

HIGH PRESSURE CO₂ ACTIVATION IN GAS PHASE WITH THE PHOENIX FLOW REACTOR™



Introduction

The emission of carbon dioxide into the atmosphere, the main cause of global warming, is still increasing every year since carbon-rich fossil fuels are still the primary source of energy.

Catalytic hydrogenation of CO₂ using sustainable hydrogen sources not only reduces the emission of carbon dioxide, but also produces valuable fuels and chemicals.

High-pressure methanol synthesis is a well-documented commercial process, its industrial implementation started already in the late 1990s.

Nowadays, the largest plant is the GO (György Oláh) Methanol Plant located in Iceland, which can convert 5500 tons/year of CO₂ (4000 tons/year of methanol). Conventional thermo-catalytic reactors operating at atmospheric pressure are excellent solutions for methane production, however, obtaining higher molecular weight products with good selectivity can be problematic.^{1,2}

This application note evaluates the performance of the Phoenix Flow Reactor™ in the production of value-added chemicals (other than methane) from a low-cost renewable carbon dioxide source.

Instrumentation

Phoenix Flow Reactor™ was utilized for converting CO₂ to methanol with high selectivity. The system is designed to perform reactions up to 450 °C. The pressure range can exceed up to 200 bar applying a back pressure regulator (**Figure 1**).

Risk assessment and hazards: The Phoenix Flow Reactor system must be placed in a well-ventilated fume hood to avoid inhalation of solvent vapours. It is forbidden to open it at high pressure or temperature. Contact with the heated parts must be avoided.

Experimental

Catalysts and sample preparation: During the synthesis of methanol, mainly copper and zinc oxide-based catalysts (CuO/ZnO/Al₂O₃, CuO/ZrO₂, CuO/ZnO/CrO₃, etc.) are applied.³

In this application, ternary CuO/ZnO/Al₂O₃ catalyst was prepared by co-precipitation method from nitrate salts and a solution of Na₂CO₃ (1 mol/L) as a precipitating agent. The precipitate was allowed to stand for one hour, filtered, washed three times, and then dried overnight at 80 °C. After grinding, the dried hydroxy carbonate precursor was calcined at 300 °C under air for 3 h, resulting in the oxide precursor (**Fig. 2a**).

The catalyst powder was pelletized under 50 kp/cm² pressure, weighted 1 g on average, and thereafter placed into the reactor between the layers of quartz wool (**Fig. 2b**).

Preliminary experiments: Before performing catalytic reactions, preliminary experiments were conducted to determine the optimal reactant gas flow rate, catalyst amount, reactor setup, pressure, and reaction temperature.

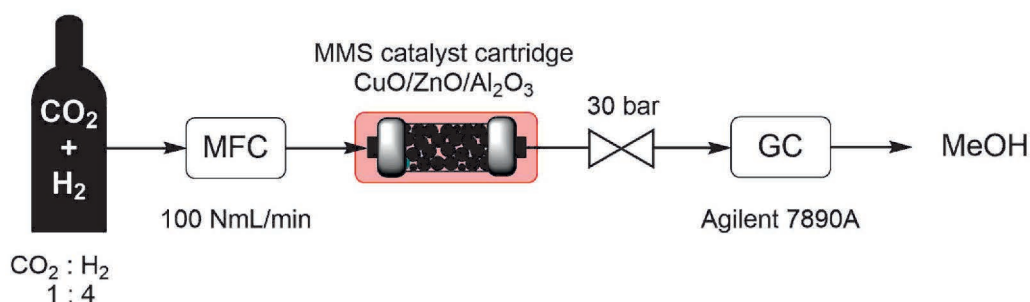


Figure 1. Schematic view of the applied system:

1: Gas Module™ (MFC), 2: Phoenix Flow Reactor™ with the catalyst column, 3: Heat exchanger, 4: Back-pressure regulator (BPR), 5: Agilent 7890A GC

Catalytic experiments: Catalytic reactions were performed in the Phoenix Flow Reactor™ system, applying a 220 mm long metal-metal sealed (MMS) column (9.4 mm inner diameter) in the heated reaction zone. The inlet CO₂/H₂ gas mixture (1/4 ratio) was fed into the system at 100 mL/min gas flow rate.

Prior to catalytic measurements, catalysts were pre-treated at atmospheric pressure: oxidized for 1 h at 300 °C, and reduced with hydrogen for 2 h at 300 °C. After pre-treatment, the samples were cooled down to 200 °C. Next, the reactor was heated up to 300 °C and equilibrated for 120 minutes.

The applied back-pressure regulator maintained 30 bar during the reaction. All products were kept in gas phase and analysed on-line by an Agilent 7890A gas chromatograph equipped with 2 columns: HP-PLOT/Q capillary column connected to a flame ionization detector (FID) and a Porapak Q+S column connected to a thermal conductivity detector (TCD).

CO₂ conversion and CO selectivity, hydrocarbons (C_nH_m), and MeOH selectivity among the carbon products without CO (including C_nH_m, MeOH) were calculated by the following equations:

$$\text{CO}_2 \text{ conversion} = (\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}) / \text{CO}_{2\text{in}} \times 100\%$$

$$\text{CO selectivity} = \text{CO}_{\text{out}} / (\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}) \times 100\%$$

$$\text{C}_n\text{H}_m \text{ selectivity} = N_{\text{C}_n\text{H}_m} / (\text{total carbon atoms of products detected by FID}) \times 100\%$$

$$\text{MeOH selectivity} = N_{\text{MeOH}} / (\text{total carbon atoms of products FID}) \times 100\%$$

CuO/ZnO/Al₂O₃ showed highly efficient catalytic performance, achieving almost 70% methanol selectivity.

Future perspective

The high-pressure/high-temperature Phoenix Flow Reactor™ gives an opportunity for obtaining a large variation of products with diverse selectivity.

By designing and testing perspective catalysts, consisting of high surface area supports (ex. H-ZSM-5), we aim to produce long-chain hydrocarbons with high selectivity, and to the subsequent development of suitable cost-effective methods for their implementation in industrial processes.

References

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- ² W. Li, H. Wang, X. Jiang, J. Zhu, Z. Liu, X. Guo, C. Song, *RSC Adv.*, **2018**, 8, 7651-7669.
- ³ J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang, T. Zhang, *Chem. Soc. Rev.*, **2020**, 49, 1385-1413.



Figure 2. a) The prepared catalyst, b) Schematic view of the applied catalyst column.



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www.thalesnano.com
 LinkedIn: /company/thalesnano-inc-
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ThalesNano Inc.
 Záhony utca 7. | H-1031 Budapest | Hungary
Phone: +36 1 880 8500
Fax: +36 1 880 8500
Email: sales@thalesnano.com
www.thalesnano.com

US Office
 50 S. Penn St. Suite B-2
 Hatboro PA. 19040
 USA
Phone: 215-534-3365
E-mail: USAsales@thalesnano.com