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Enabling high-turnover methanol-to-syngas reforming

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Abstract

Carbon-based feedstocks, including oil, coal, and natural gas, are essential raw materials for the chemical industry. This makes the transition away from fossil resources challenging compared to energy and transportation sectors. Renewable methanol has emerged as a promising liquid C1 platform that could provide a drop-in route to synthesis gas (syngas), a central intermediate in large-scale chemical production. However, homogeneous methanol-to-syngas reforming is typically performed in closed batch reactors, where accumulation of gaseous products rapidly suppresses catalytic turnover. Here we report a continuous flow system for homogeneous methanol-to-syngas reforming using Ru-MACHO-based catalysts that overcomes these limitations through continuous separation of gaseous products from the catalytic phase. Systematic optimisation using a design-of-experiments strategy identified the key operational parameters governing productivity, while ligand design enabled improved catalyst stability under flow conditions. The resulting system enables sustained syngas generation over extended operation and delivers substantially enhanced catalytic performance relative to batch operation. These findings demonstrate how combining reactor operation with molecular catalyst design can unlock new operating regimes for equilibrium-limited homogeneous catalytic transformations.

Introduction

The chemical industry underpins modern society but remains fundamentally dependent on fossil-derived feedstocks.[1] Unlike energy and transportation sectors, chemical manufacturing requires carbon as a molecular building block, rendering defossilisation uniquely challenging.[2] With the accelerating impacts of climate change already manifesting globally, urgent action is imperative. International agreements such as the *Paris Agreement* have intensified political pressure, but technological transformation remains essential.[3] The *Stockholm Declaration on Chemistry for the Future* calls for precisely such a paradigm shift; a reinvention of the chemical sciences analogous to the fossil-fuelled revolution of the twentieth century.[4] This new revolution must deliver the molecules and materials essential to modern society, while fundamentally decoupling chemical production from fossil carbon.[5,6]

Achieving a transition from fossil carbon will require more than novel synthetic methods; it demands renewable feedstocks that can integrate into existing chemical value chains. Modern large-scale chemical manufacturing plants are built around highly optimised infrastructures that rely on standardised intermediates such as synthesis gas (syngas, H_2/CO mixture), making redesign of downstream processes economically challenging. Consequently, drop-in technologies that deliver renewable carbon streams compatible with established process logic are particularly attractive. Among potential candidates, green methanol, produced from biomass or captured CO_2, has emerged as a promising renewable platform for this transition.[7] As a liquid C_1 feedstock, methanol offers clear advantages in storage, transportation, and operational safety relative to gaseous alternatives, and its renewable production capacity is expanding at industrial scale.[8] Beyond its role as an energy carrier, methanol occupies a central position in chemical manufacturing, serving as a key precursor for multiple

industrial intermediates.[9–11] Homogeneous catalytic reforming of methanol into syngas has therefore emerged as an attractive conceptual strategy, as it could allow renewable methanol to function as an upstream source for established carbonylation, hydroformylation, and Fischer–Tropsch processes. In contrast, direct syngas production via the reverse water–gas shift reaction (rWGS) remains energy intensive and continues to face challenges related to catalyst stability and process efficiency, highlighting the need for alternative approaches that leverage the rapidly expanding methanol infrastructure.[12,13]

Leitner and co-workers previously demonstrated that the molecular catalyst Ru-MACHO^{Ph} can catalyse methanol-to-syngas reforming in the absence of water (**Figure 1a**).[14] However, under batch conditions, the authors demonstrated that catalytic turnover is limited by rapid accumulation of syngas in the reactor headspace, leading to early equilibration and suppressed activity. Periodic venting of the system only partially alleviated this limitation, affording turnover numbers (TONs) of up to 9230 for H_2 and 3150 for CO after 7 x 12 hours. Recent computational and microkinetic studies further indicate that methanol-to-syngas reforming is intrinsically constrained by reaction thermodynamics and liquid–vapour equilibrium, whereby gas accumulation alters catalyst resting-state populations and limits productivity.[15,16] These limitations are exacerbated by the volatility of methanol and key intermediates at the temperatures required for catalysis. One proposed solution involves direct coupling of syngas generation with downstream syngas consumption, as independently demonstrated by our research group in collaboration with the Beller team,[17] and Leitner *et al.*[17,18] While conceptually elegant, such tandem approaches require intricate co-optimisation of multiple catalytic systems and are fundamentally misaligned with industrial syngas utilisation, which relies on decoupled and independently optimised processes. Collectively, these observations suggest that overcoming current performance limitations will require not only catalyst redesign but also a fundamental reconsideration of reactor operation.

