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CO₂ Hydrogenation to Formate with Immobilized Ru-Catalysts based on Hybrid Organo-Silica Mesostructured Materials

Hung-Kun Lo and Christophe Copéret^{*[a]}

Abstract: The hydrogenation of CO₂ to formic acid can be carried out by numerous homogenous catalysts, while efficient heterogeneous catalysts are rare. In this work, we successfully synthesize an immobilized lutidine-derived pincer-type N-heterocyclic carbene ruthenium complex based on a mesoporous organo-silica hybrid material using sol-gel direct synthesis in the presence of structure directing agents and click chemistry as the two key pillars of this strategy. This material efficiently catalyzes the hydrogenation of CO₂ into formate with turnover numbers reaching 18'000 within 24 hours, surpassing the performance of the corresponding homogeneous complexes.

Introduction

Since 2014, CO₂ emissions have exceeded 35 billion tons per year worldwide,^[1] and the number has further increased by 2% in 2017.^[2] Hence, the reduction and especially the incorporation of CO₂ into a closed carbon cycle have drawn more attention in academic and industrial research. CO₂ can be viewed as a C1-building block and/or as part of an energy cycle instead of an industrial waste^[3]. The conversion of CO₂ often requires high pressure and temperature and/or the use of "active" reactants such as H₂, methanol or epoxides to circumvent its considerable Gibbs free energy of formation ($\Delta G^\circ = -394.4$ kJ/mol). Hydrogenation of CO₂ is particularly attractive when considering that excess intermittent energy coming from wind and solar power can be used as a source of renewable H₂ to convert CO₂ into CO, methane, methanol, dimethyl ether (DME), and formic acid along with its derivatives.^[4] In particular, the high hydrogen density of formic acid (53 g/L hydrogen vs. 42 g/L for hydrogen gas at room temperature and 700 bar) makes it an efficient H₂ carrier.^[5] CO₂ hydrogenation to formic acid is however not thermodynamically favored (eq. 1) unless a base is used to shift the equilibrium (eq. 2).

Both supported bulk metal catalysts^[6] and homogeneous complexes^[7] have shown promising catalytic performances for the hydrogenation of CO₂ to formate. While, for bulk metal catalysts, turnover numbers (TONs) have reached ca. 7000 using supported Pd nanoparticles on reduced graphitic oxide nanosheets,^[8] some homogeneous catalysts can reach very high TONs and/or turnover frequencies (TOF). For instance, a lutidine-derived Ru-CNC pincer homogeneous catalyst has been shown to convert CO₂ to formate with the initial TOF and TON reaching 99'100 h⁻¹ and ca. 17'000, respectively.^[7g] The current best catalyst is based on an Ir^{III}-pincer trihydride complex,^[7h, 9] which can reach a TON of 3.5×10⁶ and a TOF of 1.5×10⁵ h⁻¹ in aqueous KOH solution. Despite the tremendous advances in

homogeneous catalysis, molecularly defined immobilized CO₂ hydrogenation catalysts are still rare.^[6, 10] One of the first examples was an organo-silica hybrid material derived from a silylated bis-phosphine Ru complex, which converts CO₂ to DMF (TON = 14'600, TOF = 970 h⁻¹) (Figure 1a).^[11] Immobilizing [RuCl₂(PPh₃)₃] or *cis*-[RuH₂(PPh₃)₄] has also been accomplished via substituting the phosphine ligands with supported bidentate phosphine ligands on a poly(styrene)-block-poly(ethylene glycol) polymer (Figure 1b-c), and these materials are also active in DMF generation from CO₂ (TON = 1'620).^[12] Supported phosphine Ru catalyst (ruthenium(II)-meta-trisulfonated triphenylphosphine) on polystyrene have also been developed to catalyze the reverse reaction (TOF = 270 h⁻¹),^[13] albeit with a lower activity than its homogeneous analogue (TOF = 600 h⁻¹)^[14] due to limited reactant diffusion rate into the pores of polystyrene. Besides immobilized phosphine catalysts, the immobilization of ruthenium N-heterocyclic carbene (NHC) complexes linked to silica matrixes was also developed (Figure 1d), but the TON to form 1-formyl-pyrrolidine is low (TON = 2'900) due to fast deactivation of the catalyst associated with metal leaching.^[15] Alternative supports based on a triazine framework have also been used to generate an hydrogenation catalyst to formate with an initial TOF of up to 5'300 h⁻¹ and TON of 4'900 within 10 hours (Figure 1e).^[16]

