

Catalytic CO₂ Conversion and *In Situ* Spectroscopy at High Pressure

Introduction

The uncontrolled consumption of the world's current primary energy supplies, of finite and non-renewable fossil fuels, are being depleted by the ever-increasing demand of energy from the modern society. The challenge in finding alternative energy sources is also accompanied by the major environmental threat, referred to as global warming induced by the greenhouse gas effect. Carbon dioxide (CO₂) is the most common waste from burning fossil fuels and it is the main greenhouse gas with an excess of 1 teraton of CO₂ in the atmosphere nowadays.

Converting this excess of CO₂ into useful fuels and chemicals could be an integral strategy to deal with the interrelated energetic and environmental problems. Heterogeneous catalytic hydrogenation of CO₂ into fuels and marketable chemicals such as methanol, carbonates, hydrocarbons, ethers, and esters offers effective solutions to convert a large amount of CO₂ in short span of time. Among other reactions, methanol synthesis holds a key position in CO₂ hydrogenation since methanol can be used as a starting feedstock in the chemical industries and as an alternative to fossil fuel.

CO₂ is a thermodynamically stable molecule and an increase in reaction pressure is known to be advantageous for efficient CO₂ activation as evident from the thermodynamic equilibrium conversion and selectivity calculations (Figure 1). The methanol synthesis processes are operated typically at about 50–100 bar with low CO₂ conversion efficiency and low methanol selectivity, often requiring extensive recycling of unconverted reactants. Although lowering the reaction pressure is generally favored because of the general perception of increased energy demands for high-pressure operations, our recent study shows that the energy demanding step is associated mainly with hydrogen production.¹

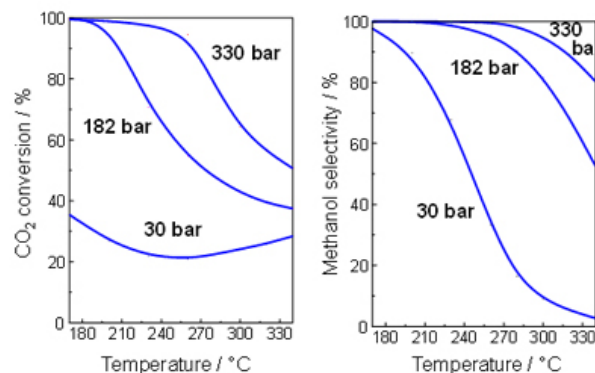


Figure 1: Theoretical thermodynamic calculations for CO₂ hydrogenation at stoichiometric ratio of CO₂:H₂ = 1:3.²

Besides the thermodynamic and kinetic advantages, high-pressure approaches can facilitate the reduction in reactor volume when reactants and/or products are compressive and handling dangerous chemicals such as hydrogen due to smaller contained volume, giving possible economic as well as safety advantages. To achieve this ambitious goal of performing reactions in continuous operation (flow condition) at very high pressure (up to 500 bar), a reactor system using Teledyne ISCO 260D syringe pump was developed [see note]. Along with the reactor system, the syringe pump was also used in the development and operation of *in situ* spectroscopic tools to study the phase behavior and reactions under the demanding high pressure operating conditions.

Using the Teledyne ISCO 260D Syringe Pump

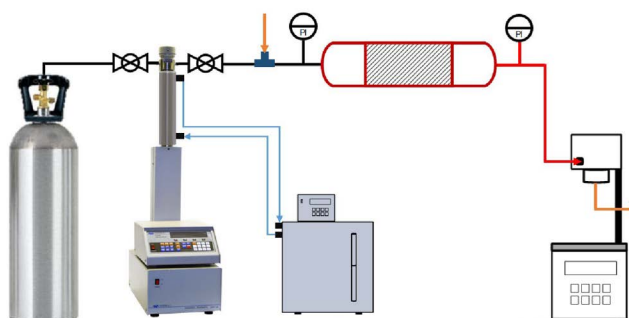


Figure 2: Schematic diagram of high pressure reaction system

The schematic diagram of the high pressure CO₂ hydrogenation setup (Figure 2) shows the Teledyne ISCO 260D high precision syringe pump. This pump was used to supply liquid CO₂ at a constant flow rate at a desired reaction pressure which is regulated by a back pressure regulator. The CO₂ dispensed from the pump was mixed with high pressure hydrogen flow regulated by a mass flow controller (not shown), and the mixture was fed to a reactor containing a Cu-based catalyst. The effluent stream from the reactor was analyzed by a gas chromatograph.

