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An Efficient and Practical System for the Synthesis of *N,N*-Dimethylformamide by CO_2 Hydrogenation using a Ru-based Heterogeneous Catalyst: From Batch to Continuous Flow

Gunniya Hariyanandam Gunasekar,[b]† Sudakar Padmanaban,[a]† Kwangho Park,[c]† Kwang-Deog Jung,[b] and Sungho Yoon*[a]

Abstract: In the context of CO_2 utilization, a number of CO_2 conversion methods have been identified in laboratory-scale research; however, only a very few transformations have been successfully scaled up and implemented industrially. The main bottleneck in realizing industrial application of these CO_2 conversions is the lack of industrially viable catalytic systems and the need of practically implementable process developments. Herein, we developed a simple, highly efficient and recyclable ruthenium-grafted bisphosphine-based porous organic polymer (Ru@PP-POP) catalyst for the hydrogenation of CO_2 to N,N-dimethylformamide, and obtained best ever turnover number (TON) of 160,000 and initial turnover frequency (TOF) of 29,000 h^{-1} in a batch process. The catalyst was successfully applied in a trickle bed reactor and utilized in an industrially feasible continuous-flow process for the first time with an excellent durability and productivity of 915 mmol h^{-1} g_{Ru}^{-1}.

For the past few decades, a number of CO_2 transformations have been identified in the field of CO_2 utilization; however, most of the reported catalytic processes are not desirable for technical realizations in industry, and thereby remain at the laboratory scale.[1-3] Therefore, the design and development of practically auspicious catalytic process systems is a key task to ensure CO_2 transformations in the chemical industry. In this regard, one conceptually challenging transformation is the synthesis of *N,N*-dimethylformamide (DMF) via CO_2 hydrogenation.[4] DMF is widely used in various areas, such as textile coatings, production of polyurethane products, acrylic fibers, electronic components, pharmaceutical products and organic synthesis. Its current industrial production is mainly from CO, i.e., through continuous-flow carbonylation of dimethylamine (DMA) using an alkali alkoxide catalyst under severe reaction conditions (150-350 °C and 30–100 MPa).[5] To surrogate this hazardous and less-sustainable CO-based route, the synthesis of DMF via CO_2 hydrogenation has been introduced in the year of 1970, and intensively investigated from then with homogeneous catalysts in a batch catalytic process.[6,7] However, advancing the homogeneous hydrogenation towards the practical realization remains infeasible owing to the serious obstacles in terms of separation of the catalysts from the highly polar product DMF and recycling of the catalyst. Nevertheless, Vorholt and co-workers recently proposed a continuous stirred tank reactor as feasible for the homogeneous hydrogenation of CO_2 to DMF using multiphase liquid–liquid extraction to separate DMF from the homogeneous catalyst.[6d-g] However, this multiphase extraction process may not be preferable and suitable in the industry particularly for a chemical like DMF, the production scale of which is relatively large, because this process is highly laborious, and most importantly, leaching of Ru metal is thus far unavoidable, which in turn reduces the economic viability of the system.

Thus, scale up of the hydrogenation process using heterogeneous catalytic systems would offer prodigious advantages over simple continuous operations and separations in industry. Unfortunately, the efficiency (TONs and TOFs) and stability of reported heterogeneous catalysts are far below the practical requirements, and sometimes non-recyclable acid additives are required for improved activity (Table S1).[7] In addition, hydrogenation catalyzed by heterogeneous catalysts in a batch-type reactor process alone has been investigated, which may not be reflected in the commercial process. Consequently, there is an imperative to develop highly efficient, selective and durable catalytic systems for the titled hydrogenation along with simple and practically viable continuous production systems.

Herein, we report a simple, highly efficient and recyclable ruthenium-grafted phosphine-based porous organic polymer (**1**) catalyst for the titled hydrogenation. The catalyst **1** shows very promising catalytic ability for hydrogenation in batch process with a maximum TON of 160,000 and an initial TOF of 29,000 h^{-1}. The catalyst was successfully applied in a trickle bed reactor and utilized in an industrially feasible continuous-flow process for the first time with an excellent productivity of 915 mmol h^{-1} g_{Ru}^{-1}. The efficiency of the catalyst is well maintained over successive runs in the batch process and the catalyst is highly durable over a long period in the continuous-flow reaction. Therefore, these results, collectively make the overall catalytic process practical in commercial operations.

