Catalysts for hydrogen, methanol, ammonia and circular CO_2

By Stephen B. Harrison, Founder and Managing Director at sbh4 consulting

Formic acid preserves animal feeds

Catalysts make reactions go faster and to the right place: they improve velocity. If there is one thing the energy transition and the pursuit of Net Zero needs, it is precisely velocity. Catalysts have a central role to play in accelerating cost-effective decarbonisation.

Decades ago, formic acid was isolated as a chemical by distilling red ants. That was a biogenic and renewable source for this animal-feed additive. However, it was never intended to be a scalable solution.

Production of low-cost formic acid from natural gas via methanol has been the default for decades. Now, the imperative is to return to a sustainable pathway to make this essential feed additive. Catalysts can support electrochemical conversion of renewable power and captured carbon dioxide (CO_2) to formic acid.

Natural gas has been the mainstream feedstocks to produce hydrogen, methanol and ammonia for decades. Catalysts are used to convert this fossil fuel to the target products in the most energy-efficient manner.

The transformation that must now take place is to conduct these operations in a climate-neutral way in support of a broader decarbonisation agenda. Catalysts will still be required, but the processes must adapt to enable cost-effective capture of CO_2 that is produced during the chemical transformations.

Hydrogen, ammonia and methanol

Steam methane reforming (SMR) of natural gas is the widespread process for pure hydrogen production. Various catalysts are used in the pre-reformer, primary reformer, secondary reformer, high-temperature shift (HTS) and low-temperature shift (LTS) reactions. This technology pathway is used to make hydrogen for refined products processing and ammonia production.

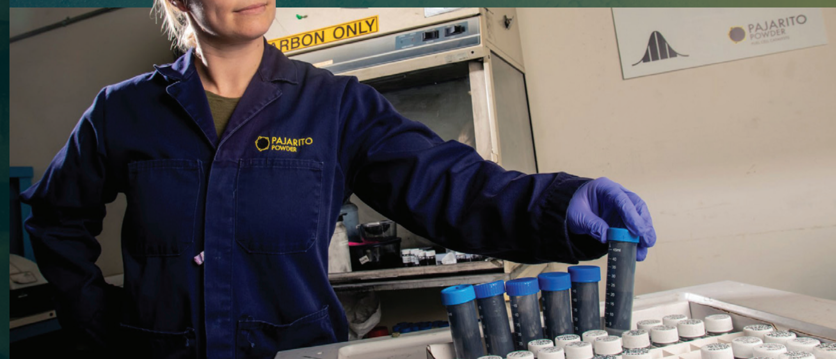
When methanol is the target molecule, syngas is required. In this case, an autothermal reformer (ATR) is sometimes favoured. "In an ATR, multiple catalysts can be used in layers," said Norbert Ringer, Global Methanol Industry Director and global Syngas Expert at Clariant.

"In case of CO-rich Syngas from partial oxidation of heavier feedstocks, HTS and LTS catalysts such as Clariant's ShiftMax 120 and ShiftMax 217 can be used to adjust the ratio of hydrogen to carbon monoxide (CO) in the syngas", added Ringer. This fine-tuning ensures the optimum stoichiometric feed for methanol synthesis.

Downstream of the syngas production, a different catalyst is used for the methanol synthesis reaction. Traditionally, methanol synthesis has been from syngas that is rich in hydrogen and CO, but with carbon dioxide (CO_2) also being present. The ability of the catalyst to withstand the presence of CO_2 is essential and if it is able to convert that CO_2 into methanol, this is a further benefit.

A modern pathway to green e-methanol is through the direct hydrogenation of CO_2 with green hydrogen from electrolysis. In this case, similar catalysts can be used to the ones that have proven themselves to be effective at converting CO_2 to methanol in the traditional 'grey' process. "We have adapted Clariant's proven MegaMax® methanol synthesis catalyst to for e-methanol production through the direct hydrogenation of CO_2 pathway", concludes Ringer.

Partially cracked ammonia can displace fossil diesel as a fuel



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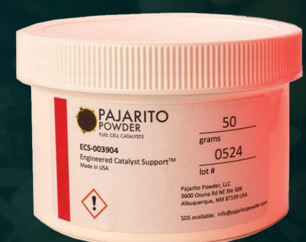

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Blue molecules

In order to decarbonise production of hydrogen, ammonia and methanol from natural gas, capture and permanent storage of the CO_2 that is produced through the reforming reactions is increasingly being proposed. If the CO_2 capture rate is sufficiently high, this can generate low-carbon hydrogen and hydrogen derivatives.

