Pt/GaN) for the first time. The utilization of

the photochemical method successfully fabricates a bifunctional interface between well-dispersed Pt nanoclusters and GaN support.³⁸ This catalytic ensemble retaining a sufficient number of Ga-N pair sites is capable of activating inert methane molecules even after deposition of Pt nanoclusters. Meanwhile, the photoreduction deposited Pt nanoclusters with rich electron density possess excellent catalytic activity for the hydrogenation of benzene with the surface-bound hydrogen in-situ generated by the non-oxidative methane-aromatization, producing the target cyclohexane efficiently with up to 89 % selectivity.

Figure 2 | Construction and characterization of Pt nanoclusters coupled with GaN interface. (a) Photoreduction process of Pt/GaN catalyst. (b) Pt 4f XPS spectra for Pt/GaN and K₂PtCl₄ sample. (c) XRD patterns of Pt/GaN (red line) and commercial GaN (blue line). (d) Representative HAADF-STEM image of Pt nanoclusters size distribution and (e) EDX mapping files of Pt/GaN sample.

Results and discussion

To obtain the highly active Pt/GaN interfacial catalyst, we chose a photochemical synthesis strategy in which methanol was used as photogenerated hole scavenger, enabling more photogenerated electrons to reduce the Pt precursor (K₂PtCl₄) to metallic Pt (Figure 2a). The X-ray photoelectron spectroscopy

(XPS) analysis indicated that Pt metal with zero-oxidation state was successfully introduced with assistance of GaN-semiconductor as photosensitizer (Figure 2b). As shown in Powder X-ray diffraction (XRD) results (Figure. 2c), commercial GaN powder with typical wurtzite structure was well maintained even after metal loading, demonstrating high tolerance and stability of GaN support against photochemical reaction media. At the same time, XRD pattern of Pt/GaN sample with no obvious characteristic peak for Pt nanoparticles reveals the presence of metal Pt possibly in the form of nanoclusters. This deduction is further reflected by the high-angle annular dark-field scanning transition electron microscopy (HAADF-STEM) image of Pt/GaN in which ultra-small Pt nanoclusters with the average particle size of ~ 1.46 nm is identified on the GaN surface (Figure. 2d). The energy-dispersive X-ray spectroscopy (EDS) mapping files show that Pt nanoclusters homogeneously dispersed on the entire GaN support (Figure. 2e), which is consistent with the HAADF-STEM results. We further finely controlled the amount of Pt metal precursors in photoreduction reaction for optimizing the effective Pt/GaN boundary exposure to gas reactant. As-generated Pt_x/GaN samples with different metal weight percentages ($x=0.5\%$, 1% , 2% and 4%) relative to GaN were used to catalyze the methane transformation.

In our previous reported research,³³ commercial GaN powder can catalyze the non-oxidative aromatization conversion of methane to benzene generation in a detectable yield under thermal condition with the reaction temperature above $150\text{ }^{\circ}\text{C}$. Based on this experimental condition, we initially tested the thermal-catalytic methane non-oxidative conversion with different semiconductor-supports in a closed reactor at $300\text{ }^{\circ}\text{C}$ for 2 h, in which 20 mg of Pt/GaN was homogeneously coated on the reactor wall using 2 mmol of high-purity methane as the single reactant. As shown in Figure 3b (Entry 1-4 of Table S1), GaN support exhibited a higher yield of benzene compared to other supports for thermal methane conversion. In the final products analysis, only aromatics including benzene (blue) toluene (orange) and xylene (green) as side-products, and hydrogen gas were generated (Figure S1). Negligible carbon oxides were observed after the reaction (Figure S1). These results demonstrated that GaN support indeed plays an essential role

for activating inert methane molecules to form benzene that will be beneficial for the further cyclohexane generation.

Figure 3 | Methane liquefaction performance. (a) Schematic representation of methane-to-liquid products via thermal catalytic condition. (b) The yield of benzene and (c) cyclohexane over commonly used supports with and without loading Pt. (d) The selectivity and conversion of methane transformation by Pt_x/GaN catalysts. (e) Catalytic performance of Pt/GaN under different reaction temperatures.

Introducing Pt metal on to the methane-active semiconductor-support to form Pt/GaN interface can prompt the challenging generation of cyclohexane from methane with a high selectivity. No desired cyclohexane was formed at 300 °C by the methane-nonactive Pt/TiO_2 sample (Figure 3c and Entry 5 of Table S1). In contrast, Pt-modified methane-active supports showed noticeable production of cyclohexane under the same reaction conditions (Figure 3c and Entry 6-8 of Table S1), in which Pt/GaN hybrids exhibits 25-fold higher catalytic performance of $6.49 \mu\text{mol g}^{-1}$ for methane conversion than those of well-controlled $\text{Pt}/\text{support}$ (here are Ga_2O_3 and ZnO) heterojunctions. All the results suggest that GaN can serve as the ideal methane-active support for Pt nanoclusters for converting methane to cyclohexane.