To date, porous organic polymers (POPs) have drawn considerable interest in the field of catalysis due to their large surface area, tunable pore size, and high chemical stability.[8] Most importantly, the integration of organic functional ligands into porous polymer backbone permits the successful immobilization of coordination complexes and thereby offers the design and development of efficient and selective solid catalysts for various catalytic applications. In this regard, porous polymer with bisphosphine backbone inspired a great deal of attention for the immobilization of various phosphine-based metal complexes

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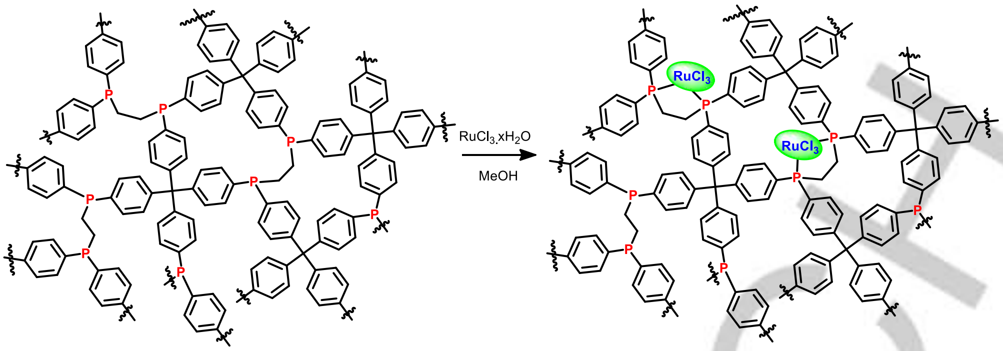

Scheme 1. Synthesis of **1**

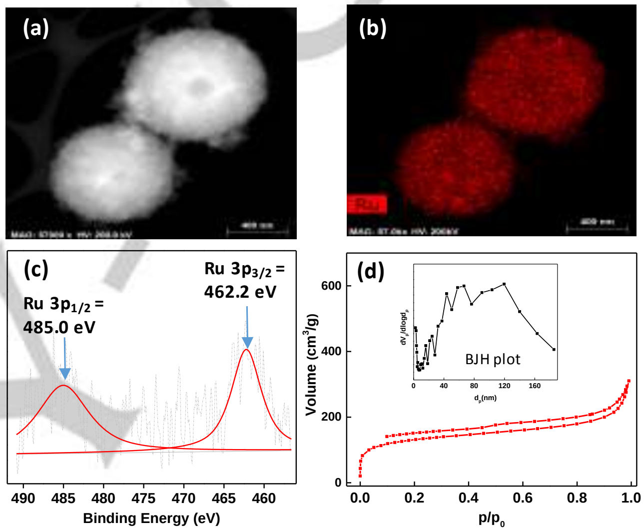

Figure 1. Characterization of **1**. (a) Scanning transmission electron microscopy (STEM) image. (b) Energy-dispersive spectroscopic (EDS) mapping of the Ru atoms. (c) Deconvoluted X-ray photoelectron spectrum of Ru-3p core level. (d) N_2 sorption measurement.

including $PdCl_2$, $RhCl(PPh_3)_3$, IrCp*, Ru(p-cymene).[9] In this context, herein we explore a ruthenium-coordinated bisphosphine-based POP for the synthesis of DMF by CO_2 hydrogenation.