Herein, we report a continuous flow system that enables syngas production via consecutive acceptorless dehydrogenation and decarbonylation of methanol using Ru-MACHO-based catalysts (**Figure 1b**). By combining reactor engineering with catalyst design, the system overcomes equilibrium limitations inherent to batch operation by continuously removing gaseous products from the catalytic phase. Systematic optimisation using a Design of Experiments (DoE) approach led to sustained syngas generation with substantially enhanced cumulative productivity. Beyond performance gains, this work establishes a strategy in which catalyst operation and gas handling are deliberately decoupled, aligning syngas generation with industrial process logic and providing a scalable route to renewable syngas-derived commodity chemicals.

Results and discussion

Motivated by previous reports indicating limited catalytic turnover under batch operation, we first examined methanol-to-syngas reforming under conventional batch conditions to identify the factors

limiting catalytic performance (**Figure 2a**). Monitoring pressure evolution revealed rapid initial gas formation followed by early plateauing largely independent of catalyst loading, further corroborating with the previous reports that catalytic activity becomes constrained by gas accumulation. Additionally, operation at elevated temperature (150 °C), combined with the volatility of methanol and key intermediates, such as formaldehyde and methyl formate, introduces a second limitation. Under these conditions, continuous gas removal in a batch reactor would require repeated cooling–heating cycles to avoid loss of volatile components during venting. Thus, rendering sustained operation impractical, particularly at scales where the thermal mass of high-pressure reactors imposes substantial energy and process penalties.

To overcome these intrinsic limitations of batch operation, we designed a continuous flow system capable of constantly separating gaseous products while recirculating the methanolic catalyst solution **(Figure 2b**). This tubular reactor concept is designed to continuously remove gaseous products outside the heated zone, thereby mitigating product accumulation and minimising the loss of volatile key intermediates. The system employs an HPLC pump to circulate the catalytic solution through a pre-heated reaction loop (1.6 mL), where the methanol-to-syngas reforming occurs. The reaction mixture then passes through a cooled loop before entering a back-pressure regulator and a gravity-driven in-line gas–liquid separator, enabling continuous separation of syngas from the circulating liquid phase. Importantly, only the reaction mixture is heated and cooled, avoiding the thermal cycling of large reactor masses required under batch operation. To enable quantitative optimisation and real-time performance analysis, the stream exiting the back-pressure regulator was combined with a constant argon flow and analysed by inline gas chromatography (see SI for experimental details).

The operational and chemical space was mapped using a DoE approach employing commercial Ru-MACHO^{Ph} as benchmark catalyst. Guided by preliminary observations and prior studies, the tubular reactor temperature was fixed at 150 °C, while flow rate, back-pressure (BPR), solvent composition (methanol/toluene), and catalyst loading were systematically varied. The first DoE explored a broad operational window to identify the parameters governing syngas productivity and ratio (see SI for experimental details). This analysis revealed back-pressure as the dominant factor controlling catalytic output, while flow rate showed a substantial but less significant effect, and methanol dilution with toluene proved statistically insignificant. Notably, operation at low back-pressure dramatically increased syngas formation, whereas increasing the pressure suppressed productivity, consistent with a process governed by gas-liquid equilibrium. The minimal influence of toluene as co-solvent further indicates that catalyst performance is primarily governed by liquid–gas equilibrium rather than bulk solvent effects.

A second DoE focused on narrowing the operational window and examining the interplay between catalyst loading, flow rate, and back-pressure (**Figure 3a**). This analysis revealed a narrow pressure regime around 75–100 psi where high syngas productivity and H_2/CO ratios were consistently achieved. Lower pressures resulted in unstable flow dynamics due to partial vaporisation of methanol and intermediates prior to the back-pressure regulator. Importantly, decreasing catalyst loading increased turnover numbers non-proportionally, as expected from the observed maximum pressures independent

of catalyst loading in batch. Based on these results, conditions of 75 psi back-pressure and 2.5 mL/min flow rate were selected as robust conditions balancing productivity, reproducibility, and catalyst efficiency. These conditions were subsequently used for catalyst optimisation studies.

Under the optimised conditions; Ru-MACHO^{Ph} (2.0 or 0.20 μmol), *t*BuOK (200 μmol), and methanol (20 mL) at 75 psi, 2.5 mL min^{-1}, and 150 °C, the continuous flow system produced 51.5 mmol of H_2 and 24.5 mmol of CO within 6 hours, corresponding to TONs of 22535 and 11335, respectively. Unless otherwise stated, results are only shown for 2.0 μmol catalyst loading, while data for lower catalyst loadings are provided in the Supplementary Information (Page S20). Notably, this performance was highly reproducible across repeated experiments performed by different operators, underscoring the robustness and operational reliability of the flow system. Despite notably surpassing previously reported batch performances regarding total production, TONs and turnover frequencies (TOFs), significant catalyst deactivation was observed, with only 11.4% activity retention (AR), with respect to CO, after 6 hours (**Figure 3b**). These observations suggest that catalyst stability is a major limitation under continuous operation.

