UTILIZING IN-SITU GENERATED HYDROGEN GAS FOR THE CONVERSION OF CO_2 INTO SUSTAINABLE FUELS OVER METAL-ORGANIC FRAMEWORKS AS CATALYSTS

INTRODUCTION

The unfortunate yearly trend of energy related record-breaking CO_2 emissions reached a new high of 37.4 Gt in 2023[1], urging researchers in the field of catalysis and process development to focus on carbon capture, storage and utilization solutions[2]. Designing highly efficient tuneable catalysts for carbon capture is the gateway to greatly reducing CO_2 emissions in the ever-growing world of global transportation and industrial sectors while harvesting the valuable fuels and chemicals yielded in the process.

In the group's work featured in this application note, the researchers utilized pure and green hydrogen generated from water using the H-Genie® Hydrogen Generator and an iron-based metal-organic framework catalyst to produce paraffin hydrocarbons (up to C_{16}) from CO_2 in continuous flow[3].

INSTRUMENTATION AND SAFETY CONSIDERATIONS

The H-Genie® utilizes patented technology to generate 99.99% purity H_2 gas from water. Designed with safety and ease of use in mind, this bench-top hydrogen generator provides accurate H_2 dosing up to 1000 NmL/min flow rate and 100 bar pressure while eliminating the risks associated with H_2 cylinders in laboratories. A multitude of built-in automated safety features such as a hydrogen sensor, over pressure protection, and leakage detection, as well as constant performance monitoring contributes to the user's peace of mind while using the instrument. The ability to connect to flow or batch reactors or to fill balloons ensures seamless transition between technologies. The group designed a one-of a kind continuous flow reactor setup for carbon capture catalyst testing with the H-Genie as the green H_2 source. This allowed the researchers to safely and effectively test their catalysts under various conditions for up to 100+ hours[3].

While the group's custom-made flow reactor provides great control over system parameters, these kinds of experiments could also be carried out in an off the shelf benchtop flow reactor like the Phoenix Flow Reactor. With heating capabilities up to 450°C, pressures up to 200 bar and various fixed bed column sizes available, scaling of parameter testing is streamlined in the system.

A built-in pressure sensor coupled with external temperature monitoring points provide further insight into stability and catalyst performance. With this instrument, safety is of utmost importance with configurable safety release valves and software features in action while using the system.

Other than H_2, various gases can also be introduced in a ThalesNano system, using the Gas Module, with a built-in MFC, allowing for the accurate dosing of 13 different gases, including CO_2 and gas mixtures, with flow rates up to 100 NmL/min and pressures up to 100 bar. The Gas Module Plus broadens the parameter scope with up to 1000 NmL/min gas dosing. To avoid the formation of dry ice during CO_2 expansion, a gas preheater is necessary while working with the gas in these systems.

The automated reaction step sequencing and high precision stability monitoring of all ThalesNano instruments are available through the THS System Controller and ReAction software. The software provides the user with the ability to write automated reaction protocols, determine fleet-wide safety triggers and monitor parameters across all instruments in the system.

DISCUSSION AND RESULTS

Ideal candidates for gas storage and catalysis, metal-organic frameworks (MOFs) possess high porosity, great surface area and are highly tuneable in functionality[4]. The novel nature of these structures still leave room for optimization in thermal and chemical stability in many cases. The group carried out reactions using one of the most studied Fe-based MOFs, MIL-100. However, the traditional synthetic methods for MIL-100 demand harsh conditions, hindering feasibility for mass production. Finding mild synthetic processes are crucial for the future of these materials, therefore the researchers developed a room temperature, easily scalable method to yield highly crystalline MIL-100 (Fe). The exact synthetic process can be found in great detail in the original paper[3]. The schematic representation of the system is depicted on Figure 1.

