

Confining the Bouncing Electrons to Get Better Catalysts

By Fusheng YAN (Staff Reporter)

Abiding to specific rules, electrons move freely around the atomic nucleus. If an external force acts upon these free-bouncing electrons and restricts their motion somehow, we shall see a change in the electron's motion state and property, or the atom's chemical activity. When the affected atoms are sitting at the catalyst's active center or pocket, it provides the possibility of controlling a catalyst's property

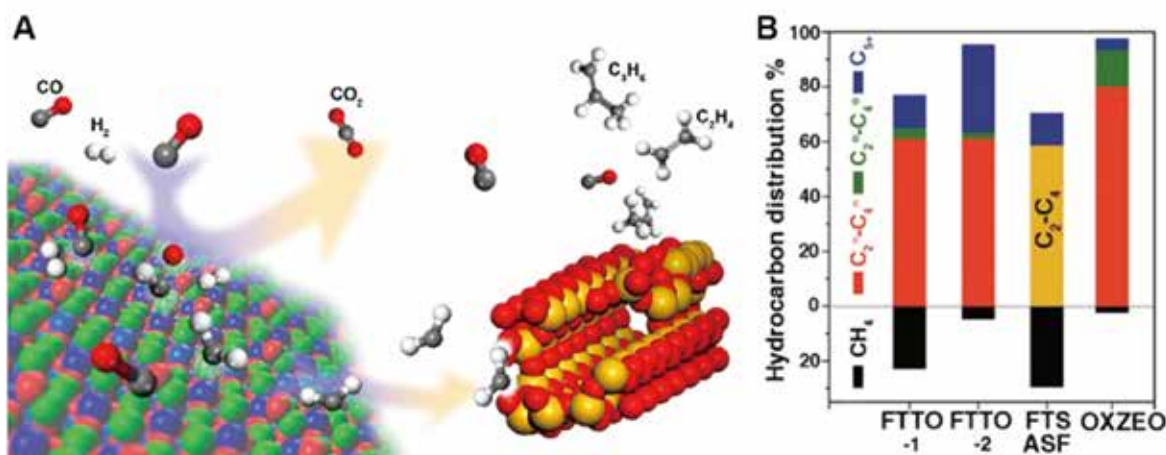
"It is like tapping a ping-pong against the table from a certain height. The ball bounces up and down. When you suddenly lower the ping-pong bat, the ball bounces much more rapidly. We could do something similar to the electrons. In that case, the electrons will vibrate more vigorously, hence changing the property of the materials," said Prof. BAO Xinhe in an interview, who leads a team at the Dalian Institute of Chemical Physics of the Chinese Academy of Sciences. "So, if we

can adjust the bouncing electrons to a certain energy, it would allow us to control many natural processes."

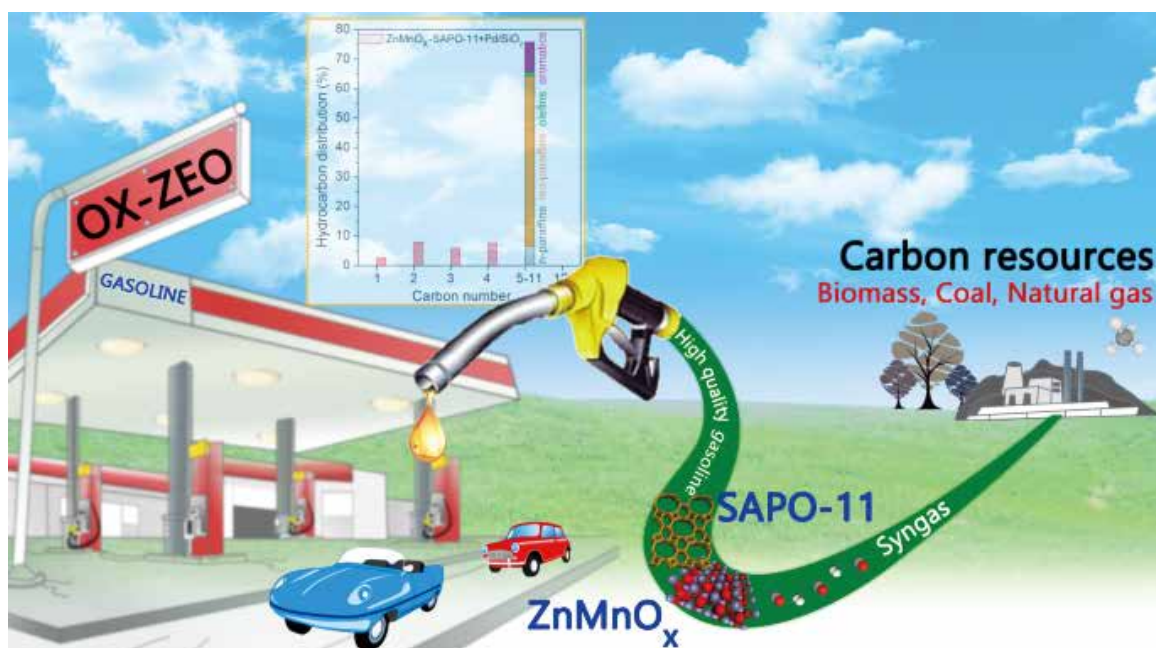
With long-lasting efforts over more than 20 years, BAO's team has developed a new concept termed "Nano-confined Catalysis," which covers confinement effects within nanospaces and at interfaces.