Catalyst deactivation pathways have been proposed for Ru-MACHO-based systems, including ligand decomposition (**Figure 3c**).[16,20–24] Following activation of Ru-MACHO^{Ph} using *t*BuOK to form the Ru-amido complex **C1**, various complexes have been observed in solution, including **C2**, **C3**, and **C4**.[14,16] While the Ru-methoxide complex **C2** is proposed to be in a dynamic equilibrium with **C1,** and the Ru-dihydride complex **C3** can undergo alcohol-assisted hydrogen release to reform **C1**, the Ru-dicarbonyl complex **C4** was proposed computationally by Nova *et al.* as a low-energy sink species.[16] Notably, Kayaki and co-workers reported that **C4** remains catalytically active in the *N*-methylation of anilines proceeding via a hydrogen-borrowing mechanism.[25] Given the close similarity between Kayaki's conditions, formation of **C4** under the reaction conditions employed here is highly plausible. Rather than representing irreversible deactivation, **C4** is therefore better described as a low-lying resting state, where accumulation of this species shifts catalyst speciation away from the productive cycle and lowers observed TOFs due to the energetic penalty required for re-entry into the active pathway as **C1**. In line with this interpretation, Prakash and co-workers demonstrated that the reactivity of related Ru-dicarbonyl complexes depends on substrate identity and phosphine substitution, underscoring how electronic and steric effects influence both catalyst speciation and intrinsic reactivity.[26] However, the relevance of these species under methanol-to-syngas reforming remains unclear. Direct identification of inactive species proved challenging due to the highly dilute catalytic regime under continuous flow operation, and neither NMR spectroscopy nor HRMS analysis allowed unambiguous assignment of deactivation products.

Alternatively, control experiments aimed at probing previously proposed pathways were therefore performed. Schneider and co-workers reported that [$RuCl_2PMe_3$(MACHO^{iPr})] complexes can form an analogous of Ru-enamido complex **C5** in the presence of excess *t*BuOK in aprotic solvents.[21,22] However, Beller and co-workers did not observe evidence for such species under basic aqueous methanol conditions, suggesting a dependence of catalyst speciation on reaction environment.[27] To probe

whether dehydrogenated species could contribute to catalyst deactivation under continuous flow conditions, an experiment including Pd/C within the gas–liquid separator was performed (see SI for experimental details).[23,24] This resulted in decreased catalytic performance, likely due to non-selective adsorption of the homogeneous catalyst on activated carbon, and therefore did not provide direct evidence for this pathway. The tripodal Ru^0-carbonyl complex **C6** reported by Schaub *et al*. retained significant H_2 evolution but produced only limited CO under reaction conditions (see SI for experimental details). This behaviour indicates that alcohol dehydrogenation remains operative, whereas decarbonylation is inhibited, consistent with computationally proposed transition states for CO release.[16,20] Additional deactivation pathways involving ligand dehydrogenation have been proposed for related MACHO systems. The hetero-nuclear ruthenium complex **C7** was neither synthesised nor assessed herein.

Previous computational analyses postulated that catalyst modification alone should not improve catalytic turnovers under equilibrium-limited batch conditions.[16] Continuous flow operation, however, reduces the dominance of equilibrium constraints and enables intrinsic kinetic differences between catalyst variants to translate into differences in overall performance. We therefore hypothesised that ligand tailoring could modulate catalyst speciation and alter the energetics of key catalytic steps under these conditions. Guided by this premise, a systematic ligand scope was investigated (Figure 4). Initial modifications focused on substituents on the phosphine aryl groups, probing both electronic and steric effects. In general, deviations from the parent phenyl substituent resulted in reduced syngas productivity. Electron-rich derivatives, Ru-MACHO$^{p(Me)}$ and Ru-MACHO$^{p(OMe)}$, as well as more sterically congested derivatives, Ru-MACHO$^{p(iPr)}$ and Ru-MACHO$^{p(3\text{-}Pe)}$, showed slightly diminished syngas productivity. Electron-deficient Ru-MACHO$^{p(CF3)}$ expelled significantly lower activity, which afforded a 42% decrease in total syngas formation relative to Ru-MACHO^{Ph}. Likewise, extension of the aromatic framework to naphthyl or biphenyl substituents resulted in poor solubility and lower overall activity. Notably, the meta-substituted Ru-MACHO$^{m,m(Me)}$ derivative displayed a distinct behaviour. While overall productivity after 6 h was only moderately improved, catalyst deactivation was significantly reduced, retaining 36.8% of the peak CO production rate compared with 11.4% for Ru-MACHO^{Ph}. This observation suggests that subtle modifications of the ligand environment can significantly influence catalyst stability under continuous flow operation.