The preparation of catalyst **1** is outlined in Scheme 1. The phosphine-based porous organic polymer support (PP-POP) was prepared in a one-pot process using tetrakis(4-bromophenyl)methane and 1,2-bis(dichlorophosphino)ethane by following a reported procedure.[9a] Post-synthetic metalation was performed by adding a methanolic solution of $RuCl_3$ to a suspension of PP-POP in methanol under N_2 atmosphere. The generated ivory solid **1** is insoluble in nearly all organic solvents and water. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDX) measurements revealed the uniform metalation of Ru throughout the solid matrix with a Ru/Cl ratio of 1:3 (Figures 1a-b and S1, and Table S2). The amount of Ru loaded into PP-POP was 0.81 wt%, as determined by inductively coupled plasma optical emission spectrometry (ICP-OES). X-ray photoelectron spectroscopic (XPS) measurement of Ru-3*p* core level suggests (Ru-$3p_{3/2}$ = 462.2 eV) that the valence state of Ru in **1** was +3 (Figure 1c and S2).[10a] Notably, the electron density of Ru in **1** was increased significantly, compared to that in the Ru precursor (Ru-$3p_{3/2}$ = 463.5 eV),[10a,b] indicating the donation of electron density from the bidentate phosphine ligands to the Ru site and successful complexation of Ru with PP-POP as depicted in scheme 1. Powder X-ray diffraction measurement (PXRD) revealed that the Ru species are present in a highly dispersed state, as there was no apparent change in the diffraction pattern of the parent polymer after Ru complexation (Figure S3). N_2 sorption analysis revealed that the structure comprised micro- and mesopores (mean pore diameter = 9.7 nm) (Figure 1d), with a Brunauer–Emmett–Teller (BET) surface area of 469 $m^2\,g^{-1}$ and total pore volume of 0.475 $cm^3\,g^{-1}$. Such hierarchical pores in **1** could gently expose the Ru sites to the reactive species and improve the mass transfer during catalysis.

Prior to evaluating the catalytic ability of **1** in a continuous-flow trickle-bed reactor, catalyst **1** was tested in a batch process to preliminarily assess the influence of various reaction parameters such as the solvent, temperature, pressure, durability, and mechanistic pathway. To select an optimal solvent, the hydrogenation was performed with various commercially available solvents in which dimethylamine (DMA) exhibits solvency ([DMA] = 2.0 M) and the results are shown in Figure 2a. Methanol was thus selected as the optimal solvent for the titled reaction as it presented the highest conversion of DMA. Along with the yield, the relatively low energy requirement for methanol distillation over water solvent during DMF isolation made methanol as the preferable solvent for the hydrogenation.

Along with DMF, as shown in Figure 2a, the generation of dimethylammonium formate (FA) was observed in all cases, albeit in various ratios. It is commonly considered that the synthesis of DMF by CO_2 hydrogenation is accompanied by FA generation, followed by dehydration, as shown in Figure 2b. However, there is another possible route that involves the generation of CO via the reverse water gas shift reaction, followed by DMA carbonylation (Figure 2b).[6g] To acquire insight into the pathway, a series of experiments was carried out. While performing time-dependent kinetic studies with **1**, FA was detected as a major intermediate during the hydrogenation as the initial rapid generation of FA declined steadily and the formation of DMF increased constantly with respect to the reaction time (Figure 2c). In line with this result, the hydrogenation with FA added to the starting solution gave a higher yield than that without FA (Table S3). Moreover, no CO was detected by gas chromatographic analysis of the gas mixtures (Figure S4). CO_2 hydrogenation in the presence of CO produced a significantly lower yield of the