As the first proof of concept, BAO's team demonstrated that a non-precious metal Fe catalyst encapsulated within carbon nanotubes exhibits high activity and stability as a fuel cell cathode catalyst. Later, they extended this confinement concept to other catalytic settings, such as at the interface and within the lattice. They, therefore, developed better catalysts of notably improved performance that convert coal to ethanol via syngas and selectively remove CO from excess H₂ for fuel cell applications.

Notably, by integrating interface and nanospace



OXZEO bifunctional catalyst concept for syngas conversion to light olefins. (A) Scheme and (B) hydrocarbon distribution in comparison. (Image by BAO's team)



The one-step synthesis of high-quality gasoline from syngas, empowered by a new bifunctional composite catalyst. (Image by BAO's team)

confinement effects within an oxide-zeolite-based composite, BAO's team developed a new design, namely OXZEO, for selective conversion of syngas to light olefins (*i.e.*, $C_2=C_4$, olefins containing two to four carbon atoms and at least one double bond).

In work published in *Science* in 2016, they reported a new OXZEO catalyst that converts syngas to light olefins with a selectivity reaching 80% and to C_2-C_4 with a selectivity of 94%, which well-surpass the theoretical limit of 58% for C_2-C_4 hydrocarbons via the conventional Fischer-Tropsch synthesis (FTS) route.

Syngas, or synthesis gas, is an important intermediate in the chemical industry. Any carbon-containing feedstock such as coal, natural gas, or biomass can be converted into a mixture of carbon monoxide (CO) and hydrogen (H_2) via steam reforming or gasification. The FTS process catalytically converts CO and H_2 in the syngas into hydrocarbons of various molecular weights, including the desired ones (C_2-C_4) and the methane (C_1) and long hydrocarbons (C_{5+}) byproducts. Though extensively studied, FTS is still limited by low olefin selectivity and a high byproduct ratio of C_1 . As described by the Anderson-Schulz-Flory (ASF) model, the selectivity of C_2-C_4 does not exceed 58%.

To enhance the ratio of C_2-C_4 and reduce other hydrocarbon byproducts, BAO's team creatively developed a new bifunctional composite catalyst that contains an oxide ($ZnCrO_x$) and a mesoporous SAPO zeolite (MSAPO). Notably, OXZEO separates CO activation and C-C coupling onto two different types of active sites with complementary properties. CO and H_2 are activated over a partially reduced oxide ($ZnCrO_x$) surface, whereas C-C coupling is controlled within the confined acidic pores of zeolites. As a result, OXZEO can reach high C_2-C_4 selectivity up to 94% (including 80% $C_2=C_4$) of all hydrocarbons while curbing the C_1 byproduct (CH_4) to only 2%.

They reckoned that this bifunctionality of the catalyst is the main reason it works so well because they found that, in the absence of MSAPO, syngas was converted mainly to CH_4 (up to 53%). Selectivity to C_2-C_4 hydrocarbons was only 38% over $ZnCrO_x$. When adding another layer of MSAPO below the oxide, they observed a clear product shift: increased C_2-C_4 selectivity (up to 69%) and a plummet in CH_4 selectivity (dropped to 26%). Based on this result, they speculated that reaction intermediates generated over the oxides must have transported in the gas phase toward the active sites of MSAPO, where they were converted to

C₂–C₄ hydrocarbons, rather than hydrogenated to CH₄ over the oxide or in the gas phase.

By increasing space velocities that facilitates the transport of intermediates in the gas phase from oxides to MSAPO, they observed a further improvement in catalytic selectivity over C₂–C₄. In addition, when they packed the oxides and MSAPO in an alternating sequence, the C₂–C₄ selectivity increased further because of the reduced distance for transporting the intermediates. When they well-mixed these two components, they observed an even higher selectivity of C₂–C₄ (80%), with overall C₂–C₄ selectivity reaching 94% and only 2% CH₄.

Thus, the C₂–C₄ selectivity of this new bifunctional composite catalyst is far beyond the maximum predicted by the Anderson-Schulz-Flory (ASF) model in FTS. Moreover, as evidenced, the OXZEO composite catalyst is robust and shows no sign of deactivation within 110 hours.

This new catalyst design will undoubtedly impact the development and application of coal and natural gas in the chemical industry.

An expert review in the same issue of the journal *Science*, titled “Surprised by selectivity,” also praised the work.

By applying the same bifunctional design, BAO’s team developed another OXZEO composite catalyst that enables the selective synthesis of gasoline-range hydrocarbons C₅–C₁₁ directly from syngas. The gasoline selectivity reached 76.7% among hydrocarbons, with only 2.3% CH₄. This new process may enable the one-step synthesis of environmentally friendly high-quality gasoline from various carbon resources via syngas.

The power of bifunctional catalyst design and Nano-confined Catalysis has brought a new wave of innovation into academia and the chemical industry. What it holds for the future is alluring.

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