Given the influence of steric and electronic effects observed within the aryl series, attention was next directed towards alkyl-substituted Ru-MACHO derivatives, which allows further systematic modulation of steric demand around the metal centre. Interestingly, a trade-off between catalytic activity and stability emerged across this series. Compared to Ru-MACHO^{Ph}, Ru-MACHO^{Et} exhibited 65.0% activity retention although with comparatively modest turnover numbers (H_2: 12405, CO: 5650). Increasing steric bulk to Ru-MACHO^{iPr} substantially enhanced productivity (H_2: 25370, CO: 12385), albeit at the expense of stability, with only 41.7% of the peak CO production rate maintained after 6 h. Interestingly, further increasing steric demand to cyclohexyl substituent, Ru-MACHO^{Cy} produced a more balanced profile by

combining high turnover numbers (H_2: 24320, CO: 11423) with improved activity retention (62.1% after 6 h). In contrast, excessive steric encumbrance in *tert*-butyl and adamantyl derivatives (Ru-MACHO^{tBu} and Ru-MACHO^{Ad}) resulted in near-complete loss of activity, indicating that overly hindered environments likely impede access to the metal centre. Although these observations provide insight into catalyst speciation under flow conditions, the precise origin of long-term deactivation remains unresolved and is the subject of ongoing investigation.

Encouraged by the stability of Ru-MACHO^{Cy}, efforts were directed towards scaling the continuous flow system. More specifically, the tubular reactor volume was increased from 1.6 mL to 32 mL, thus increasing the fraction of catalyst solution constantly exposed to the heated section from ~8% to ~71%. To maintain stable operation and retain a constant concentration of Ru-MACHO^{Cy} under these conditions, an additional HPLC pump was integrated with an automated feedback protocol that continuously adjusted methanol feed based on CO production (see SI for details). This automated methanol replenishment prevented reservoir depletion and enabled steady-state operation during long-term experiments. Following a minor re-optimisation (see SI for experimental details), the flow system delivered a continuous syngas stream over 84 hours when employing 4.0 ppm Ru-MACHO^{Cy} (**Figure 5**). The outcome was astonishing record turnover numbers of 269347 for H_2 and 130829 for CO, corresponding to average TOFs of 3207 and 1557, respectively. Importantly, the system achieved 47.5% activity retention relative to the post-induction steady-state regime (180 minutes). These results demonstrate that combining catalyst design with continuous flow operation enables sustained, high-turnover syngas generation from methanol, providing a modular and scalable strategy compatible with existing syngas-based chemical infrastructure.

Conclusion

We have presented a continuous flow system for on-demand syngas generation from methanol that overcomes key limitations associated with batch methanol-to-syngas reforming. Through continuous separation of gaseous products from the catalytic phase, the developed system decouples gas handling from catalyst operation, suppresses equilibrium limitations, and enables sustained catalytic turnover under mild conditions. Systematic optimisation using Design of Experiments, identified back-pressure as the dominant operational parameter controlling productivity, establishing a narrow operating regime in which efficient syngas formation at a H_2/CO ratio of 2:1 was achieved. Although catalyst deactivation remains a central challenge, mechanistic control experiments and ligand modification studies revealed that catalyst speciation and stability can be strongly influenced by steric and electronic tuning of the MACHO scaffold. More specifically, a cyclohexyl-derivative, Ru-MACHO^{Cy}, proved long-term catalyst stability under flow conditions, enabling continuous operation over extended timescales. Translation of the optimised system to a larger reactor configuration afforded sustained syngas production over 84 hours, reaching record turnover numbers for both hydrogen and carbon monoxide. Beyond performance improvements, this work demonstrates that reactor design and catalyst development must be considered together to unlock new operating regimes inaccessible under batch conditions. By aligning

renewable methanol-to-syngas reforming with established syngas-demanding processes, this modular flow system provides a scalable strategy for integrating renewable syngas into existing chemical infrastructures.

Methods

See supplementary Information for further methods.

Declarations

Data Availability

All reported data is available in the supplementary information.

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Author contributions

Conceptualisation and writing/revising of the original draft were carried out by A.B., G.M.F.B. and T.S. Experiment design and experimental investigations were carried out by A.B., G.M.F.B. and M.G. Funding acquisition was carried out by T.S. All authors reviewed the final manuscript.

Competing interests

T.S. is co-owner of SyTracks A/S, which commercialises CO tubes.