Figure 1. Selected heterogeneous Ru catalysts in CO₂ hydrogenation

While these immobilized catalysts offer significant advancements, the TONs still fall short of the respective homogeneous catalysts, which is likely due to deactivation from leaching or changes in the metal coordination sphere. Since bidentate NHC-Ru catalysts^[18] belong to some of the most robust homogeneous systems, we investigated and report here the synthesis and the catalytic property of a Ru NHC-pincer complex supported on a mesostructured porous silica material **1** (Figure 2a-b), prepared from the propyl azide materials obtained via direct synthesis followed by a post-functionalisation using click chemistry (Figure 2c). Using this approach, the immobilized catalyst is able to reach 18'000 TONs in 24 hours under batch

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conditions, while its homogeneous counterpart is limited to 9'250 TONs.

Results and Discussion

Synthesis of the immobilized Ru NHC-pincer complexes

The catalyst **1** was prepared in three key steps from an azidopropyl SBA material^[17] by first incorporating the NHC ligand via click chemistry, followed by a passivation of the surface and then incorporation of Ru (Figure 2a-b).^[18] First, the functional mesostructured SBA-type propylazido silica material was synthesized by co-condensation of tetraethoxysilane and (3-azidopropyl)trimethoxysilane in the presence of the structural directing agent (P123), and the resulting product has large surface area (706 m²g⁻¹) and narrow distribution of small pores (7.2 nm)^{[19]-[20]}. Its porous vermicular structure was confirmed with transmission electron microscopy (Figure S1b). The material was then post-functionalized through click chemistry^[21] in the presence of a catalytic amount of CuSO₄·5H₂O in DMF using the alkynyl substituted pincer ligand **3** (Scheme 1), which was prepared in five steps from readily available starting materials with an overall yield 47% (Scheme S1).^[22] Prior to the incorporation of Ru, the surface of the material was carefully washed to remove excess Cu using a chelating agent, sodium diethyldithiocarbamate, and passivated with chlorotrimethylsilane (Me₃SiCl) in order to make the surface more chemically inert (by protecting accessible surface OH groups), i.e. by avoiding side reaction when Ru precursor was introduced to the material. The IR spectrum of **5** (Figure S5) shows a significant decrease in the azido band intensity at 2111

cm⁻¹ and the disappearance of the isolated silanol band at 3740 cm⁻¹. However, some azido residue remains unreacted, suggesting that they are not accessible and are likely present in the micropores.^[18] Furthermore, the solid-state ¹³C NMR spectrum of the ligand-functionalized material (**5**) shows analogous peaks to the spectrum of **3** in solution ¹³C NMR spectroscopy. Figure S8 shows that the most distinctive peaks are from the methyl groups of mesitylene (ca. 20 ppm), the C2 (167 ppm), C4 and C5 (ca. 55 ppm) positions of the imidazolium ligand, and the Me₃Si resonances (-1.8 ppm) from protection of surface OH groups. Finally, Ru was incorporated, by first reacting the imidazolium with LiHMDS in the presence of LiBr^[15, 23], followed by the addition of RuHCl(CO)(PPh₃)₃ as the molecular precursor. After ligand functionalization under click conditions and Me₃Si-passivation on the material, the surface area dropped from 706 to 451 m²g⁻¹, which is likely due to the surface modification with Me₃Si groups and post-functionalization of the propyl azido groups with the very large molecular structure.^[24] Introduction of the Ru precursor further caused the surface area of the material to drop to 312 m²g⁻¹ but the porous vermicular structure remained intact (Figure 3b). The absence of coordinated PPh₃ according to IR spectroscopy shows that most grafted Ru species are present as bis-NHC-Ru complex (Figure S10). In addition, the IR band at 1951 cm⁻¹, which is observed at 1875 cm⁻¹ in the molecular analog **6** (Table 1), is attributed to coordinated CO, possibly interacting with the material surface. The elemental analysis of the immobilized Ru-catalyst gave ruthenium and nitrogen weight contents of 0.62% and 1.67%, respectively. Based on the measured Ru/N molar ratio (1/20) by comparison to the theoretical molar ratio (1/8), the estimated conversion of the supported imidazolium precursor to Ru-NHC is about 40%.