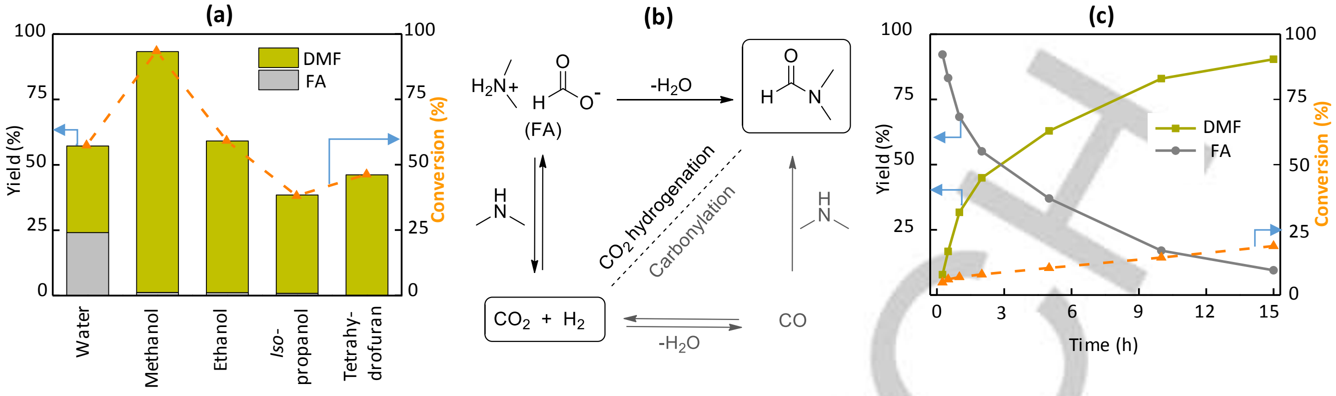

Figure 2. (a) 20.0 mg of **1** in 2.0 M DMA in corresponding solvent (20.0 mL); T = 140 °C; $p(CO_2)/p(H_2)$ = 2/2 MPa; (b) Possible pathways for production of DMF from CO_2/H_2. (c) 10.0 mg of **1** in 2.0 M DMA in methanol, T = 100 °C; $p(CO_2)/p(H_2)$ = 2/2 MPa.

Table 1. CO_2 hydrogenation in batch process[a]

Entry	T (°C)	P (MPa)[b]	Yield$_{FA+DMF}$ (%)[c]	TON$_{FA+DMF}$[d]
1	80	2	10	5,000
2	100	2	19	9,400
3	120	2	27	13,600
4	140	2	36	18,250
5	140	3	56	27,300
6	140	4	65	31,700
7	140	6	84	41,300
8	140	8	98	48,250 (29,000)[e]
9[f]	140	8	80	160,000
10[g]	140	8	2	700

[a]Reaction conditions: 10.0 mg of **1** in 2.0 M DMA in methanol, time = 15 h. [b]Total pressure at room temperature with $p(CO_2)/p(H_2)$ = 1. [c]Calculated based on ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard, and the yields were with respect to DMA. [d]TON = $(mol_{FA+DMF})/mol_{Ru}$. [e]Value in parenthesis represents the initial TOF, which was calculated after 15 min of the reaction. [f]2.5 mg of **1** for 40 h; [g]$p(CO_2)$=3.9 MPa + $p(H_2)$ = 3.9 MPa + p(CO) = 0.2 MPa

products, indicating that **1** is very resistant to carbonylation (table 1, entry 10). Therefore, these results collectively indicate that the formation of DMF is accompanied by FA generation and the pathway related to carbonylation is very unlikely in **1** catalyzed hydrogenation. Notably, there was no discernible distinction in the point of selectivity for FA versus DMF during the heterogeneous hydrogenation, because FA, if present, in the reaction medium, can be converted to DMF during thermal treatment in the DMF isolation step, which has also been reported by Vorholt and co-workers during distillation of the solvents in the DMF isolation step.[6d-g] Henceforth, the word “yield” in this manuscript indicates the combined FA and DMF yields.

As shown in Table 1, the studies on the temperature and total pressure dependence revealed a proportional relationship with the yield, indicating that the chemical equilibrium is more readily shifted towards product side at higher temperature and pressure (Table 1, entries 1-8). The initial TOF and maximum TON for the catalyst were 29,000 h^{-1} (entries 8 and 9) and up to 160,000, respectively, under the optimized reaction conditions without any additives. Surprisingly, these are the best values among those reported for heterogeneous catalysts. Notably, the product yield with respect to the CO_2 feed (15.6 g, 0.354 mol, for entry 8) was calculated to be 11.1%, which is comparable to that of the current process for CO_2 hydrogenation to methanol (~15%),[11] highlighting the industrial viability of **1** for scale up of the hydrogenation.

Before checking the recyclability in the batch process, a filtration test was conducted to evaluate the heterogeneous