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Figures

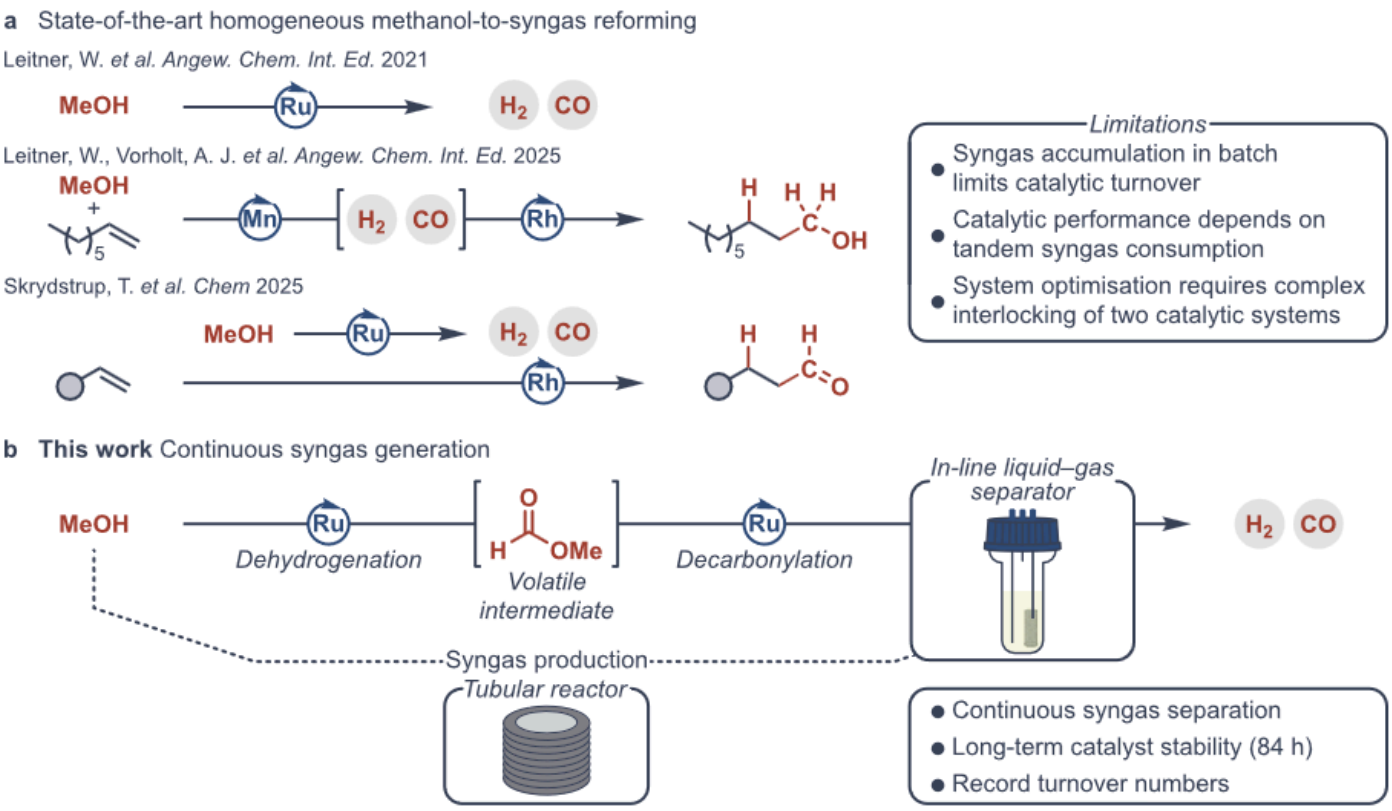


Figure 1

a Previous reports on homogeneous methanol-to-syngas reforming in batch. **b** This work, continuous methanol-to-syngas reforming in flow.