In case of spectroscopic studies the laboratory reactor was replaced by a specially designed high pressure microreactor cell made of materials transparent in the light frequency used for excitation. Often specialized *in situ* spectroscopic studies are performed at external facilities (e.g. synchrotron light facility for X-ray absorption spectroscopy). In these cases, it is impossible to transport all the infrastructure associated with compression system (e.g. to generate high pressure H₂) installed in the home laboratory.

The great advantages of the syringe pump in this respect are its transportability with minimal installation time and its capability for compression. The syringe pump is very flexible to be operated with liquid/gas mixtures. Also, the temperature of cylinder can be easily kept up to 100 °C to maintain a single phase of the mixtures for homogeneous dispensing.

In order to accurately evaluate and quantify the reaction performance, it is of extreme importance to maintain the precise feeding flow rates of H₂ and CO₂. The Teledyne ISCO syringe pump provides accurate flow rate control at a precision of 0.5% or better of a set point value. It was possible to operate the pump as low as 2 µl/min flow of CO₂ over a wide pressure range (<500 bar). It should be noted that in liquid state the density of CO₂ changes very sensitively by temperature variations, possibly affecting the actual dispensed flow rate.

To avoid such problems, the pump is equipped with an external jacket around the syringe to maintain constant temperature of fluids. In this case the temperature of the syringe was kept at 20 °C by means of circulating water from a constant temperature bath. Unlike the reciprocating pumps the flow delivered by the syringe pump was truly pulse-less thus ensuring the reproducibility of the reaction results.

Performing reactions at high pressure involving the use of flammable gas like H₂ requires all the safety precautions in place. Teledyne ISCO pumps have inbuilt flow rate and pressure limits alarms to trigger the shut-down as well as to alert the user upon any abnormal change in operation conditions. Using the LabVIEW driver, provided with the pump, made it possible to control the pump remotely and in an automated mode over a prolonged time period of weeks. This remote control feature enabled another safety element in terms of software-triggered system shutdown in case of abnormal

change in other reaction parameters e.g. overshoot of temperature and sudden pressure increase.

Results Summary

For a hydrogenation process operated continuously by passing CO₂ and H₂ through a reactor filled with a catalyst packed inside, an indicative parameter to measure the process performance and efficiency is the weight time yield (WTY) often expressed in gram of methanol produced per gram of catalyst per hour (g_{MeOH}·g_{cat}⁻¹·h⁻¹). WTYs of >1 g_{MeOH}·g_{cat}⁻¹·h⁻¹ are considered as an excellent performance. From the commercial point of view, this value has to be above 1 to be practically attractive and viable. A breakthrough in the history of CO₂ hydrogenation reaction was achieved by almost fully converting CO₂ at one-pass through the reactor (i.e. no recycling) and also with the highest WTY ever reported.² The representative results of our catalytic tests are presented in Figure 3.

The figure summarizes the effects of feed composition on CO₂ conversion and product selectivity over the Cu/ZnO/Al₂O₃ catalyst at 260 °C, 360 bar, and gas hourly space velocity (GHSV) of 10,471 h⁻¹. At the conventional CO₂:H₂ molar ratio of 1:3 defined by the stoichiometry of CO₂ hydrogenation to methanol, the highest obtained CO₂ conversion was 37% with methanol selectivity of 72%. Drastic rise in CO₂ conversion and methanol selectivity was observed when H₂ partial pressure was further increased to CO₂:H₂ = 1:10. At this ratio CO₂ conversion was outstanding (95%) with high methanol selectivity (98%), suppressing CO formation to a negligible extent. Under this condition the methanol weight time yield (WTY) was found to be 1.2 g_{MeOH}·g_{cat}⁻¹·h⁻¹. It has been clearly demonstrated that the capability of testing high pressure reactions enabled by the syringe pump and the steady concentration of reactants by means of accurate flow of reactants were extremely crucial to achieve the outstanding catalytic results.