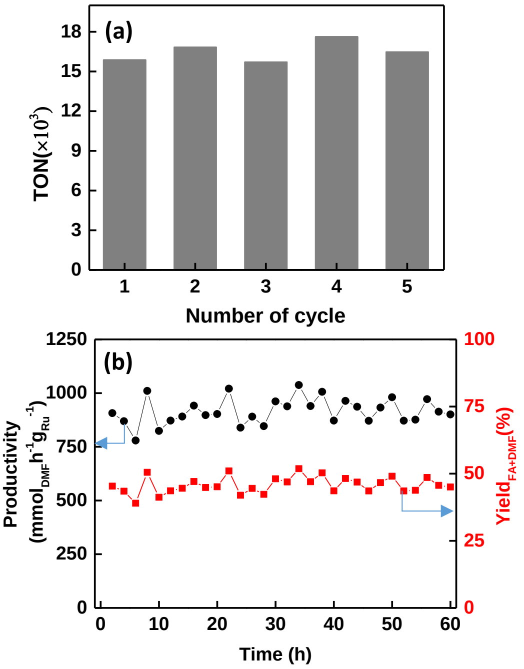

Figure 3. (a) Recyclability of **1** in batch process. (b) CO_2 hydrogenation in continuous-flow process using **1**.

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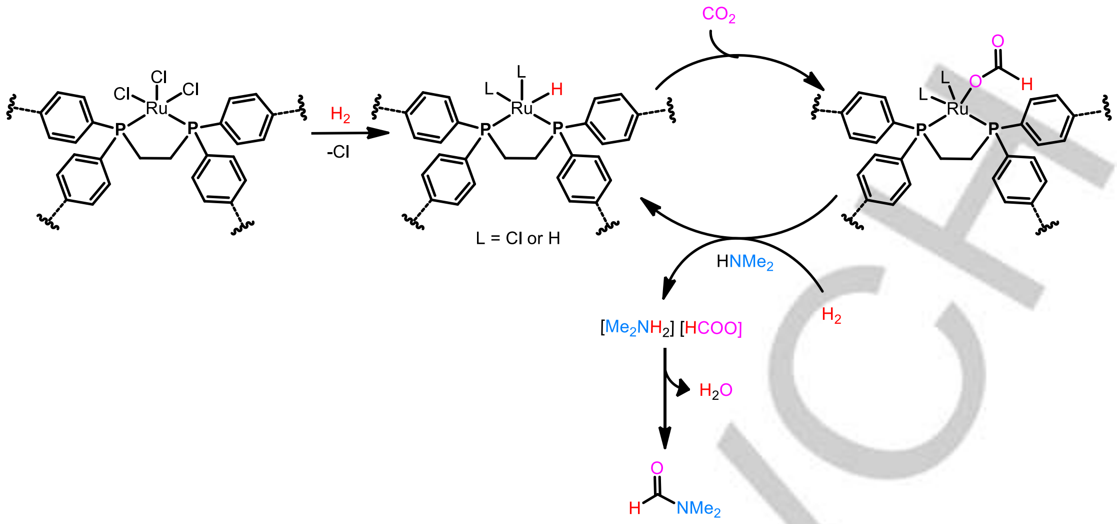

Figure 4. Plausible mechanism for the synthesis of DMF over **1**.

nature of **1**. The test results clearly show that **1** functions in a purely heterogeneous fashion as the filtered solution failed to catalyse the hydrogenation even after a prolonged reaction time (Figure S5). Moreover, ICP-OES analysis of the filtered solution revealed that no Ru metal were leached out during the hydrogenation, indicating the strong binding of the Ru ion to the PP-sites in **1**. To further understand the robustness, catalyst **1** was reused for multiple runs via simple filtration after each cycle. Figure 3a shows that the catalytic efficiency of **1** was well maintained over five consecutive cycles, and the cumulative TON was ~ 80,000 during these runs. As shown in Figures S6 and S7, the characterization of recovered catalyst by STEM-EDX and XPS analysis revealed that the Ru is still intact to the support without any change in its binding energy ($Ru3p_{3/2}$ = 462.2 eV). However, the presence of Cl element was reduced to below the detection limit of the SEM-EDX measurement, suggesting the inactive role of Cl in the catalysis (Table S4). These results indicating that the original motif of Ru is well intact with PP-POP albeit with slight changes in its coordination environment.

Based on our experience and previous literature,[6g, 12] a plausible mechanism for the synthesis of DMF via formate pathway by CO_2 hydrogenation over **1** is proposed (Figure 4). The pathway involves the generation of Ru-H intermediate through substitution of Cl ligand with H_2 followed by CO_2 insertion into Ru-H intermediate to generate Ru-formate species, which then releases out the formate from the catalytic cycle by the oxidative addition of H_2 and regenerates the Ru-H species. The formate extruded from the catalytic cycle finally undergoes dehydration and produce DMF.