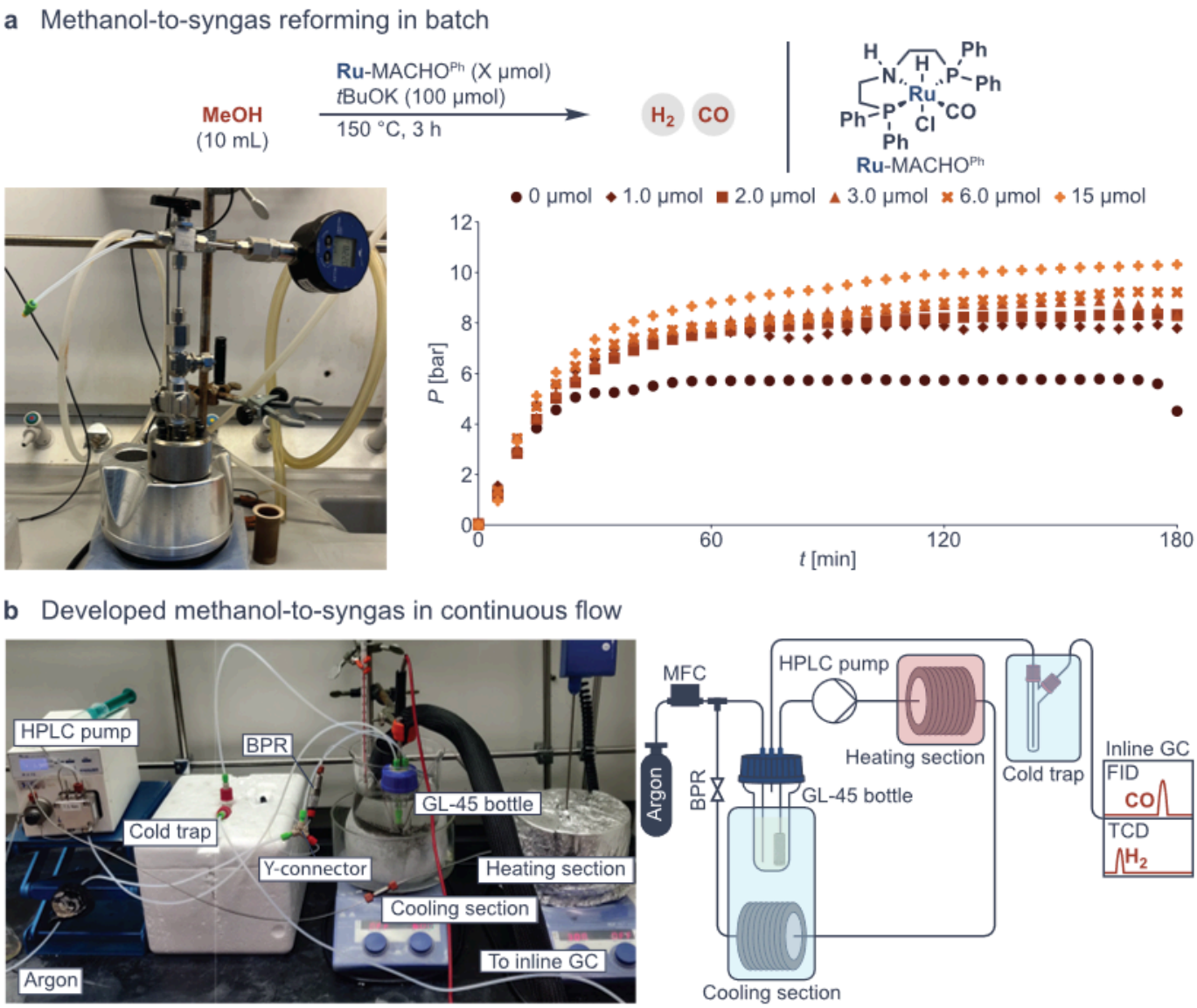


Figure 2

a Reaction conditions and pressure response over time for methanol-to-syngas reforming in batch with varying Ru-MACHO^{Ph} loadings. **b** The developed continuous flow system and a schematisation thereof.

