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Nonthermal Plasma-Promoted CO_2 Hydrogenation in Presence of Alloy Catalysts

Nonthermal plasma (NTP) is used to activate CO_2 molecules for hydrogenation into alternative fuels at low temperatures, also enabling the conversion of renewable electricity to chemical energy. Researchers from Tokyo Tech combined experimental and computational methods to investigate the hydrogenation pathway of NTP-promoted CO_2 on the surface of Pd_2Ga/SiO_2 catalysts. The mechanistic insights from their study can help improve the efficiency of catalytic hydrogenation of CO_2 and allows the engineers to design new concept catalysts.

Climate change accelerated by excess CO_2 emissions has been a major concern over the past few years. To deal with this problem, technologies that can not only reduce and remove excess CO_2 emissions but also transform them into value-added chemicals are being developed. One such method is the hydrogenation of CO_2 using renewable hydrogen to produce alternative fuels.

Over the years different strategies have been developed to improve CO_2 hydrogenation in the presence of metallic catalysts. The most promising among them is nonthermal plasma (NTP). It promotes hydrogenation of CO_2 beyond the thermodynamic limit even at low temperatures without deactivating metallic catalysts, which are vulnerable to higher temperatures. Despite the rising popularity of this technique, the interactions between the NTP-activated species and metallic catalysts are still not well understood.

Fortunately, a team of researchers from Tokyo Institute of Technology (Tokyo Tech), Japan, led by Prof. Tomohiro Nozaki, devised a study to overcome this gap in understanding. In their recent breakthrough, published in the *Journal of the American Chemical Society*, the researchers revealed the reaction dynamics for NTP-assisted CO_2 hydrogenation on the surface of Pd_2Ga/SiO_2 alloy catalysts that lead to the formation of formate. Prof Nozaki explains "Reaction mechanisms like Eley-Rideal or E-R pathway have been proposed to explain efficient CO_2 conversion at lower temperatures and the activation energy for this reaction decreases dramatically. Moreover, NTP produces a copious amount of vibrationally activated CO_2 which is the key to enhancing CO_2 conversion beyond the thermal equilibrium."

The team investigated the reactions between NTP activated CO_2 and Pd_2Ga/SiO_2 alloy catalysts in a fluidized-bed dielectric barrier discharge reactor (Figure 1 and Videos) and compared them to conventional thermal catalysis. The results revealed that the CO_2 conversion into formate was more than two-fold in the case of NTP-assisted hydrogenation when compared to thermal conversion. To further establish the mechanics of the mentioned conversion, the scientists adopted *in situ* spectroscopic analysis and density functional theory (DFT) calculations.

The results revealed that the NTP activation gave rise to vibrationally excited CO_2 molecules which directly react with hydrogen atoms adsorbed by the Pd sites on the catalyst via the E-R pathway. One of the O atoms from the reacted species then got adsorbed at the neighboring Ga site resulting in the formation of monodentate-formate or m-HCOO. The DFT calculations also deduced a decomposition pathway for the same m-HCOO species.

This experimental-theoretical study showed that NTP can promote CO_2 hydrogenation to limits those conventional thermal methods can hardly reach. It also provided mechanistic insights into NTP activated CO_2 and catalyst interaction, which can be utilized to develop better catalysts and improve the hydrogenation process. "With our research, we wanted to accelerate the waste to wealth initiative. Capturing CO_2 and using it as feedstock for synthesis of fuels and valuable chemicals will not only help us deal with climate problem but also slow down fossil fuel depletion to some extent," concludes Prof. Nozaki.

Reference

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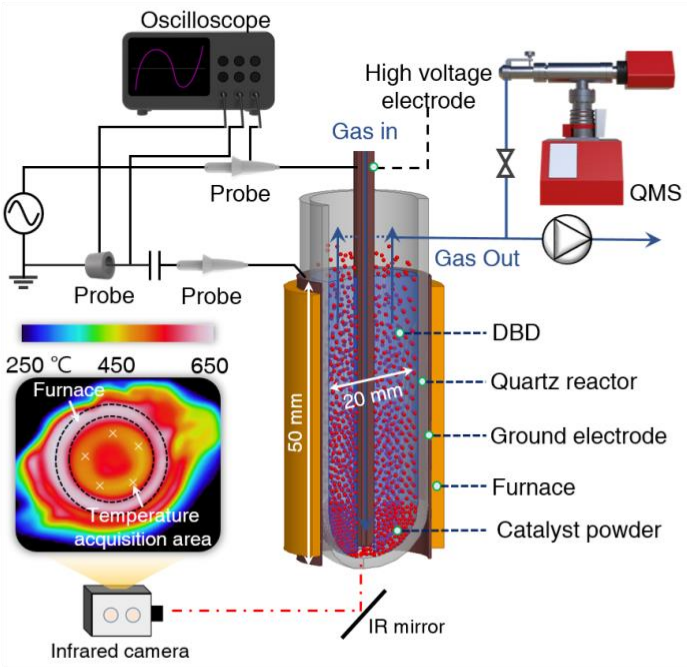


Figure 1. Carbon dioxide recycling - innovative plasma-catalysis concept

Fluidized-bed dielectric barrier discharge reactor was used for CO_2 hydrogenation over Pd_2Ga/SiO_2

