

Technology Offer

Inexpensive and highly efficient catalysts for the production of propene and related light olefins

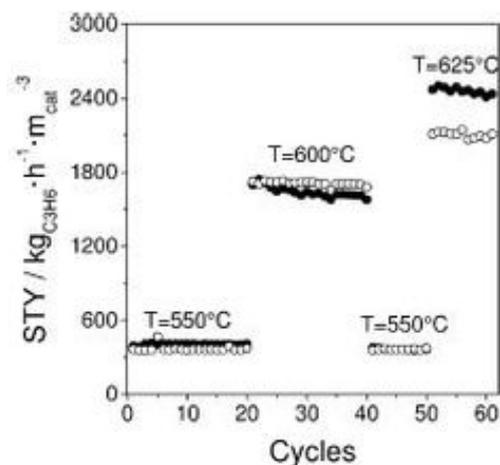
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Challenge

Light olefins such as propylene and ethylene are among the most important feedstocks in the chemical industry. They are employed in the production of a vast array of chemicals, including polymers, solvents, dyes, resins, fibers and drugs. Most common methods for obtaining light olefins are steam cracking and fluid catalytic cracking (FCC) of naphtha, light diesel and other oil byproducts. However, given the high market demand for olefins, the limited reserves of petroleum and the low selectivity of the cracking processes towards the production of particular olefins, the industry is looking for an alternative, more economical and efficient technology.

One particular promising alternative is provided by the conversion of shale gas, which in the last decade has become vastly available and cheap. In addition to methane, natural shale gas contains considerable amounts of natural gas liquids (NGL) such as ethane and propane, which can be easily separated from methane and converted into light olefins by non-oxidative dehydrogenation. Indeed, non-oxidative propane dehydrogenation (PDH) has become an established large-scale process, and in 2012, about 5 million metric tons of propylene (over 6% of total worldwide production) have been produced by PDH. This number is expected to increase significantly in the next couple of years as new PDH plants have been announced or are already under construction.

Despite the maturity of PDH in terms of large-scale propylene production, the process faces considerable challenges, particularly with regard to catalyst development. Indeed, state-of-the-art processes use chromium- or platinum-based catalysts, which either are toxic and possess limited selectivity (CrO_x) or are expensive (Pt). Furthermore, catalyst durability is an issue, prompting researchers to search for more suitable alternatives based on supported oxides of metals or transition metals. In this context, an Al_2O_3 -supported catalyst, consisting of two typical propane dehydrogenation components, namely Pt and Ga_2O_3 , provided promising results, but long-term tests over 150 cycles of repeated hydrogenation and regeneration revealed a loss of the initial activity of about 30% during the first twenty cycles. Hence, more efficient and durable PDH catalysts are still needed.



Space-time yield (STY) of propene over Cu(0.05 wt%)/LaZrO_x (filled circles) and Cr(19.6 wt%)-K(0.9 wt%)/Al₂O₃ (open circles) in a series of 60 PDH/regeneration cycles at 550, 600, and 625°C

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Comprehensive studies of alternative PDH catalysts composed of unconventional components revealed that lattice defects of the support are the actual catalytically active sites. Such defects can be generated under PDH conditions by metal oxides. ZrO₂ promoted with other metal oxides is a typical representative, which has been used before as support for catalytically active Pt, CrO_x or GaO_x species. In these previous studies, however, the loading with noble metal or metal oxide was too high to interrogate the intrinsic activity of the support.

Mechanistic analyses now revealed that coordinatively unsaturated zirconium cations (Zr_{cus} , where cus = coordinatively unsaturated) are the active sites, which possess PDH activity and selectivity comparable to those of industrially relevant CrO_x-based catalyst. The concentration of Zr_{cus} can be adjusted by varying the kind of ZrO₂ promoter and/or by supporting tiny amounts of hydrogenation-active metal. As a proof of concept, a number of catalysts with Cu, Ni, or Co species supported on LaZrO_x have been prepared, whereat it should be noted that none of these metals had ever been reported before to be active in PDH reactions. Nonetheless, all these catalysts revealed up to five-times higher rates of propylene formation than LaZrO_x, and, surprisingly, a Cu(0.05 wt%)/LaZrO_x catalyst was only two-times less active than the best-performing Ru(0.05 wt%)/LaZrO_x catalyst. A comparative study of the proprietary Cu(0.05 wt%)/LaZrO_x and the industrial-relevant Cr(19.6 wt%)-K(0.9 wt%)/Al₂O₃ clearly showed that the Cu(0.05 wt%)/LaZrO_x gives a similar or even higher space-time yield (STY) and does not significantly change its performance over many cycles of dehydrogenation and regeneration. The catalyst also showed propylene selectivity well above 90%, and main side products were light

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- high olefin selectivity
- excellent space-time yield