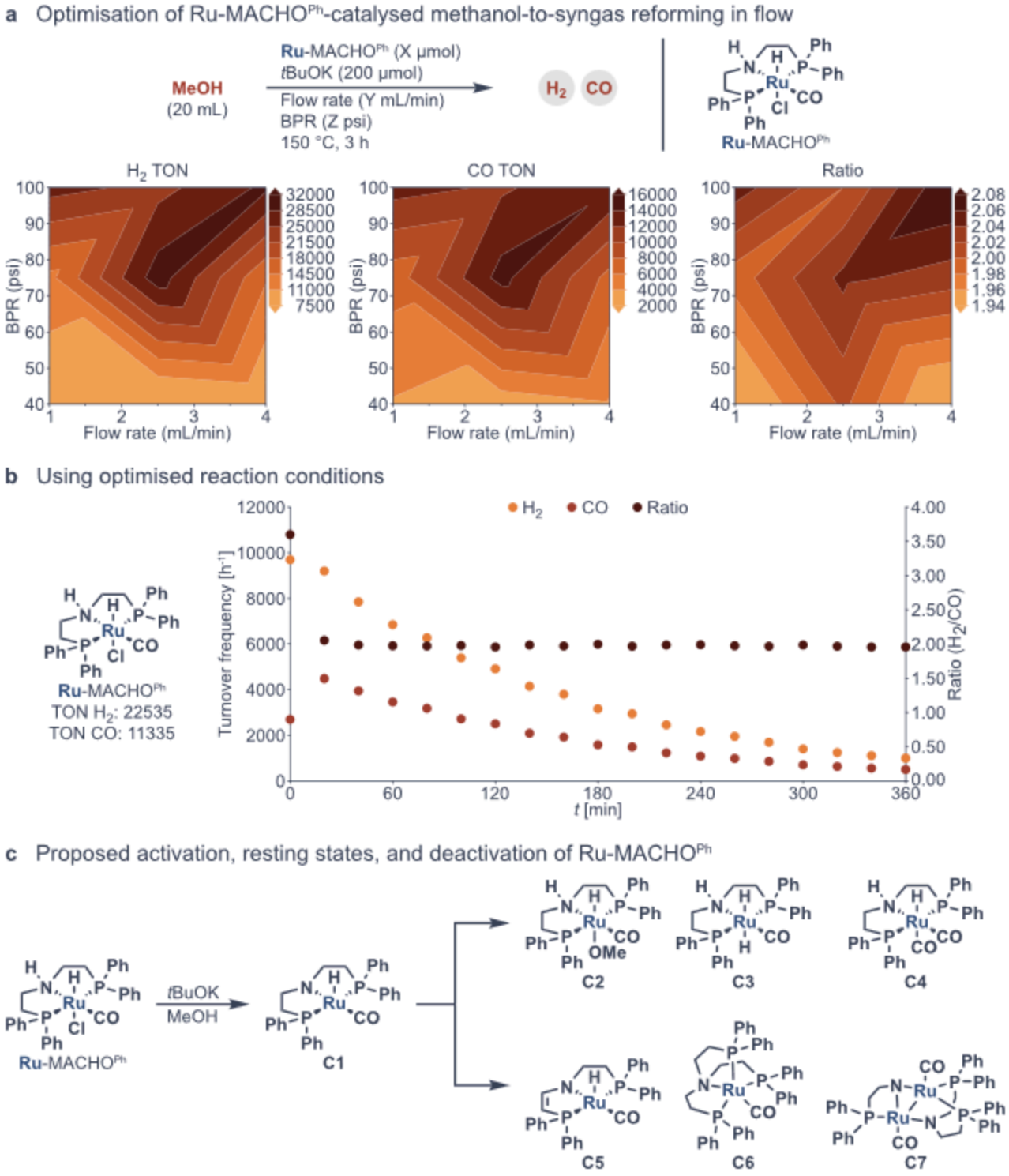


Figure 3

a Selected contour plots for the second DoE displaying syngas production and ratio for flow rate against back-pressure. **b** Time-dependent catalytic activity and syngas ratio using optimised reaction conditions and Ru-MACHO^{Ph} (2.0 μmol). **c** Proposed complexes.[14,16,19–22]