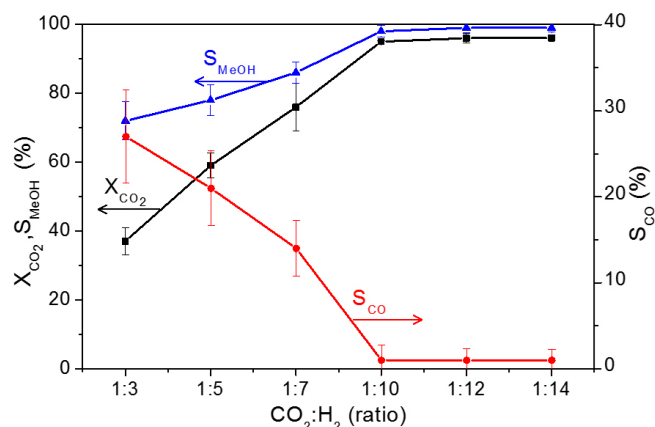


Figure 3: Effects of the CO₂:H₂ feed ratio on CO₂ conversion (X_{CO₂}) and selectivity to CO (S_{CO}), and methanol (S_{MeOH}) in CO₂ hydrogenation over the Cu/ZnO/Al₂O₃ catalyst. Reaction conditions: T = 260 °C, P = 360 bar, GHSV = 10,471 h⁻¹. Adapted from [2] with permission.

The ability of the syringe pump to operate in a wide range of flow rates with high precision made it possible to largely vary flow and thus GHSV conditions as shown in Table 1. Outstanding conversion level of CO₂ and very high methanol selectivity were obtained at low GHSV values. Increase in GHSV up to an extremely high level (182,000 h⁻¹) resulted in lowering CO₂ conversion from 95.8 to 65.8 % along with a decrease in selectivity towards methanol, but relatively high CO₂ conversion and methanol selectivity were maintained. Under this condition WTY of 7.7 g_{MeOH}·g_{cat}⁻¹·h⁻¹ was obtained, which is by far superior to any WTY values reported to date.

S.V. / h ⁻¹	CO ₂ Conv. / %	Selectivity / %				Yield / mg·g _{cat} ⁻¹ ·h ⁻¹			
		CO	CH ₄	MeOH	EtOH	CO	CH ₄	MeOH	EtOH
425	94.8	1.4	5.9	92.5	0.2	4.9	11.8	370.4	1.18
10,000	95.8	1.4	0.0	98.6	-	10.1	0.0	797.7	-
20,000	95.7	1.8	0.0	98.2	-	24.7	0.0	1582.0	-
40,000	89.9	4.9	0.0	95.1	-	128.0	0.0	2890.1	-
80,000	78.8	10.3	0.0	89.7	-	474.0	0.0	4778.3	-
131,000	71.8	19.9	0.0	80.1	-	1359.5	0.0	6314.3	-
182,000	65.8	22.7	0.0	77.3	-	1972.4	0.0	7729.1	-

Table 1: Catalytic activity test for commercial methanol synthesis catalyst at various GSVs, at T = 260 °C, P = 360 bar and CO₂:H₂ = 1:10. Adapted from [2] with permission.

The advantageous use of the syringe pump was further exploited for high pressure *in situ* Raman and X-ray absorption spectroscopic (XAS) studies. The plug and play nature of the pump helped us to perform XAS study at a synchrotron light facility. In this experiment, a mixture of CO₂ and H₂ with a predefined molar ratio was charged into the pump, compressed to a desired pressure, and dispensed to an *in situ* cell made of polymer-coated fused silica capillary which functioned as a packed-bed catalytic reactor (OD: 662 μm, ID: 247 μm, 15 cm in length).³ The *in situ* XAS study revealed that the active copper in the methanol synthesis catalyst remains in the metallic state under the reaction conditions of 200 bar.