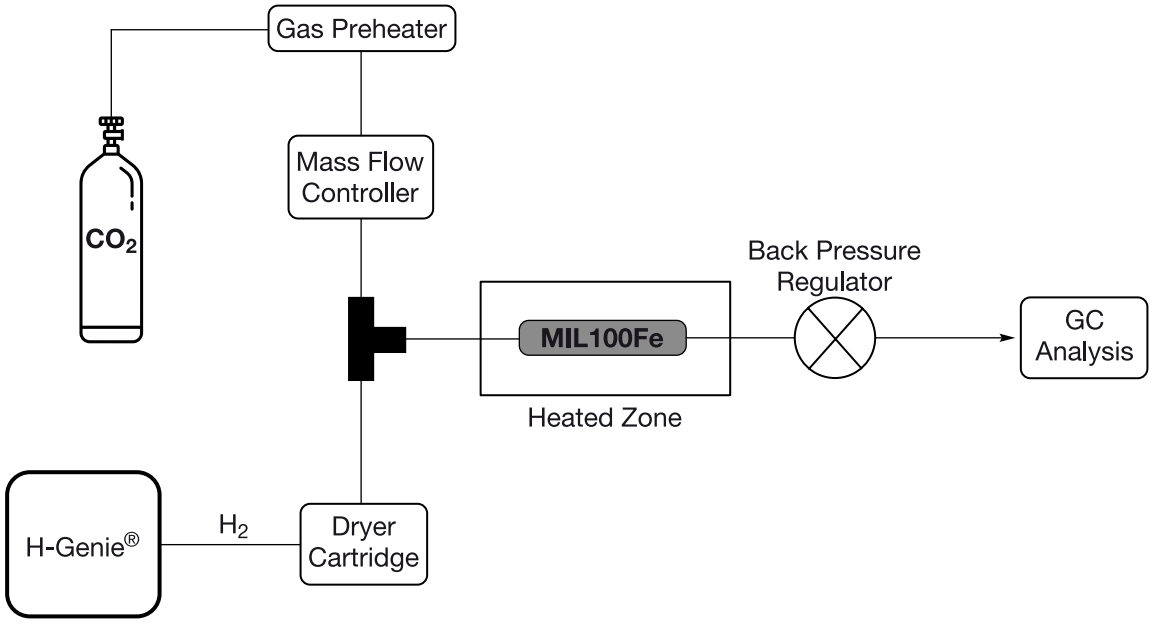

Figure 1: Schematic representation of the flow chemistry reactor platform

The catalytic performance was studied and optimized using a stainless steel high pressure continuous flow reactor equipped with a 10 mm internal diameter fixed-bed where CO_2 hydrogenation experiments were conducted with the H-Genie®'s on-demand generated H_2.

The in-situ reduction of the catalyst was carried out at 340°C (rate of heating was 10°C min^{-1}) for 24h of constant 45 mL/min syngas flow to ensure iron carbide and iron oxide phase presence. During their experiments the group used 1.5 g of catalyst diluted with SiC. The pressure range of 10-30 bar and temperatures of 300°C and 340°C were examined.

The H_2/CO_2 3:1 gas hour space velocity was 2400 mL g_{cat}^{-1} h^{-1}. The group installed a separate purification after the H_2 gas outlet of the H-Genie® to achieve 99.999% H_2. A GC/TCD system was used to analyse gas composition.

Increasing the temperature to 340°C the CO_2 conversion reached 44.1% from 29.4% without major changes in CO and CH_4 selectivity. In the experiments high reaction temperature limited the liquid fraction's carbon range to C_5-C_{12} with a maximum of 10% side product formation. At 340°C raising the pressures to 30 bars a significant CO_2 conversion improvement (from 34.2% at 10 bar to 44.1% at 30 bar) coupled with an increase in chain growth probability was observed (Figure 2).