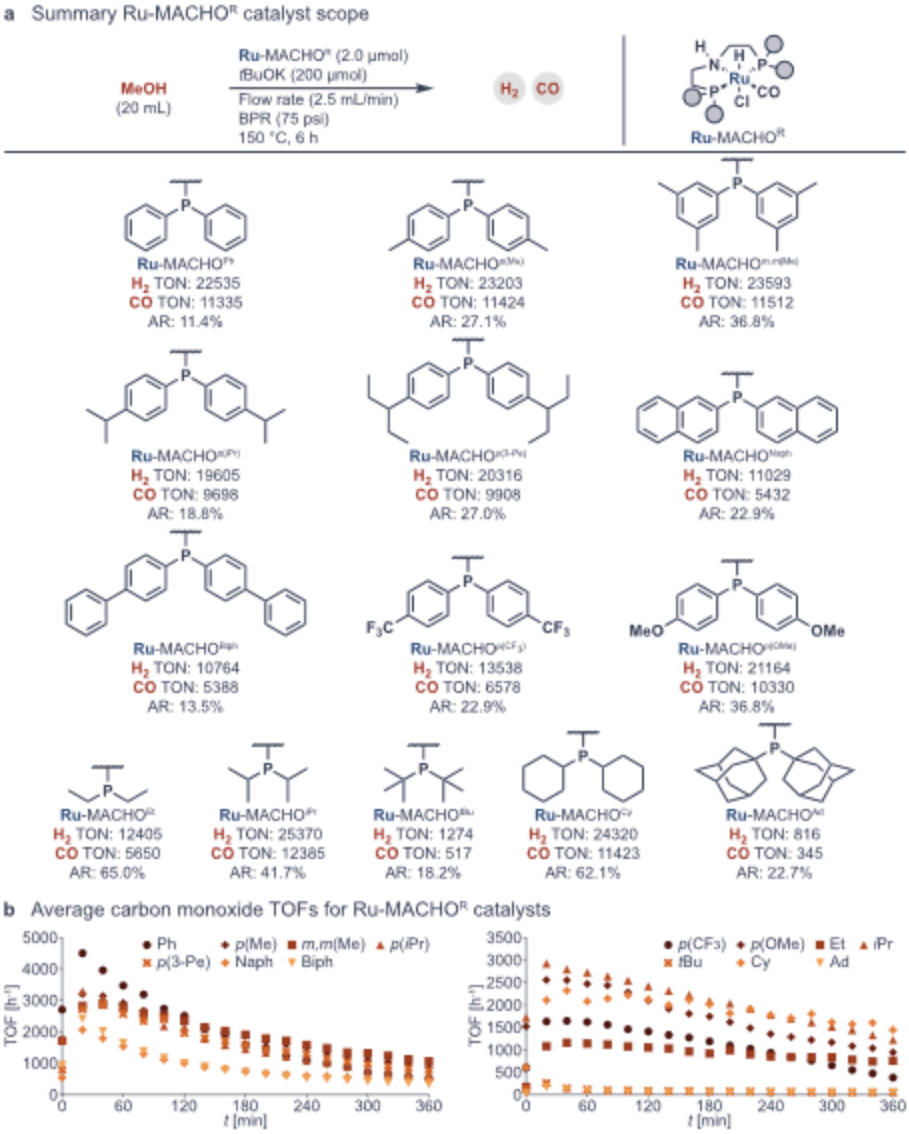


Figure 4

a Scope of Ru-MACHO-derivatives. **b** Time-dependent catalytic activity, showing only CO TOFs (see SI for experimental details).

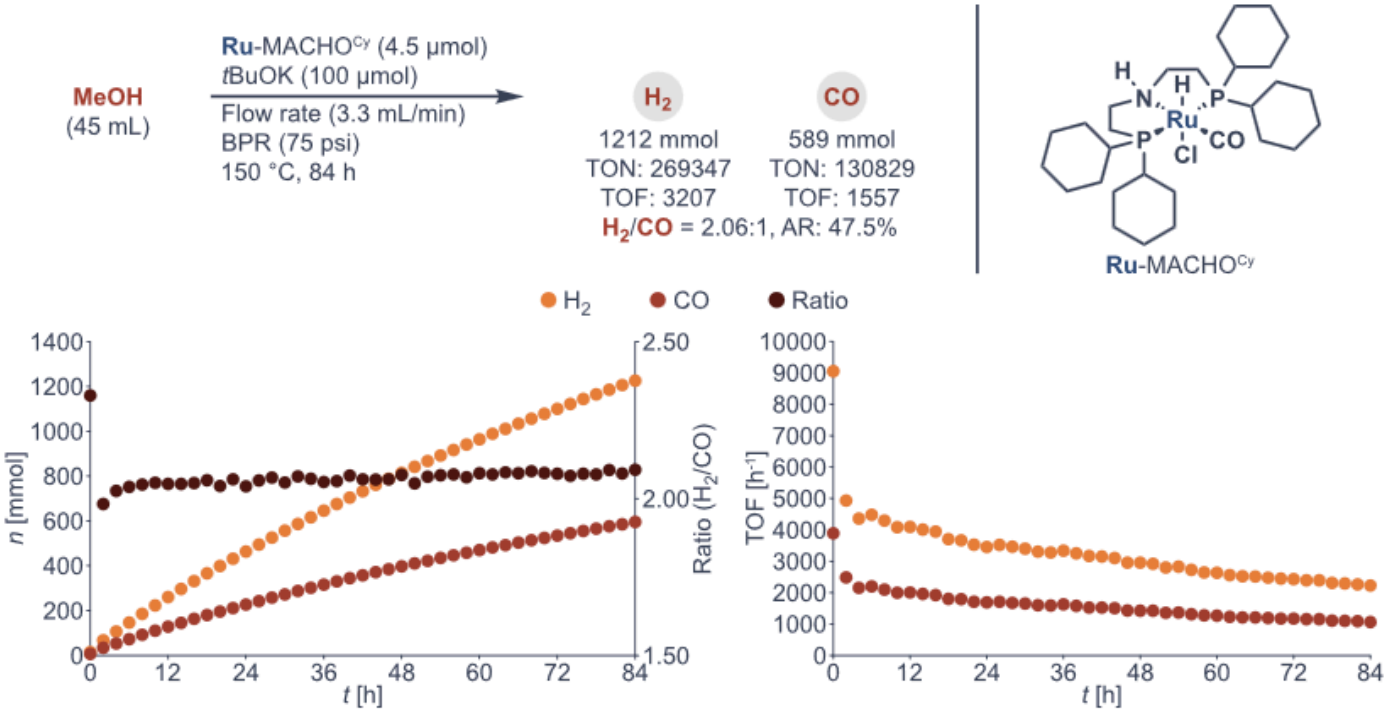


Figure 5

Reaction conditions for scaled flow system along with time-dependent catalytic activity and cumulative syngas production and ratio over time (see SI for experimental details).

Supplementary Files

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