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Highlight

A new horizontal in C1 chemistry: Highly selective conversion of syngas to light olefins by a novel OX-ZEO process

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The most challenging goal of C1 chemistry is the control of C–C coupling to produce chemicals or fuels from C1 feedstocks, in particular syngas (H_2/CO), which can be derived from various carbon resources such as coal, natural gas or shale gas, and biomass. Light olefins including ethylene, propylene and butenes ($C_2^=$–$C_4^=$) are important building-block chemicals, which are currently produced from naphtha. The synthesis of light olefins from syngas is a promising alternative. Fischer–Tropsch (FT) synthesis, which has a history of more than 90 years, is currently the major process for the direct conversion of syngas to hydrocarbons including light olefins, but the $C_2^=$–$C_4^=$ selectivity is limited because of the FT mechanism, which involves the C–C coupling of CH_x (x=1–3) intermediates formed via CO dissociation on metal (typically Fe, Co or Ru) surfaces [1]. The C–C coupling on open metal surfaces is uncontrollable, leading to wide distribution of hydrocarbon products following the Anderson–Schulz–Flory (ASF) distribution. The maximum selectivity of C_2–C_4 hydrocarbons (including paraffins and olefins) is 58% [1]. Light olefins may also be produced from syngas via a two-process route, i.e., methanol synthesis and methanol to olefins (MTO), but this indirect route is water- and energy-intensive.

The Bao group at Dalian Institute of Chemical Physics, Chinese Academy of Sciences has recently made a significant breakthrough by designing a new OX-ZEO process, in which CO activation and C–C coupling proceed separately on reduced spinel $ZnCrO_x$ oxide surfaces and in zeolite pores in a composite catalyst (Fig. 1a) [2]. The $C_2^=$–$C_4^=$ selectivity reaches ~80% at a CO conversion of 17% at 673 K under a syngas (H_2/CO=2.5) pressure of 2.5 MPa. This $C_2^=$–$C_4^=$ selectivity is markedly higher than that reported on the optimized FT to olefin (FTTO) catalyst based Fe (~60%) [3], and breaks the limitation by the ASF distribution (Fig. 1b). The composite catalyst works synergistically; methane was formed as the major product over $ZnCrO_x$ oxide alone and the combination of MSAPO shifted the major products to $C_2^=$–$C_4^=$ olefins.

The synchrotron vacuum ultraviolet photoionization mass spectroscopy (SVUV-PIMS) provides evidence for the formation of a ketene radical, i.e., CH_2CO, from the $ZnCrO_x$ oxide surface under atmospheric pressure of syngas. The CH_2CO radical was proposed to be the key intermediate for light olefin formation. Further characterizations and DFT calculations reveal that the partially reduced $ZnCrO_x$ surface is the key, which exhibits weak binding of CH_x, allowing the formation of CH_2CO radical in the gas phase (Fig. 1a), and thus prevents the uncontrollable polymerization of CH_x species. The product formation occurs in the confined pore of MSAPO with proper acidity, favoring the selectivity of light olefins.

The concept of reaction coupling has recently resulted in significant progress in tuning the product selectivity in syngas conversions [3–5]. The work of Bao and co-workers represents a milestone in the direct synthesis of light olefins by a new OX-ZEO process. The activity and selectivity can be tuned by manipulating the two active sites, thus breaking down the "seesaw" effect of activity and selectivity observed in many catalytic systems. Moreover, oxygen from CO is believed to be turned into CO_2 instead of H_2O, and thus there is no need of the energy-intensive water-gas shift reaction to regulate the H_2/CO ratio. The catalyst is applicable to the conversion of syngas with a wide range of H_2/CO ratios (0.5–3.0) and is useful for the direct utilization of coal- and biomass-derived syngas.

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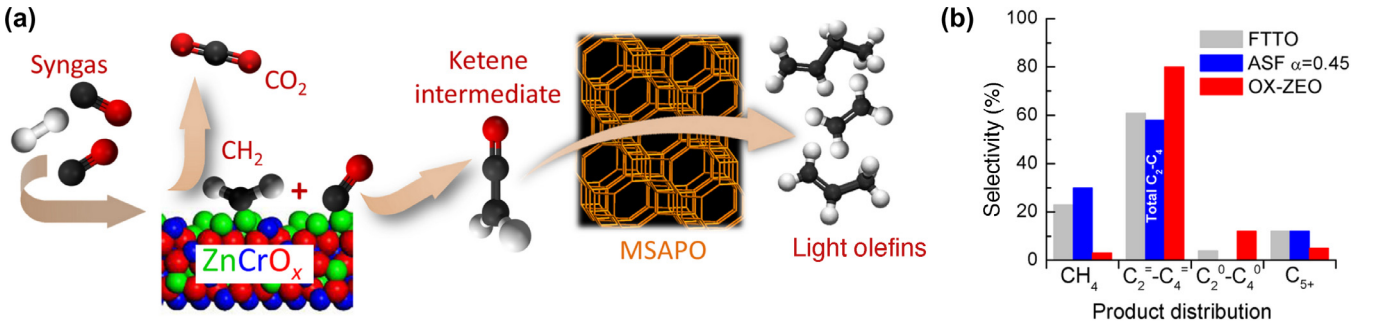


Fig. 1. (a) Reaction scheme for selective conversion of syngas to light olefins catalyzed by a composite of $ZnCrO_x$ and MSAPO. (b) Comparison of product distributions for the OX-ZEO process, reported FTTO catalyst [3], and the ASF distribution with a chain growth probability (α) of 0.45.

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