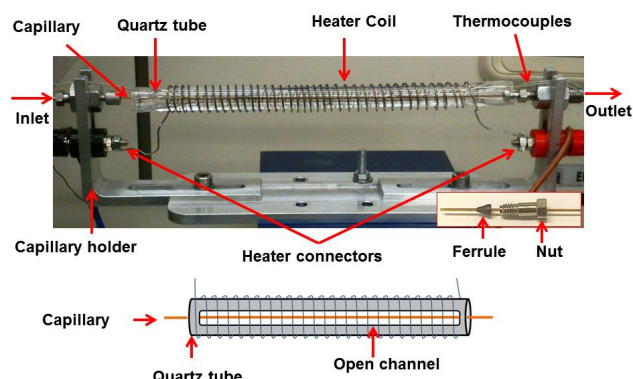


Figure 4: Capillary microreactor cell used for high pressure *in situ* XAS study. Reproduced from [3] with permission

In another study, the syringe pump was used for *on-chip* Raman study to investigate the concentration profiles of reactants and products along the axial direction of a catalyst bed and also the phase behavior of a heterogeneously catalyzed reaction (cyclohexene hydrogenation) performed at high pressure (>100 bar) in supercritical CO₂.⁴ Figure 4 shows the photograph of fully assembled glass-Si microreactor where a Raman laser was focused on the micro-channel (catalyst bed of Pd/Al₂O₃) of the reactor. Two syringe pumps were used to feed CO₂ and also reactant (cyclohexene). In addition, using the *on-chip* Raman approach, phase behavior of dense CO₂ could be studied, clearly separating characteristic features of Raman spectra for gas, liquid, and supercritical states.

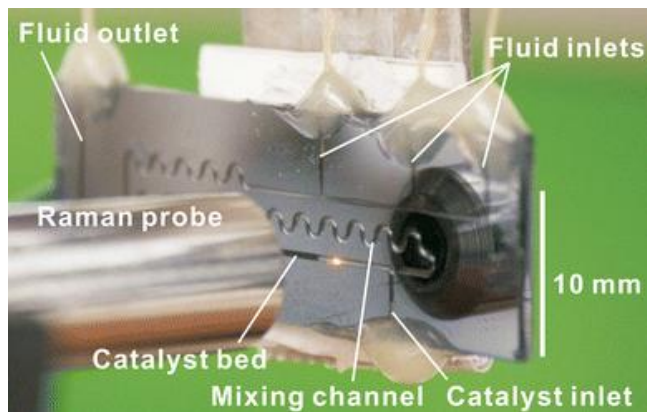


Figure 5: On-chip Raman analysis using Teledyne ISCO syringe pump in supercritical CO₂ [4] - Reproduced by permission of The Royal Society of Chemistry.

Conclusion

In summary, the Teledyne ISCO syringe pump was found to be extremely versatile and powerful to study high pressure catalytic reactions and to gain spectroscopic insights.

Note:

The 260D model pump, which was used during the original experiment, is discontinued. Current model 260x is the recommended replacement for the older 260D model.

The following models of Teledyne ISCO pumps for such high pressure applications are recommended:

	260x	65x
Pressure Range (psi)	0-9,500	0-20,000
Flow Range (ml/min)	0.001-107	0.00001-25

*December 21, 2015; revised November 8, 2023
Product model names have been updated in this document to reflect current pump offerings.*

Reference

1. Tidona, B.; Koppold, C.; Bansode, A.; Urakawa, A.; Rudolf von Rohr, P., CO₂ hydrogenation to methanol at pressures up to 950 bar. *J. Supercrit. Fluids* 2013, **78**, 70-77.
2. Bansode, A.; Urakawa, A., Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products. *J. Catal.* 2014, **309**, 66-70.
3. Bansode, A.; Guilera, G.; Cuartero, V.; Simonelli, L.; Avila, M.; Urakawa, A., Performance and characteristics of a high pressure, high temperature capillary cell with facile construction for operando x-ray absorption spectroscopy. *Rev. Sci. Instrum.* 2014, **85**, 084105.
4. Urakawa, A.; Trachsel, F.; Rudolf von Rohr, P.; Baiker, A., On-chip Raman analysis of heterogeneous catalytic reaction in supercritical CO₂: phase behaviour monitoring and activity profiling. *Analyst* 2008, **133** (10) 1352-1354.

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