

SPECTROSCOPY

Giving oxygenates a new spin

Elucidating the reaction mechanism of a catalytic process is very challenging. Now, advanced solid-state nuclear magnetic resonance experiments demonstrate the importance of oxygenates to regulate the conversion of synthesis gas over an oxide–zeolite–based bifunctional catalyst material.

Marc Baldus and Bert M. Weckhuysen

Synthesis gas, a mixture of carbon monoxide and hydrogen, is considered one of the important building blocks to make our future chemicals and fuels as it can be produced from almost any carbon source, including waste, biomass and natural gas¹. Although historically, Fischer–Tropsch synthesis catalysts, based on iron and cobalt^{2,3}, are used, oxide–zeolite–based bifunctional catalysts, coined as OXZEO materials, have more recently been explored as valuable composite materials to produce light olefins, long-chain hydrocarbons and aromatics from synthesis gas^{4,5}. The emerging success of the OXZEO system is illustrated by among others, its industrial exploration at the Shaanxi China pilot plant facility⁴, but the mechanism behind this novel catalyst material remains elusive. It has been assumed to consist of two consecutive, but classical steps in which methanol is first synthesized on the oxide phase and subsequently converted into a variety of hydrocarbons according to the hydrocarbon pool (HCP) mechanism on the zeolite phase⁶. However, the presence of these HCP-type species in an OXZEO catalyst and their active involvement in the formation of, for example, light olefins and aromatics has not been experimentally proven.

Now, writing in *Nature Catalysis*, Hou and colleagues have used a combination of quasi in-situ solid-state nuclear magnetic resonance (ssNMR) and online gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) to investigate this catalytic process in great detail⁷. This combination of techniques provided both chemical and structural information on the processes taking place in the main OXZEO catalyst under study, namely ZnAlO_x/H-ZSM-5. It identified for the first time several carboxylates and other oxygenates present during the conversion of synthesis gas, thereby revealing a so-called oxygenate route in the reaction mechanism (Fig. 1a).

Initially, ²⁷Al and ¹H ssNMR spectroscopy were used to study the properties of the OXZEO materials under investigation,

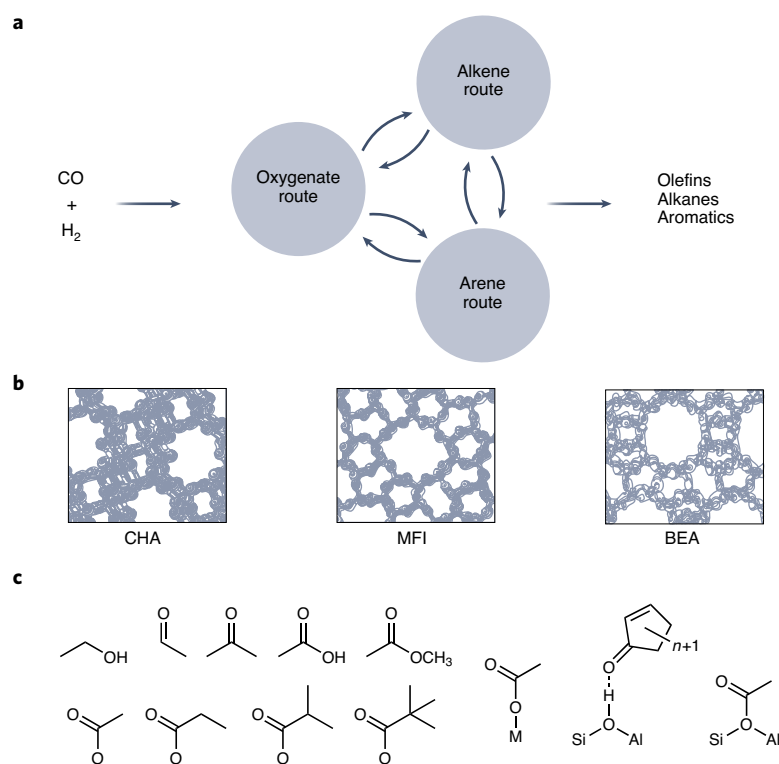


Fig. 1 | Oxygenates detected during CO and H₂ conversion over oxide–zeolite–based catalysts.

a, Conversion of synthesis gas towards the various reaction products not only requires the more classical alkene and arene route, which is taking place in the methanol-to-hydrocarbons process, but also an oxygenate route. It is however clear from this study that more advanced characterization studies, as well as kinetic measurements, are needed to fully link the different oxygenate species in one additional, third reaction cycle, which is fully connected with the dual alkene–arene cycles. **b**, Different zeolite framework structures — that is, CHA (8-membered ring), MFI (10-membered ring) and BEA (12-membered ring) — that lead to distinct oxygenate species. **c**, Different oxygenated end products, as well as adsorbed oxygenate species, as detected by quasi in-situ solid-state nuclear magnetic resonance and online gas chromatography and gas chromatography–mass spectrometry.