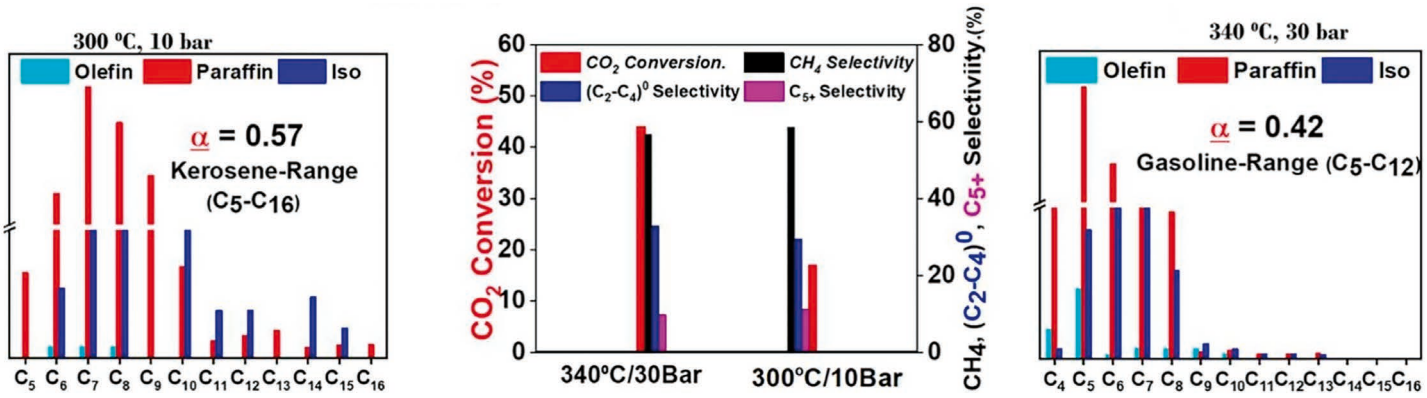

Figure 2: Conversion and selectivity charts of experiments at 300°C 10 bar and 340°C 30 bar[3].

By decreasing pressures and temperatures, the carbon range of liquid fraction shifted to the kerosene regime (C_5-C_{16}). It was determined that the natural gas range (C_1-C_4) bears the largest share of CH selectivity (approx. 90%). The C_3-C_4 liquified petroleum gas fraction makes up approximately 50% of the light paraffin portion (C_2-C_4).

To determine industrial feasibility, long term catalytic stability studies were carried out. It was found that after 100 hours of continuous tests, no sign of observable deactivation was detected (Figure 3).

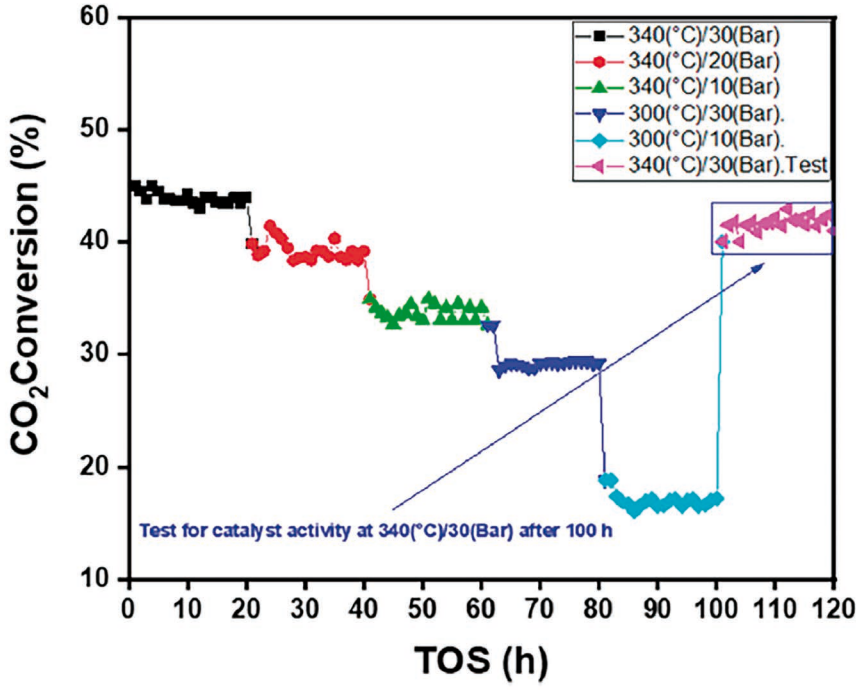

Figure 3: Catalytic performance stability studies[3]

SUMMARY AND CONCLUSIONS

From the stability to the scalability and ease of parameter monitoring in continuous flow showcasing the reality of utilizing these technologies to solve real-world environmental concerns, The group's work sets a great example for chemists and engineers in the field of green chemistry and sustainable process development for carbon capture.

REFERENCES

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