The technologies that are likely to be favoured to produce blue hydrogen or blue syngas for low-carbon methanol are partial oxidation (POx) and gas heated reforming (GHR). POx is generally a non-catalytic process, but the GHR uses similar catalysts to those in an ATR.

POx and GHR are aligned to 'blue' molecule production because CO_2 is produced at high-concentration and high-pressure within the process. This facilitates cost effective capture of CO_2 with a high overall CO_2 capture rate, ensuring certification of the hydrogen, ammonia or methanol product as 'low-carbon'.

Unlike SMR and ATR technologies, GHR and POx systems avoid the requirement for fired process heaters or hot-box burners which result in low-pressure, low-concentration, post-combustion CO_2 emissions which are more expensive to capture.

Point of use ammonia cracking catalysts

Ammonigy, based in Germany, has been developing heavy-duty engine systems that can utilise blue or green ammonia as a decarbonised fuel.

CEO Christian Hermle said liquid ammonia is an excellent hydrogen carrier and energy vector in its own right. The volumetric and gravimetric energy density of ammonia are excellent, and it can be produced from green hydrogen without the need to identify a CO_2 source that is required to build circular hydrocarbons.

"Ammonia burns with a slow, or 'lazy'

flame," explained Hermle. "Our solution is to partially crack ammonia so that a mixture of ammonia, hydrogen and nitrogen is produced. This blend of gases burns with similar properties to diesel or natural gas."

The technology Ammonigy has innovated can be used upstream in conventional engines that are commonly used in trains or maritime applications. The partially cracked ammonia can be fed onto these engines and thereby accelerate the deployment of clean fuels and turbo-charge the energy transition.

"We have experimented with a range of ammonia cracking catalysts during the development of our proof-of-concept solution", added Hermle. Nickel works well at high temperatures and platinum group metals can be used to crack ammonia at lower temperatures.

"At the moment we favour platinum-based catalysts. They achieve better conversion at a lower temperature. This translates to acceptable costs for the overall system."

High conversion means the reactor is smaller which reduces the amount of material required and ensures a compact design to integrate into the engine system. Furthermore, at moderate operating temperatures, commonly available grades of steel can be selected to ensure affordability.

When ammonia is used in combustion applications, the emissions of oxides of nitrogen must be considered and mitigated.

"A major focus of our research has been to avoid NOx and nitrous oxide emissions from the engine", added Hermle. "Again, specialised catalysts can mitigate emissions of the pollutant and greenhouse gases."

Circular CO_2 to hydrocarbons

'Decarbonisation' is often used to describe the direction of travel towards Net Zero climate impact. However, many useful chemicals contain carbon. So, defossilisation or carbon circularity may be more accurate descriptions. Increasingly, there is a drive towards CO_2 circularity: utilisation of CO_2 emissions to re-create chemicals that would otherwise have been produced from fossil fuels.

Oxylum in Belgium has been innovating technology in this area. Bert De Mot, Co-founder and CEO, said it is working on the electrochemical conversion of CO_2 into chemical feedstocks.

"In our first business case we focus on the production of green formic acid as an energy vector and circular chemical," he said.

Formic acid has a variety of use-cases, for example it is added to animal feeds to reduce the need for antibiotics and is a processing agent for textile dyeing and finishing. It also has applications in the pharmaceutical sector, as cleaning agent and for de-icing runways.

Ammonia and methanol are also high-potential hydrogen carriers, but formic acid has advantages due to ease of storage and handling.

"An exciting potential new application of formic acid is as a clean hydrogen carrier," added De Mot. "After all, formic acid is a food additive and with appropriate packaging and precautions, it can be used in a diverse range of settings."

Oxylum converts CO_2 to formic acid using catalytically stimulated electrochemical reactions. "There is a host of published research in this area," said De Mot. Tin and bismuth catalysts have been shown to be affective for electrolytic conversion of CO_2 to formic acid. "But we can also target other chemicals, for example CO by using gold or silver catalysts."

The use of a copper-based catalyst shifts the conversion towards the production of Ethylene, ethanol or methane.

"Our work has leveraged the state of the art and taken electrolysis of CO_2 to a new level with superior catalysts which increase the energy efficiency, reaction conversion and selectivity towards the target molecule", concluded De Mot.

AEM and PEM electrolyser catalysts

In the EU and the USA, the production of green hydrogen must align with the use of renewable power. However, wind and solar power generation is inevitably variable and sometimes intermittent. To work in these conditions, careful selection of the electrolyser technology and vendor is essential.