Credit: Journal of the American Chemistry

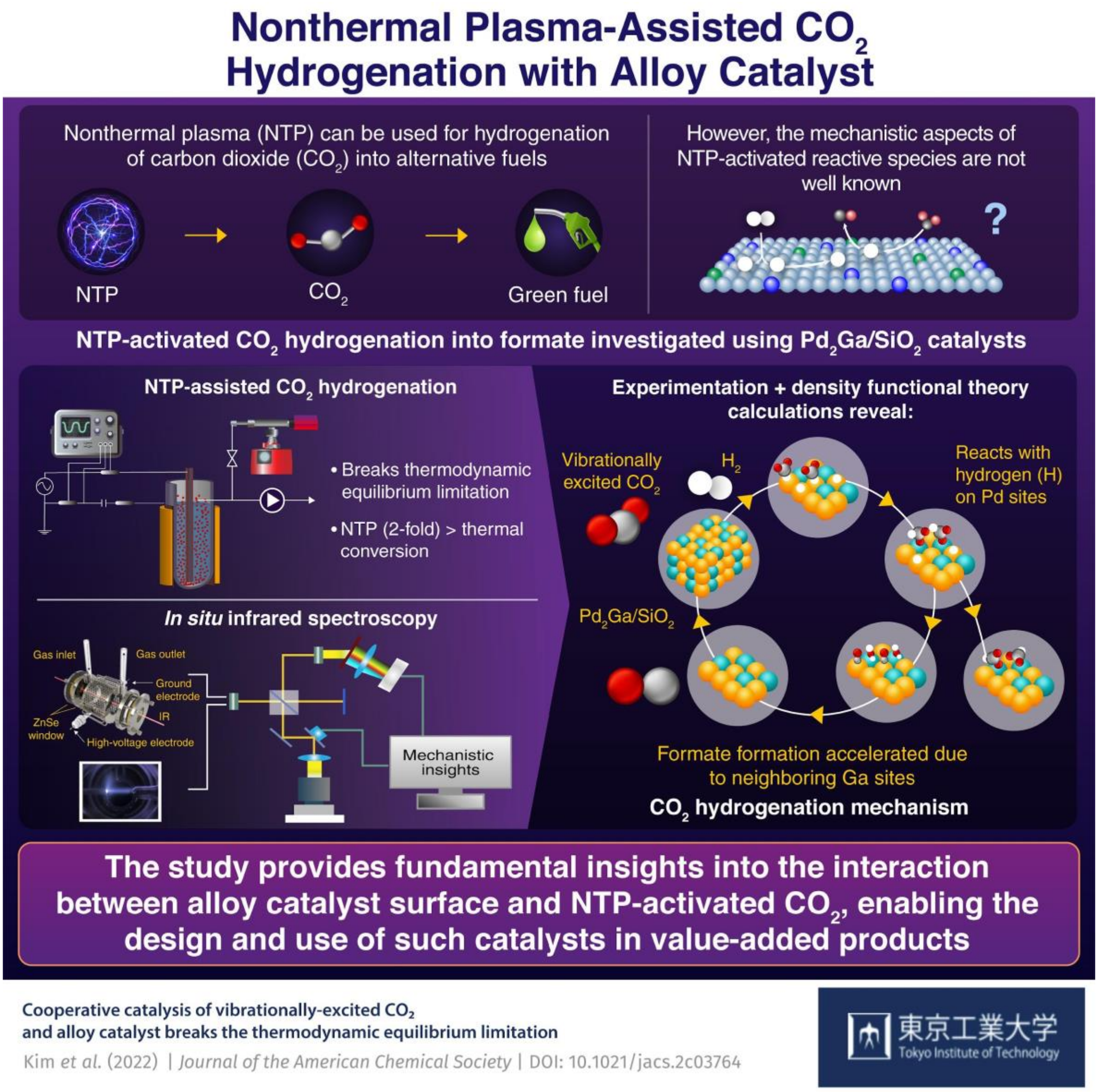
Videos: DBD generated in fluidized bed reactor

Side view, https://youtu.be/Bqvv3MK1mQM

Top view, https://youtu.be/HnTq8RoyAXw

Refer to the manuscript for detailed conditions.

Credit: Professor Tomohiro Nozaki of Tokyo Institute of Technology



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Tokyo Tech stands at the forefront of research and higher education as the leading university for science and technology in Japan. Tokyo Tech researchers excel in fields ranging from materials science to biology, computer science, and physics. Founded in 1881, Tokyo Tech hosts over 10,000 undergraduate and graduate students per year, who develop into scientific leaders and some of the most sought-after engineers in the industry. Embodying the Japanese philosophy of "monotsukuri," meaning "technical ingenuity and innovation," the Tokyo Tech community strives to contribute to society through high-impact research.
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Founded in 1876 as Sapporo Agricultural College, Hokkaido University is one of the oldest, largest, and most prestigious universities in Japan. The university attracts prospective students all around the globe with the diverse degree programs offered and the all year round scenic beauty. The campuses are located in the cities of Sapporo and Hakodate of Hokkaido and 21 facilities are spread throughout Hokkaido and mainland Japan, contributing towards the resolution of global issues.
https://www.global.hokudai.ac.jp/

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