Catalysts for hydrogen production and processing

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Catalysts make reactions go faster and to the right place: they improve velocity. If there is one thing the emerging hydrogen economy needs, it is precisely that: velocity.

Natural gas has been the mainstream feedstock to produce hydrogen and its main derivatives, 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 taking place is for these operations to be net-zero to support industrial decarbonisation. Catalysts will still be required, but the processes must adapt, and new generations of catalysts will emerge.

Modern methanol catalysts

Steam methane reforming (SMR) of natural gas is the default 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 speciality chemicals firm Clariant.

“In case of carbon monoxide (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 CO in the syngas,” Ringer explained. This fine-tuning ensures the optimum stoichiometric feed for methanol synthesis.

Downstream of 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 CO_2 also being present. The ability of the catalyst to withstand the presence of CO_2 is essential. 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 those 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 for e-methanol production through the direct hydrogenation of CO_2 pathway,” Ringer said.

Catalytic and non-catalytic options for RWGS

The reaction of green hydrogen and captured, recycled CO_2 produces a renewable, circular syngas. This is a clean alternative to the production of syngas from natural gas reforming. During this process, hydrogen combines with CO_2 to produce water and CO. This is the reverse water gas shift (RWGS) reaction.

Clariant’s ShiftMax 100 RE catalyst enables the RWGS reaction and is aligned to the conversion of CO_2 and hydrogen to clean syngas. It is used by Ineratec in its electrofuels production process, which is being demonstrated at its Era One pilot facility in Frankfurt, Germany.

Shell has patented (WO 2020/114899 A1) a non-catalytic partial oxidation (POx)-based RWGS system that operates between 1,000 and 1,500°C enables RWGS without a catalyst. The equipment would resemble classical natural gas-fed POx reactors currently used by industrial gases majors, such as Linde’s POx reactor at La Porte and Singapore. And, as with the classical POx units, an air separation unit (ASU) or pipeline could be used to supply the oxygen.

Johnson Matthey has patented (US 2023/0264955 A1) a nickel-based catalyst for their catalytic POx process (CPOx). This technology would resemble an ATR. It proposes using oxygen co-product from the hydrogen electrolyser to feed the RWGS POx reactor. This process integration would reduce or eliminate the need for ASU oxygen supply.

VTT, a Finnish research institute, patented (WO 2019/175476 A1) a CPOx process for RWGS using a rhodium-based catalyst. This process operates at 800 to 950°C and 20 bar, lower than the range proposed by Shell in its non-catalytic RWGS POx reactor. It is generally the goal that a catalyst will enable a process to operate at a reduced temperature.

Ammonia cracking catalysts

German-based Ammonigy 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 is 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,” Hermle added. “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.”

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The technology that Ammonigy has created can be used upstream of conventional engines that are commonly used in trains or maritime applications. The partially cracked ammonia can be fed onto these engines.

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

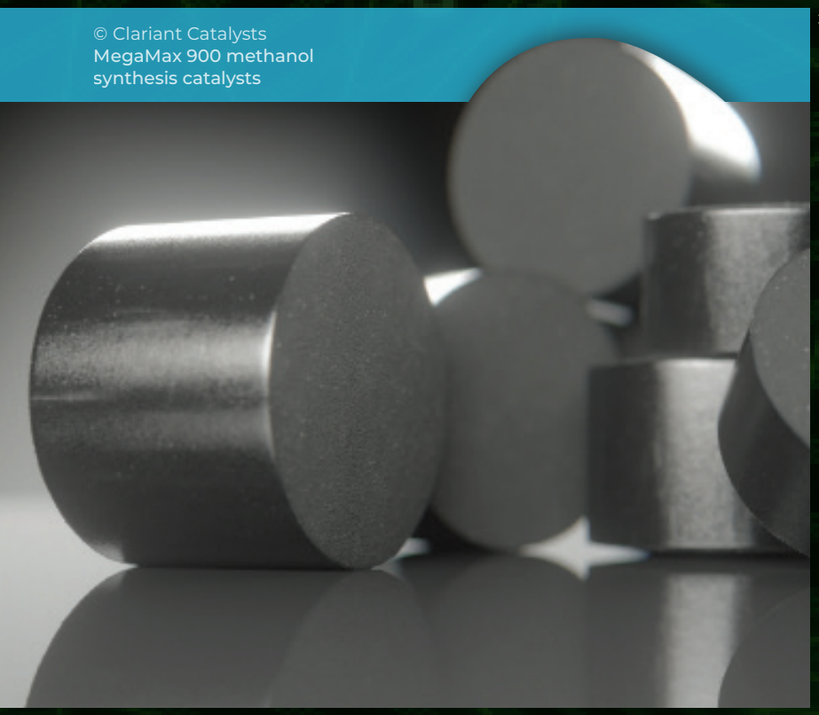
“At the moment, we favour platinum-based catalysts. They achieve better conversion at a lower temperature. This translates to acceptable costs for the overall system.”

