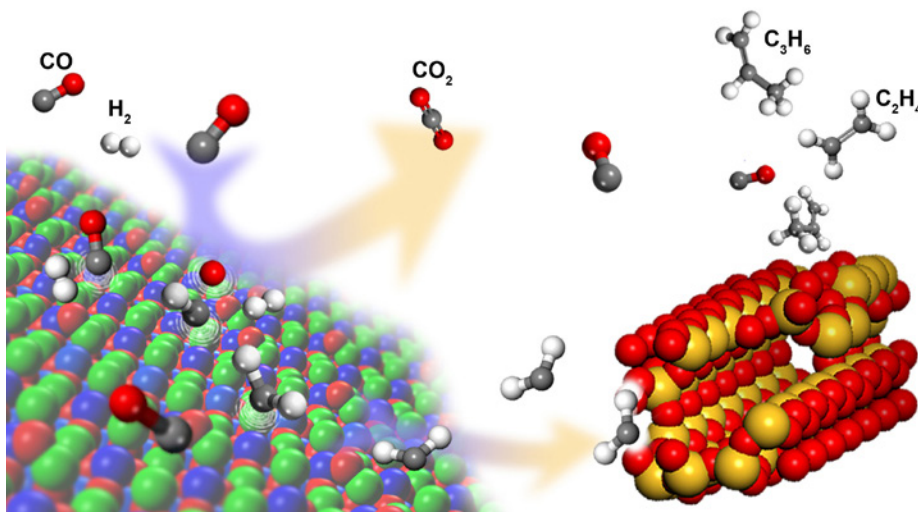
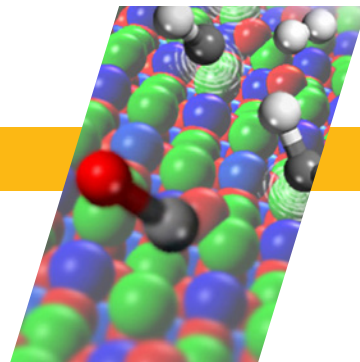


New Catalyst Boosts Selective Formation of Olefins from Syngas



Schematic of the catalytic process from syngas (H_2 and CO) to light olefins (C_xH_{2x}). The bifunctional nanocomposite catalyst has two types of active sites: a metal oxide surface, depicted on the left, and a zeolite pore, depicted on the right. (Image by Xiumei Jiang and Feng Jiao.)

Experiments at the ALS have helped to explain how a new catalyst significantly boosts the selective formation of light olefin molecules—important building blocks in the petrochemical industry—from a basic gas mixture called syngas (synthesis gas). A research team from China recently developed the nanocomposite catalyst and used ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) to investigate the chemical changes occurring at the catalytic surface in the presence of various reaction gases. The results showed that the boost in olefin production is enabled by the bifunctionality of the catalyst, which affords two types of active sites with complementary properties. The research should be of interest to both academia and industry, and the new technique could become a serious competitor for many older industrial processes, allowing for the use of alternative syngas feedstocks that can save water and energy.

Syngas (a mixture of H_2 and CO gases) can be converted into light olefins and other hydrocarbons through Fischer-Tropsch synthesis (FTS), a long-standing gas-to-liquid process involving metal-based catalysts. In FTS, H_2 and CO are catalyzed to form CH_x monomers. These monomers then undergo polymerization on the catalyst's metal surface, leading to the formation of a wide range of hydrocarbons of different chain lengths. The percentage of a given hydrocarbon species produced (selectivity) depends on variables such as temperature, syngas composition (ratio of H_2 to CO), pressure, catalyst type, and catalyst composition. A widely used statistical model of the process predicts that the maximum selectivity for hydrocarbons with two to four carbon atoms (C_2 – C_4 hydrocarbons), including olefins, is around 58%.

Now, researchers from the Dalian Institute of Chemical Physics in China have developed a nanocomposite catalyst

Synthesis, Catalysis, Analysis

We extract hydrocarbons from the earth in many different forms: coal, crude oil, natural gas, and biomass, for example. To transform these raw materials into useful products, we need to break down their hydrocarbon chains into simpler building blocks that we can then recombine and/or rearrange as needed. The building blocks discussed here—light olefins such as ethylene (C_2H_4), propylene (C_3H_6), and butylene (C_4H_8)—are used to synthesize a wide variety of products, including plastics, fibers, solvents, fuels, lubricants, paints, and medicines. Hundreds of millions of tons of light olefins are produced worldwide per year, mostly from the steam cracking (heating) of crude oil. Higher oil prices and environmental concerns have led to a vigorous search for alternative feedstocks and better catalysts. In this work, Jiao et al. describe their analysis of a promising, long-lasting catalyst for the direct production of olefins under more energy-efficient and water-conserving conditions.

consisting of a metal oxide (ZnCrO_x) and a mesoporous zeolite (a mineral with acidic pores). With this catalyst, they were able to achieve a surprisingly high selectivity of 80% for light olefins and 94% more generally for C_2 – C_4 hydrocarbons. Syngas with a lower ratio of H_2 to CO (such as coal or biomass) can be used, avoiding the need to increase the proportion of H_2 via the water-gas shift reaction, an energy-intensive and water-consuming process.

To better understand the functionality of the catalyst, the team carried out *in situ*

ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) measurements of the ZnCrO_x surface, working with scientists at Beamline 9.3.2 of the ALS, where the AP-XPS technique was pioneered. The resulting spectra indicate that the surface undergoes partial reduction (removal of oxygen) upon exposure to H_2 and CO , leading to the formation of CO_2 and surface carbon species. This latter carbon deposition, which might otherwise limit catalyst lifetime, can be removed by exposure to H_2 to form the hydrocarbon building block, CH_2 . The AP-XPS data is consistent with characterization results from other methods such as time-of-flight mass spectrometry and density functional theory calculations.

The overall reaction mechanism that emerges for this catalyst has two distinct stages, occurring at different functional sites. First, CO activation on the ZnCrO_x surface leads to the formation of gas-phase intermediate hydrocarbon species (CH_2). Then, the linking up of the intermediates into longer hydrocarbon chains (C-C coupling) takes place within the confines of the acidic (H^+ -donating) pores of the zeolite, where the length of the chains can generally be controlled by the size and acidity of the pores. Because the catalyst allows the use of syngas with a lower ratio of H_2 to CO , the energy-intensive water-gas-shift reaction can be avoided. More generally, these findings open up promising new avenues for the development of syngas-to-olefin technology.



Left: The two components of the catalyst, ZnCrO_x and zeolite (MSAPO), are shown in catalyst beds in four different packing modes, buffered by inert layers of quartz wool. Selectivity for $\text{C}_2\text{-C}_4$ products increased with greater mixing of the components. **Center:** *In situ* AP-XPS spectra of the ZnCrO_x surface showed a new signal with a lower Zn 3d binding energy in the presence of H_2 or CO gas, indicating that the Zn species can be partially reduced under process conditions. **Right:** *In situ* AP-XPS carbon 1s spectra of ZnCrO_x exposed to a sequence of H_2 and CO atmospheres at various temperatures and pressures. The data show a strong surface C signal upon exposure to CO (curve II), which attenuates in H_2 (curve III) before vanishing at 450°C (curve IV). The signal returns when the surface is re-exposed to CO (curve V).

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