including the elucidation of their structural and acidic properties. Subsequently, Hou and colleagues elegantly combined ¹³C labelling and two-dimensional ssNMR spectroscopy to track the various reaction intermediates formed during catalytic operation — lasting from as little as 30 seconds, to over tens of minutes and even up to several hours (for example, 4 h) —

two ZnAlO_x/H-ZSM-5 materials possessing the same MFI framework structure (Fig. 1b) but differing in their acidity. To spectroscopically detect the reaction products under conventional ssNMR instrumental conditions, they adapted a pulse–quench catalytic reactor method, as originally developed by Haw et al., in which reaction intermediates are rapidly

immobilized at low temperatures⁸. These samples were subsequently transferred to the ssNMR sample container and analysed by ssNMR. At the same time, online GC and GC–MS methods were used to follow the reaction products formed, thereby directly allowing catalyst performance to be linked with reaction intermediate formation. For example, various oxygenated compounds, such as formate, methanol and dimethylether (DME) species adsorbed on the catalyst (Fig. 1c) were detected within reaction times as short as 30 s, suggesting the quick establishment of the formate-to-methanol/DME pathway over the metal oxide component. Furthermore, spectroscopic evidence was found for ethene as an initial gas-phase species in the product stream. Extending the reaction time to 2 min led to the accumulation of rich carboxylates/carboxylic acids on the catalyst material, followed by the formation of aromatics and different, more complex oxygenates, such as methylcyclopenten-1-ones, appearing after a reaction time of 10 and 20 min (Fig. 1c). Importantly, other products, including ethoxy, propoxy and butoxy groups, which have not all been detected during the more classical methanol-to-hydrocarbons (MTH) process⁶, were also observed experimentally in this study (Fig. 1c). Ultimately, steady-state conditions were reached after ~4 h, with a multitude of reaction products identified. To further dissect the dominant catalytic process under the steady-state conditions, Hou and colleagues adapted the measurement protocol by starting the reaction with ¹²C-labelled CO, which is largely invisible for the ssNMR experiments used, and then switching to the ¹³CO/H₂ reaction mixture after 20 h of operation. Again, these experiments led to the identification of a variety of surface intermediates and reaction products, and revealed important differences in the steady-state reaction cycles for the two different catalyst materials under study.

All together, these ssNMR results allowed a full mechanistic model to be constructed for the complex reaction network of the synthesis gas conversion over ZnAlO_x/H-ZSM-5, thereby demonstrating the important role of the oxygenate-based route alongside the more classical HCP

dual-cycle MTH reaction mechanism⁶. Indeed, the existence of these oxygenate reaction intermediates and their role in the proposed third reaction cycle somewhat contrasts with the initial involvement of methanol as the starting point of the classical HCP dual-cycle mechanism⁶. In order to illustrate the general validity of the role of oxygenates as important reaction intermediates, similar ssNMR characterization experiments were performed for ZnCr and ZnGa oxides dispersed in zeolite H-ZSM-5, as well as for ZnAlO_x/H-SSZ-13 (with the CHA framework structure) and ZnAlO_x/Beta (with the BEA framework structure) (Fig. 1b). Hou and colleagues found that multi-carbon oxygenates were present for all these catalyst materials. Interestingly the small pores in SSZ-13 favour the aromatic-based cycle, while the wider pores in zeolite H-Beta allow larger carboxylate species to be made. One may expect that other zeolite framework structures and chemical compositions will lead to an even wider variety of oxygenated reaction intermediates and products. However, although a third reaction cycle with several oxygenated molecules has now been proposed (Fig. 1c), it is not fully clear how the different oxygenates are interconverted and mechanistically linked to the other two, more classical, reaction cycles (that is, the alkene and arene cycles) of the MTH process⁶. More advanced characterization studies, alongside detailed kinetics, are needed to further substantiate these points of debate.

From an analytical point of view, the ssNMR experiments employed are already informative, but more detailed knowledge may be obtained in the future. For example, ¹³C–¹³C and ¹³C–¹H ssNMR two-dimensional experiments with a low- and medium-field NMR instrument were used to spectrally resolve a variety of molecular species during different reaction time points and at steady state. Extending ssNMR experiments to three spectral dimensions may help to reduce spectral overlap and assignment ambiguities⁹. In parallel and as shown elsewhere¹⁰, molecular mobility and the influence of the zeolite pore geometry could be further investigated as a function of zeolite framework

type. Conducting these experiments at ultra-high-field NMR conditions, in combination with proton (¹H)-detected ssNMR⁹ and hyperpolarization methods, such as dynamic nuclear polarization, would offer unprecedented spectral resolution and sensitivity. These analytical advancements would further broaden the use of ssNMR to elucidate complex catalytic reactions in time and chemical space for other zeolite-based catalyst materials.

Finally, recent developments in the field of tandem catalysis¹¹, together with the latest study of Hou and colleagues, show that catalyst scientists are on their way to developing relevant structure–performance relationships under reaction conditions to elucidate complex reaction networks in multifunctional catalysis. This also demonstrates that the more classical ideas on catalysis functioning should always be verified by experimental methods as unexpected reaction intermediates may be operative. Only once this is done can new, more active or selective solid catalysts be designed and ultimately utilized in practice. □

Marc Baldus¹✉ and Bert M. Weckhuysen^{1,2}✉

¹NMR Spectroscopy, Bijvoet Center for Biomolecular Research, Utrecht University, Utrecht, the Netherlands. ²Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Utrecht, The Netherlands.

✉e-mail: M.Baldus@uu.nl; B.M.Weckhuysen@uu.nl

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Competing interests

The authors declare no competing interests.