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Single-Pass Catalytic Conversion of Syngas into Olefins via Methanol

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Light olefins (ethene, propene and butenes) are key building blocks in the petrochemical industry, with an annual production of more than 120 million metric tons.[1] They are mainly produced by naphtha and ethane cracking, but during the last decade, rising oil prices combined with the shale-gas revolution have been strong incentives for a gradual transition from oil to natural gas and coal as raw materials for the petrochemicals industry. Two industrial processes for the conversion of methane (the main component of natural gas) and coal into C_{2+} hydrocarbons saw remarkable growth during this period: The Fischer–Tropsch (FT) process for the production of mainly liquid-range hydrocarbons, and the methanol to olefins (MTO) process for the production of light olefins, in particular propene and ethene.[2]

Both processes are indirect, and proceed via a common intermediate, namely synthesis gas, or syngas, which is a mixture of CO and H_2. The industrial importance of syngas stems from it being the thermodynamically favored product from balanced mixtures of hydrocarbons and oxidants such as O_2, CO_2, and H_2O at temperatures above 800 °C. In a next step, the FT process converts syngas into higher hydrocarbons, while the MTO process requires yet another step, the conversion of syngas into methanol, before higher hydrocarbons are formed in the MTO reaction.

Syngas-based processes will potentially become even more attractive in the future, when renewable carbon sources (biomass, CO_2) are expected to gradually replace fossil fuels. Therefore, efforts to optimize syngas-based processes for the production of light olefins are sky-rocketing, with particular focus on the FT process for the production of light olefins, so-called Fischer–Tropsch to Olefins (FTO), and combined FT and cracking processes.[1] More recently, a combination of a mixed-oxide catalyst with the MTO catalyst for the single-reactor conversion of syngas into olefins via an oxygenate intermediate was developed[3,4] (Figure 1).

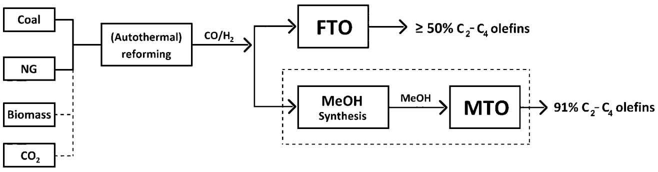

Figure 1. General scheme for the FTO (upper) and MTO (lower) processes.

The two approaches are mechanistically very different. The FT process uses supported Fe- or Co-based catalysts. Product formation proceeds through a surface carbide mechanism, giving mainly linear olefins and paraffins. The chain-length distribution is determined by the relative rates of CH_2 insertion and chain termination reactions, the so-called Schulz–Anderson–Flory distribution, and the catalyst and reaction conditions may be tuned to favor products ranging from methane and light olefins at one end, to heavy waxes at the other. It has been shown that the addition of sodium and sulfur to Fe-based catalysts promotes the formation of C_2–C_4 olefins while suppressing methane formation, thereby leading to stable performance with 50 % selectivity for C_2–C_4 olefins at more than 70 % CO conversion.[5]

The industrial methanol to olefins (MTO) process proceeds over a crystalline microporous silico-aluminophosphate catalyst, H-SAPO-34. An exceptional 91 % C_2–C_4 olefin yield is obtained at full methanol conversion.[6] The exceptional selectivity for C_2–C_4 olefins is due to the structure of H-SAPO-34 (Figure 2), combined with a modest acid strength. Its pore structure consists of large cavities with a diameter 7.3 Å × 12 Å that are connected by small windows with a diameter 3.8 Å × 3.8 Å. Partial substitution of lattice P atoms by Si creates Brønsted acid sites, which catalyze carbocation-based methylation, oligomerization, aromatization, cracking, and dealkylation reactions, thereby leading to a mixture of branched and linear olefins, paraffins, and aromatic hydrocarbons.[7] The H-SAPO-34 windows allow only linear hydrocarbons to escape, which means that the process is shape selective, and other product ranges may be obtained by using zeolite and zeotype catalysts with larger pore sizes.[7]

Cheng et al[4] recently described the successful combination of the production of methanol from syngas with further conversion of methanol into olefins. A binary Zr-Zn oxide is used as a catalyst for methanol synthesis, and is combined with the preferred MTO catalyst, H-SAPO-34. The reaction is