Two modern electrolyser technologies that have the potential to align to variable power input are proton exchange membrane (PEM) and anion exchange membrane (AEM) systems. In each of these technologies, a thin polymer membrane is coated with catalysts that facilitate the required electrochemical reactions to split water and then recombine it as oxygen gas and hydrogen gas.

Pajarito Powder, based in New Mexico, has developed a wide range of catalysts for AEM and PEM electrolysis. Thomas J. Stephenson, CEO and Chairman, said, "Some of our catalyst powders for electrolysis contain conventional platinum and iridium oxide ingredients, and others have been innovated to be 'precious metal free', or PMF."

"AEM electrolysers can use iron, nickel and cobalt based catalysts. These are 'earth-abundant' materials. They are affordable and plentiful and will enable scale up of the AEM technology without potential disruptions to the supply chain or the threat of high materials costs."

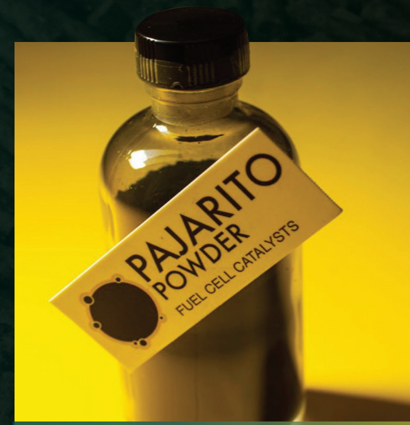
On the other hand, most commercial PEM systems rely on platinum and iridium oxide as catalysts. "Platinum is expensive, and iridium is super-expensive," added Stephenson. "And beyond the issue of cost, there are some concerns about the availability of iridium at scale to support an expansion of PEM electrolyser production."

Reducing the amount of iridium in PEM catalysts will result in cost reductions. However, the efficacy of the catalyst must remain high so that a high current density and small surface area of the electrode and catalyst coating is required.

This minimises the overall size of the electrolyser stack and, in turn, reduces the costs of the other stack components such as the bipolar plates and porous transport layers, which results in a more affordable PEM electrolyser stack.

Stephenson said it is targeting a 40-60% reduction in the iridium loading compared with conventional PEM catalysts.

"And of course, we want to achieve that whilst preserving the current density. We are also convinced that recycling of older stacks to recover precious metals and introduce circularity will reduce dependence on freshly mined iridium and secure the future of PEM electrolysis in a sustainable manner." gw



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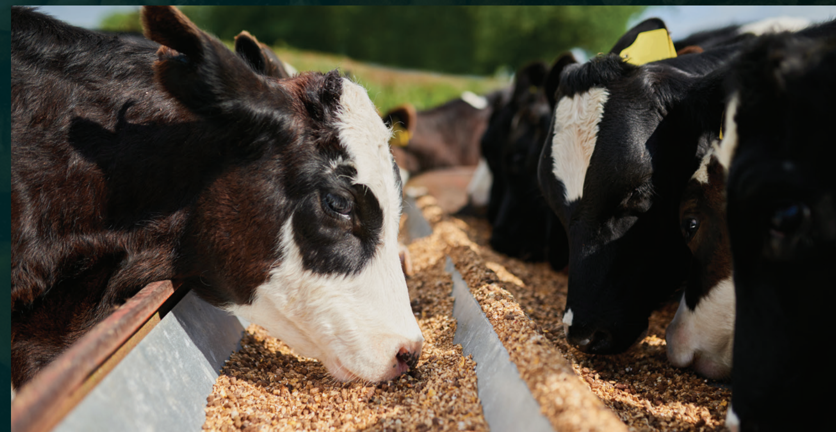
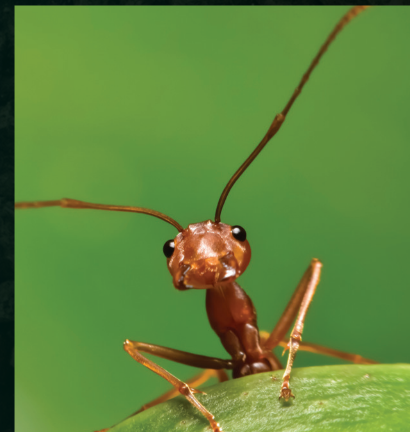

Formic acid is an additive to animal feed


Red ants use formic acid to defend their nest

ATR for Ammonia Production