The optimization of metal loading on GaN surface was used to accommodate the conversion rate of benzene hydrogenation to well match the methane dehydrogenation step, thus ensuring Pt/GaN with high chemoselectivity and productivity for methane-to-cyclohexane conversion (Figure 3d). The Pt_{0.5}/GaN sample with a low metal content decreased the methane conversion from 0.14 % to 0.0046 % (Entry 9 of Table S1) without generating cyclohexane due to methane-active Ga-N pairs covered by Pt nanoclusters. These results reveal that the active sites to activate methane locates at the GaN support surface rather than the supported metal. The best-performance for methane liquefaction in both conversion (0.040 %) and selectivity (88.90 %) toward cyclohexane was obtained with the aid of Pt₁/GaN with 1 wt. % Pt content. Further increasing the Pt loading on the surface of GaN inevitably induced aggregation of metal clusters (Figure S2), losing their catalytic reactivity at the cluster/GaN boundary (Figure 3d and Entry 10-11 of Table S1). These results demonstrate the key role of highly dispersed Pt/GaN interface to simultaneously catalyze the methane aromatization and the subsequent hydrogenation for synthesizing cyclohexane in an ultra-selective manner.

The reaction temperature has imperative impact on delicately balancing methane aromatization and benzene hydrogenation rates with the aim of converting more methane to cyclohexane via the proposed methane-benzene-cyclohexane process (Figure 3e and Entry 12-14 of Table S1). Decent cyclohexane selectivity (92.67 %) but quite low methane (0.00049 %) conversion was observed at a lower temperature of 250 °C (Entry 12 of Table S1). When the reaction temperature was raised to 300 °C (Entry 8 of Table S1), the cyclohexane generation rate reaches an optimal value in the temperature-dependent reactivity profiles wherein superior chemoselectivity is comparable to the one at 250 °C. To further enhance methane conversion for practical applications, higher temperatures of 350 °C and 400 °C were also effective in our catalytic system (Entry 13-14 of Table S1) except with the lower selectivity to cyclohexane. Such reaction temperatures-dependent trade-off correlation between cyclohexane selectivity and methane conversion presented by the optimized Pt/GaN again indicates that synergistic mechanism working at the Pt/GaN interface is likely responsible for this novel methane-to-cyclohexane process.

Figure 4 | Methane conversion mechanism studies. (a) Time-dependent yield of cyclohexane (red sphere) and benzene (black) with the mixture of commercial Pt/C and GaN and (b) Pt/GaN and as catalysts. (c) Yield of cyclohexane over Pt/GaN via benzene reacting with hydrogen gas and the corresponding schematic illustration. (d) Proposed methane conversion pathway for production of cyclohexane catalyzed by Pt/GaN interface.

To gain in-depth insight of the catalytic methane transformation process on Pt/GaN surface, we compared time-dependent reaction performance for as-formed Pt/GaN and a mechanical mixture of commercial Pt/C and bare GaN (Figure 4a-b and Table S2-3) of which there is similar Pt loading. We found that only trace non-oxidative methane conversions occurred in the presence of Pt/C and GaN mixture even after 5 h under the standard thermal conditions owing to non-existence of the effectively integrated interface between Pt/C and GaN (Figure 4a). In contrast, the yield of cyclohexane has obviously increased after using Pt/GaN and was accompanied with a small amount of benzene generated from aromatization of methane (Figure 4b). Such results demonstrated that the overall reaction pathway indeed involves successive aromatization and hydrogen transfer steps near the boundary of Pt clusters and GaN support. Further control experiment was carried out to verify the essential feature of such a surface hydrogen auto-transfer process where the equivalent amounts of benzene and H_2 gas are as much as those of theoretical production of our standard methane liquefaction reaction over Pt/GaN (Figure 4c). As we expected, the

hydrogenation of benzene towards cyclohexane with hydrogen gas did not take place significantly (Figure S3). These results unravel that the in-situ generated H-atoms on the surface of GaN via methane dehydroaromatization are quite prone to migrate to the adjacent Pt metal surface for the subsequent hydrogenation driven by active metal hydride intermediate rather than undergoing two separate steps of dehydrogenation-hydrogenation to accomplish the successive hydrogenation of benzene (Figure. 4d).

Given the nature of heterogeneous catalysts, the Pt/GaN interface showed good recyclability without obvious attenuation in terms of production rate of cyclohexane under the thermal condition for up to 5 cycles (Figure 5a and Entry 1-5 of Table S4). The electron density states of fresh and the used catalysts stay the same as reflected by the Pt XPS results in Figure 5b, suggesting the considerable stability of highly active Pt/GaN boundary.

Figure 5 | Reusability of Pt/GaN for catalyzing methane-to-cyclohexane. (a) Yield of cyclohexane over reused Pt/GaN. Reaction conditions: 2 mmol of methane, 20 mg of catalyst, 300 °C, 2 h. (b) Pt 4f XPS spectra of fresh and used Pt/GaN.

Conclusions

In summary, we have uncovered a novel means for methane liquification via the highly selective generation of cyclohexane, by using Pt clusters supported on GaN as catalysts. The method converts methane gas into liquid cyclohexane with extremely high selectivity. Homogeneously dispersed Pt clusters on GaN are essential to achieve methane activation and the subsequent benzene hydrogenation via hydrogen-transfer process with the surface bound H-atoms for efficient production of cyclohexane. The catalyst

system is very stable and can be reused for multiple times without diminishing the catalytic activity. Such a green and sustainable conversion of methane to value-added and portable liquid products with high selectivity exhibits great application potentials in large-scale industrial practice.

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Author contributions

C.-J. L proposed the research idea and supervised the project. L.-D. T. designed and prepared catalyst, characterized samples, and performed catalytic measurements. H. S. and L.-D. T. participated in mechanistic studies. H. S. and L.-D. T., and J.-T. H. wrote the manuscript. M.-X. L revised the manuscript and

participated in critical discussions. All authors interpreted the results and contributed to the development of the manuscript.

Additional information

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