Figure 2. (a) The NHC pincer-type ruthenium complex developed by Pidko et al. and the corresponding modified structures (b) Strategies to immobilize catalysts on the well-defined hybrid material: SBA material with click reaction (c) Comparison of directly grafted material and hybrid material

Scheme 1. Key synthetic steps for the heterogeneous Ru catalyst (**1**)

Figure 3 (a) The Ru catalysts on the porous SBA material (b) TEM micrographs (c) nitrogen adsorption/desorption isotherm at 77 K of **1**. ^{13}C solid-state NMR of the ^{13}C -labeled (d) ligand-functionalized material (e) heterogeneous Ru catalyst and (f) the mass spectrum of the dissociated immobilized catalyst from ToF-SIMS

In order to obtain molecular-level characterization of the surface species, the corresponding ^{13}C -labeled catalyst at the NHC carbenic carbon was prepared with ^{13}C -labeled 1-mesityl-1H-imidazole.^[25] The immobilized ^{13}C -enriched imidazolium precursor – ca. 93% labeled at the C2 position – gave an intense signal at $\delta = 137$ ppm in the ^{13}C NMR spectrum, consistent with the formation of this organic functionality (Figure S18). After introducing Ru, the intensity of the peak decreased significantly and a new peak appeared at $\delta = 192.05$ ppm, which confirmed the formation of Ru-NHC bond (Figure 3d-e). Another characteristic peak assigned to the Ru-H was also found at $\delta = -15.5$ ppm in the ^1H solid-state NMR (Figure S11), similarly to its molecular counterpart ($\delta = -15.57$ ppm).^[7] The immobilized Ru-catalyst was also analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS), which confirms the structure of the proposed surface sites. In particular, a peak of $m/z = 624.70$ was detected, consistent with the presence of the Ru complex fragment (Calc. 624.18) – (Figure 3f). The ToF-SIMS spectrum also shows a strong bromide signal, which could result from the physical absorption of salt byproducts on the material surface or coordination to Ru. To conclude, the solid-state NMR, IR and ToF-SIMS spectra show that the SBA-supported Ru heterogeneous catalyst has been synthesized successfully.

The CO_2 hydrogenation activity of this material was then evaluated under batch conditions and compared to the analogous molecular complexes. The typical hydrogenation reaction conditions are as follows: 85 °C reaction temperature, 40 atm total pressure, and in the presence of DBU as a base (Table 1).^[79] While the material without Ru does not show any significant activity to convert CO_2 to formate, the immobilized Ru-based catalyst (**1**) can reach 18'000 TON within 24 hours, which greatly exceeds what is obtained with the Ru molecular precursor (4'030 TONs for $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$) and the

molecular analogue **6** (9'250 TONs). However, the CO_2 conversion barely increased when the reaction was extended to 48 hours (19'000) indicating deactivation. Hot filtration experiment (see ESI) suggests that no active species are leached from the heterogeneous catalyst during the reaction.

Table 1 CO_2 hydrogenation results with different catalysts

CO_2 + H_2 $\xrightarrow[30 \text{ mL DMF, } 85^\circ\text{C}]{5 \text{ mL DBU}}$ $\text{HCOOH} \cdot \text{DBU}$ 5 bar 35 bar Catalyst Internal standard					
Entry	Catalyst	Amount of cat. (mg)	Formate (mmol)	Time (h)	TON
1	$\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$	5.0	21.2	24	4034
2	1	10.0	10.8	24	18000
3	1	10.0	5.9	5	9800
4	5	10.0	0.90	24	-
5	6 ^[a]	0.6	7.4	24	9250

[a] Molecular counterpart (**6**) of the Ru heterogeneous catalyst (**1**)

Structure of **6**:

Conclusion

In summary, we successfully developed a simple strategy to immobilize the Ru-NHC pincer homogeneous catalyst through click chemistry on a highly ordered silica-based (SBA) material. The structure of the ruthenium heterogeneous catalyst was confirmed by infrared spectroscopy, ToF-SIMS and solid-state NMR with the use of ^{13}C -labelling. This immobilized catalyst effectively catalyzes the CO_2 hydrogenation into formic acid-base adduct reaching 18'000 in 24 h, surpassing its homogeneous counterpart. However, while this immobilization strategy improves the stability of this catalyst compared to its homogeneous analogue allowing increasing the number of TON, it still suffers from deactivation. We are currently trying to understand the deactivation mechanism in order to develop more robust catalysts and possible regeneration strategies.

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Keywords: CO_2 hydrogenation • heterogeneous catalysis • ruthenium • carbene • mesostructured silica

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