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,” Hermle stressed. “Again, specialised catalysts can mitigate emissions of the pollutant and greenhouse gases.” >>

Catalysts for reforming, Power-to-Liquids, ammonia and Power-to-X pathways

Process	Reaction	Enthalpy of reaction	Temperature / ° C	Typical catalysts	Commercial catalyst examples
Steam methane reforming (SMR)	$CH_4 + H_2O \rightarrow CO + 3H_2$	– 206 kJ / mol	700–950	NiO-based	Clariant REFORMAX 330 LDP
Oxygen-fed partial oxidation (POx)	$2CH_4 + O_2 \rightarrow 2CO + 4H_2$	– 24.5 kJ / mol	700–1,100	CaAl12O19	Clariant REFORMAX 420 with REFORMAX 330 LDP
High-temperature water gas shift (HT WGS)	$CO + H_2O \rightarrow CO_2 + H_2$	– 131.2 kJ / mol	320–450	Fe_2O_3 / Cr_2O_3 with Cu promoter	Johnson Matthey KATALCO 71 range, Clariant ShiftMax 120
Low-temperature water gas shift (LT WGS)	$CO + H_2O \rightarrow CO_2 + H_2$	– 131.2 kJ / mol	180–270	CuO & ZnO on alumina	Johnson Matthey KATALCO 83 range, Clariant ShiftMax 217
Reverse water gas shift (rWGS)	$CO_2 + H_2 \rightarrow CO + H_2O$	– 41.5 kJ / mol	700–900	Ni-based	Clariant HyProGen R-70
Catalytic POx rWGS	$2CO_2 + 2O_2 + 6H_2 \rightarrow 2CO + 6H_2O$	Δ H < 0	800–950	Ni on metal oxide, Rh on alumina	Johnson Matthey HyCOgen, VTT
Dry methane reforming (DMR)	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$	– 247.1 kJ / mol	800–950	Ni oxides	BASF SYNSPIRE G1-110, Clariant HyProGen R-70
Methanation of CO_2	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	– 165.0 kJ / mol	300–400	NiO / alumina	Clariant METH 135, Topsøe MCR-2
Methanol synthesis from syngas	$CO + 2H_2 \rightarrow CH_3OH$	– 90.4 kJ / mol	200–300	CuO / ZnO / MgO on alumina	Topsøe MK-121, Johnson Matthey KATALCO 51, Clariant MegaMax 900
Methanol synthesis via CO_2-hydrogenation	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	– 49.5 kJ / mol	200–300	Cu-based	Johnson Matthey eMERALD, Clariant MegaMax 800
Methanol to olefins (ethylene)	$2CH_3OH \rightarrow C_2H_4 + {}_2H_2O$	– 11.72 kJ / mol	400–500	SAPO-34, ZSM-5	UOP MTO-600
Methanol to olefins (propylene)	$3CH_3OH \rightarrow C_3H_6 + {}_3H_2O$	– 30.98 kJ / mol	400–500	SAPO-34, ZSM-22	Clariant MTPROP
Methanol reforming to syngas	$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$	– 49,2 kJ / mol	240–320	CuO / ZnO/MgO on alumina	Topsøe MDK-20
DME synthesis from methanol	$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$	– 23.5 kJ / mol	250–300	$Al2O_3$ or zeolite based	Topsøe DME-99-ECO
DME to paraffins	$CH_3OCH_3 \rightarrow 2(– CH_2–) + H_2O$	Δ H < 0	320–380	Zeolite based, with iron promoter	Nanostructured ZSM-5
Formic acid synthesis via CO_2-hydrogenation	$CO_2 + H_2 \rightarrow HCOOH$	– 31.2 kJ / mol	<100	RuCl2(PTA)4, CU-MOF-5	Emerging