Building on the promising results obtained with **1**, continuous-flow CO_2 hydrogenation was performed in a specially designed trickle-bed reactor (TBR) system, where liquid and gas substances are continuously introduced into a fixed (packed) bed of catalyst particles with simple operations. TBRs are widely used in industry particularly for the three-phase reaction (solid, liquid, and gas),[13] The reactor system can offer auspicious advantages in terms of mixing, heat management, scalability, energy efficiency, and sustainability, etc., during the reaction.[13] Although this type of reactor may show a lower TOF than the stirred batch reactor under the same condition, the simple design and operation have practical advantages over the stirred tank reactor. Additionally, no requirement of the recovery of catalysts during the reaction makes this type of reactor feasible for commercialization.

A schematic diagram of the setup is presented in Figure S8. A stainless steel tubular reactor with an internal diameter of 7 mm and length of 460 mm was positioned vertically and the flow stream was consistently set from top to bottom. The setup can maintain simultaneous flow of the liquids (DMA in methanol) and gases (CO_2 and H_2) to the reactor. DMA in methanol and CO_2 were delivered using a HPLC pump and H_2 was delivered through a mass flow controller. The gases and liquids were temperature equilibrated and thoroughly mixed in the preheating system before entering into the reactor. The liquid in the collecting vessel could be removed periodically to analyze the solution through ^1H NMR analysis.

For hydrogenation in the trickle bed reactor systems, catalyst **1** was uniformly mixed with silicon carbide and loaded into the reactor with glass wool plug, and fitted into the rig. Before starting the experiment, the system was thoroughly flushed with N_2 to remove oxygen from the setup. Based on the results of the batch process, continuous hydrogenation was carried out at 140 °C at a total pressure of 12 MPa using 0.5 g of catalyst. During this continuous process, the liquids were periodically collected from the rig for the product analysis. As shown in Figure 3b, the generation of products (FA+DMF) over the time stream was well maintained for a long period (60 h) with an excellent productivity of 915 mmol h^{-1} $g_{active\ metal}^{-1}$, indicating that the catalytic system is highly durable. Notably, this value is significantly high compared to industrial catalyst of methanol synthesis by CO_2 hydrogenation (5.45 mmol h^{-1} $g_{active\ metal}^{-1}$)[11] emphasizing that the developed catalytic process is potentially economical. Therefore, this catalytic process is scalable, simple, and has the potential viability for DMF synthesis via CO_2 hydrogenation in the industry.

In summary, a practically viable catalytic process for the synthesis of DMF by CO_2 hydrogenation was demonstrated using a ruthenium grafted phosphine-based porous organic polymer catalyst. The catalytic system shows best ever activity in the batch (initial TOF of 29,000 h^{-1} and TON of 160,000) and continuous-flow process (productivity of 915 mmol h^{-1} g_{Ru}^{-1}). The catalyst shows excellent stability during both hydrogenation processes, with good selectivity. The simplicity of the catalytic process, with high efficacy and durability, thus provides a promising venue for realizing industrial-scale hydrogenation of CO_2 to DMF.

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Keywords: DMF synthesis via CO_2 hydrogenation • Phosphine-based heterogeneous catalyst • Continuous flow CO_2 hydrogenation • Porous organic polymer • Heterogeneous CO_2 hydrogenation.

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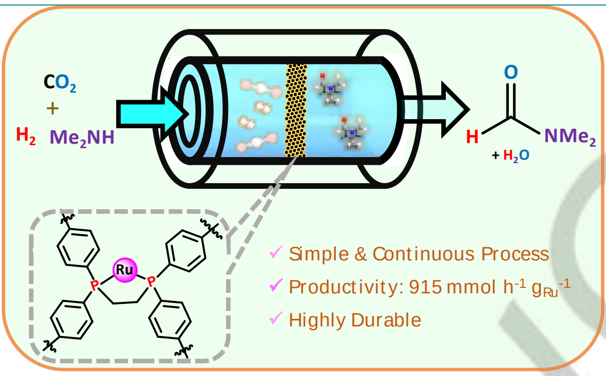
A simple and continuous process has been developed using a highly durable and efficient heterogeneous Ru catalyst.



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