

 CARBON DIOXIDE UTILIZATION

A carbon-neutral energy cycle

“oxygen vacancies on In_2O_3 are key to the catalytic conversion of CO_2 ”



Our reliance on fossil fuels results in CO_2 emissions that affect climate and the environment to such an extent that our recent history is referred to as the Anthropocene. The challenge in lowering these emissions can, in principle, be met by using energy technologies with a lower carbon footprint. Another approach — capturing atmospheric CO_2 and converting it to fuels — could also be effective in enabling a sustainable carbon cycle.

The urgent need for efficient CO_2 capture has led to the emergence of nanoporous metal–organic frameworks that show promising CO_2 uptake. But CO_2 sorption is only the first of many steps in processes that ideally would afford products such as CH_4 , CH_3OH , CO and HCO_2H . The conversion of CO_2 into these single-carbon (C_1) molecules has been developed to a greater extent than have conversions into heavier products, underscoring the inertness of CO_2 and the high kinetic barriers associated with C–C bond formation. These shortcomings have been tackled head-on with a catalyst system that combines high-surface-area In_2O_3 with a hierarchical microporous and mesoporous zeolite (HZSM-5). Indeed, this bifunctional material effects the hydrogenation of CO_2 to gasoline products with

carbon numbers that are predominantly in the range C_5 – C_{11} , as a team led by Yuhan Sun and Liangshu Zhong describe in *Nature Chemistry*.

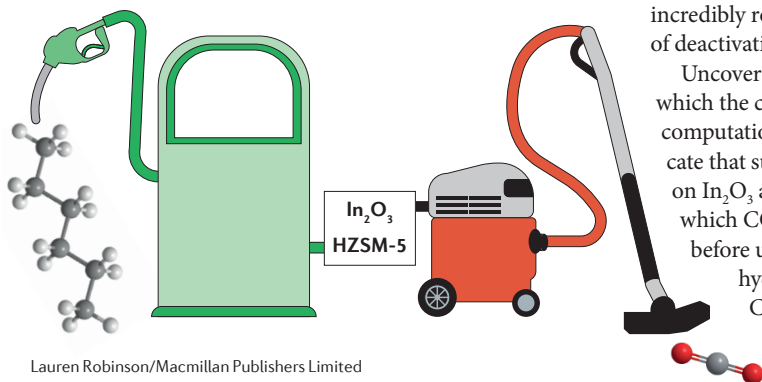
Gasoline is widely used in internal combustion engines for transportation and industry. One way to build carbon chains from CO and H_2 is the Fischer–Tropsch synthesis, an adaptation of which uses Fe-based catalysts to directly use CO_2 as a feedstock to give C_{5+} hydrocarbons. However, “the Anderson–Schulz–Flory distribution sets the limit on the C_5 – C_{11} hydrocarbon fraction to ~48%, with an undesirable CH_4 fraction of ~6%,” notes Zhong. The problem faced by many chemists, including the team of Sun and Zhong, is how to encourage chain growth while also suppressing CH_4 formation. These two points are addressed by the two active components of the present complementary catalyst. A defective In_2O_3 surface readily mediates CO_2 hydrogenation, and, in tandem, the zeolite offers pores in which the reduced products can meet each other and undergo C–C coupling to produce gasoline-range hydrocarbons. This methodology, at a CO_2 conversion of 13.1%, gives rise to selectivities for C_{5+} hydrocarbons as high as 78.6% while evolving CH_4 at only 1%. Moreover, the hybrid catalyst is incredibly robust, showing no signs of deactivation over 150 hours of use.

Uncovering the mechanism by which the catalyst operates called for computational studies, which indicate that surface oxygen vacancies on In_2O_3 are the reactive sites at which CO_2 is first chemisorbed before undergoing stepwise hydrogenation to give CH_3OH . The product then makes its way to acidic sites within

the zeolite, where it is converted into hydrocarbons through aromatic hydrocarbon pool intermediates such as carbocations. The formation of CO — the key feedstock in Fischer–Tropsch chemistry — is suppressed by the In_2O_3 surface, which stabilizes key intermediates *en route* to CH_3OH . The system thus mediates direct conversion of CO_2 into liquid C_{5+} hydrocarbons, rather than a process in which CO_2 is reduced to CO , which then dissociates from one catalyst and undergoes further reactions elsewhere.

Demonstrating the practical utility of their bifunctional system, the team reproduced their laboratory results when evaluating a pellet form of the catalyst in trials conducted under industrially relevant conditions. Nevertheless, the design of Sun, Zhong and co-workers certainly has room for improvement in terms of its control and stability. The obvious parameters to tune include the pellet shape, the surface structure of the oxide and the ratio between oxide and zeolite. Also, “the tight contact of bifunctional active sites significantly lowers the number of strongly acidic sites, deactivating HZSM-5 towards C_{5+} formation,” laments Sun. The team is now optimizing the catalyst, noting that oxygen vacancies on In_2O_3 are key to the catalytic conversion of CO_2 . “We foresee that stabilizing these vacancies — for example, by strengthening dispersion interactions between In_2O_3 and the support — will greatly enhance the efficiency of this methodology,” they note.

Yaoqing Zhang, Associate Editor,
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