CO-based fischer-tropsch synthesis (CO FTS)	$CO + 2H_2 \rightarrow (– CH_2–) + H_2O$	– 152 kJ / mol	180–250	Co-, Fe-based	Johnson Matthey FT CANS, Greyrock GreyCat
CO_2-based fischer-tropsch synthesis (CO_2 FTS)	$CO_2 + 3H_2 \rightarrow (– CH_2–) + 2H_2O$	– 111 kJ / mol	30 –350	Na or K modified Co-Fe based	Emerging
Ammonia synthesis (Haber Bosch)	$N_2 + 3H_2 \rightarrow 2NH_3$	– 45,9 kJ / mol NH_3	350–550	Fe-based	Topsøe KM1
Low temperature ammonia cracking	$2NH_3 \rightarrow N_2 + 3H_2$	– 45,9 kJ / mol NH_3	400–500	Ru, PGM-based	Johnson Matthey KATALCO 27-612, Clariant HyProGen 850 DCARB
High temperature ammonia cracking	$2NH_3 \rightarrow N_2 + 3H_2$	– 45,9 kJ / mol NH_3	600–800	Ni-based	Johnson Matthey KATALCO 27-2, Topsøe H_2Retake, Clariant HyProGen 820 DCARB
PEM electrolyser cathode reaction (HER)	$4H^+ + 4e– \rightarrow 2H_2$	– 285.83 kJ / mol water	50–80	Pt	Pajarito Powder Pt/ECS, Johnson Matthey Platinum black HSA
PEM electrolyser anode reaction (OER)	$2H_2O \rightarrow 4H^+ + 4e– + O_2$	– 285.83 kJ / mol water	50–80	Ir	Pajarito Powder EEC-IrOx, Johnson Matthey Iridium-black
PEM fuel cell cathode reaction	$4H^+ + 4e– + O_2 \rightarrow 2H_2O$	– 285.83 kJ / mol water	ambient–55	Pt-based	Pajarito Powder Pt/ECS-3701, Heraeus H2FC-50Pt C700
PEM fuel cell anode reaction	$H_2 \rightarrow 2H^+ + 2e–$	– 285.83 kJ / mol water	ambient–55	Pt	Pajarito Powder Pt/ECS, Heraeus H_2FC-30Pt-C60T
AEM electrolyser cathode reaction (HER)	$2H_2O + 2e– \rightarrow 2OH^- + H_2$	– 285.83 kJ / mol water	ambient–55	non-PGM	Pajarito Powder Pt/ECS
AEM electrolyser anode reaction (OER)	$4OH^- \rightarrow 2H_2O + O_2 + 4e–$	– 285.83 kJ / mol water	ambient–55	Ni, Co, Fe-based	Pajarito Powder EEC-PbRuOx



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MegaMax 900 methanol synthesis catalysts

>> Hydrogen electrolyser catalysts

In the EU and the US, the production of green hydrogen must align with the use of renewable power. However, wind and solar power generation is inevitably variable and sometimes also 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 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 in the US, has developed a wide range of catalysts for AEM and PEM electrolysis. CEO and Chairman, Thomas Stephenson, 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’.”

“AEM electrolysers can use iron, nickel and cobalt-based catalysts. These are ‘earth-abundant’ materials,” Stephenson said. “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,” he added. “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 a small surface area of the electrode and catalyst coating are 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 explained, “We are targeting a 40–60% reduction in the iridium loading compared to 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.”

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