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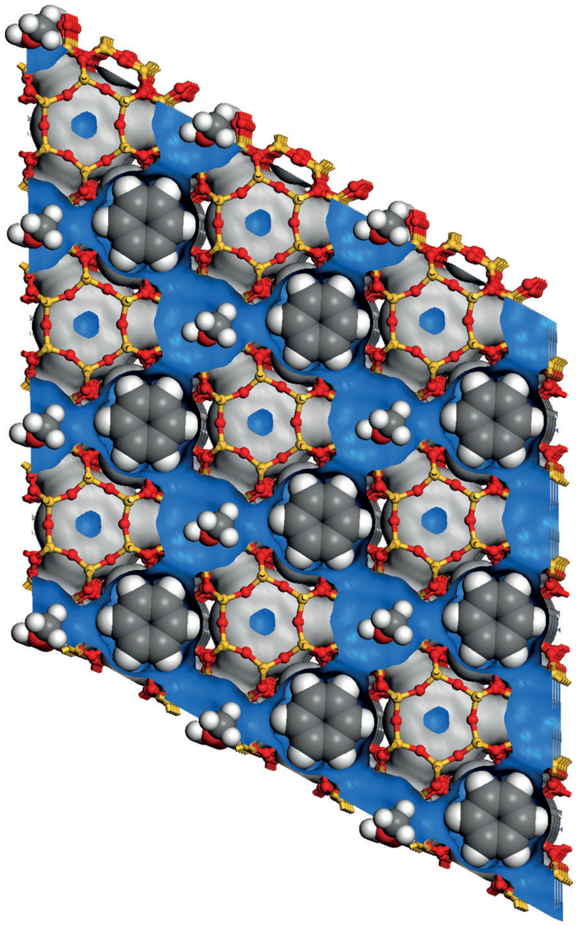

Figure 2. The cavity–window structure of H-SAPO-34. Lattice Al, P, Si atoms are shown in yellow, while oxygen atoms are shown in red. The void space is shown in blue (interior) and grey (exterior). Benzene and methanol molecules are inserted to illustrate the cavity and window size. Image courtesy of K. P. Lillerud.

carried out under typical MTO conditions; 400 °C and 10 bars, with $H_2/CO = 2:1$. The catalyst combination yielded a very promising 74 % selectivity for C_2–C_4 olefins at 11 % CO conversion. In a long-term experiment under slightly different conditions, CO conversion and C_2–C_4 olefin selectivity values of 9.2 % and 68 %, respectively, were maintained for 100 h of reaction.[4]

The beautifully simple rationale behind the contribution of Cheng et al. is to overcome the thermodynamic limitation of methanol formation under the preferred MTO conditions by applying Le Chatelier's principle (see Figure S1 in the Supporting Information of the Cheng et al. Communication). The task is far from trivial, however, with the first challenge being to find a catalyst that is able to selectively convert syngas into methanol at 400 °C. After identifying the binary Zr-Zn oxide as a catalyst that is selective for methanol production, Cheng et al. demonstrated the successful implementation of Le Chatelier's principle by comparing the CO conversion obtained over the binary Zr-Zn oxide alone to that obtained over a mixture of the binary Zr-Zn oxide and H-SAPO-34. A ten-fold increase in CO conversion was observed, and methanol was completely converted into hydrocarbons over the mixed catalyst. Intimate mixing of the two catalysts, preferentially by ball milling, was observed to significantly influence the CO conversion.

A major challenge with the mixed process is the strong thermodynamic drive for hydrogenation of C_2–C_4 olefins to the corresponding paraffins at 400 °C. Cheng et al. demonstrate that H-SAPO-34 alone is capable of hydrogenating C_2–C_4 olefins to their saturated analogues under elevated H_2 pressures, and that the hydrogenation ability of H-SAPO-34 decreases with decreasing Si content. The observation of full methanol conversion but only partial CO conversion under the applied test conditions may suggest that the activity of the MTO catalyst could be reduced even more, thereby potentially enhancing the olefin/paraffin ratio at high CO conversion.

It is also interesting to note a parallel contribution using a similar approach.[3] Jiao et al. combined a partially reduced $ZnCrO_x$ catalyst with SAPO-34 and reported 80 % selectivity for C_2-C_4 olefins at 17 % CO conversion at 400 °C, 25 bars, and $H_2/CO = 1.5$. The olefin/paraffin ratio was 6.3, compared to 2.2 in the work by Cheng et al. Further studies are required to determine whether the difference between the two systems can be ascribed to the catalyst or the conditions used, or to a combination of both.

The single-pass conversion of CO into C_2–C_4 olefins in the combined processes is presently too low to compete with the two-stage MTO process. However, by demonstrating the ability to overcome several obstacles of the combined system, Cheng et al. and Jiao et al. bring inspiration to scientists all over the world for finding even better combinations of active sites and reaction conditions, thereby improving the kinetic selectivity of the combined process for industrial implementation.

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