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Shaping Covalent Triazine Framework for the Hydrogenation of Carbon Dioxide to Formic Acid

Anastasiya V. Bavykina*^[a], Elena Rozhko^[a], Maarten G. Goesten^[a,b], Tim Wezendonk^[a], Beatriz Seoane^[a], Freek Kapteijn^[a], Michiel Makkee^[a], and Jorge Gascon*^[a]

Abstract: A facile one-step method to shape Covalent Triazine Frameworks (CTFs) for catalytic applications is reported. Phase inversion of the CTF powder using a polyimide as binder in a microfluidic device results in the formation of composite spheres with accessible CTF porosity and a high mechanical and thermal stability. The fabricated spheres can be used to host organometallic complexes. The obtained shaped catalysts, Ir@CTF spheres, are active and fully recyclable in the direct hydrogenation of carbon dioxide into formic acid under mild reaction conditions (20 bar and 50-90 °C) and in the dehydrogenation of formic acid.

Introduction

Covalent Triazine Frameworks, CTFs, are a class of solid, porous organic polymers, formed by the trimerization of aromatic nitriles. Within materials chemistry, CTFs have recently attracted considerable attention for they provide a unique combination of high porosity, high thermal and chemical stability, and a high degree of chemical tunability.^[1] Most interestingly, tuning of their solid-state properties is possible by varying their starting building blocks.^[2] For instance, the use of pyridinic precursors leads to an inherently basic material, highly suitable for the activation of small molecules. Recently, we reported the application of such a CTF as non-innocent support for Ir(III)Cp* and the use of the resulting catalyst in the dehydrogenation of formic acid, demonstrating that the CTF framework does not only immobilize the metal complex, but itself promotes the catalytic cycle by deprotonating formic acid in acidic conditions^[3].

In the frame of reversible hydrogen storage, essential in a hydrogen economy, the reversibility of the abovementioned reaction – the hydrogenation of CO₂ to yield formic acid – is particularly important. Progress in realizing this challenge has, to large extent, relied on homogeneous catalysts, often based on Ir^[4], Rh^[5], and Ru^[6]. Although the performance of such catalysts is generally outstanding from the perspective of turnover frequencies (TOFs), they usually operate under very low concentrations, making them unsuitable for process-intense operation. It is, therefore, logical that there exists a surging quest for efficient heterogeneous systems capable of catalyzing this reaction^[7]. Some promising step-forwards have already been presented, mainly in the form of molecular heterogeneous catalysts; Ru-based by Zhang *et al.*^[8] and most interestingly, a

CTF-supported Ir-based system by Park *et al.* of great similarity to the one employed by us in the dehydrogenation of formic acid.^[9] While this clearly shows that CTF-based catalysts carry great promise as solid molecular catalysts, laboratory practice still relies on using the catalyst in a slurry operation as a powder. Notably, the use of powder invokes a number of problems in prospective application, most particularly the partial loss upon sampling or recovery in catalyst recycling, yet the all-important aspect and potential of CTFs in catalyst formulation, shaping or embedding in applied reactor conditions has remained unexplored.

In attempt at bringing the use of CTF-based molecular catalysts a step closer to industrial reality, we herein report a one-step method for the production of porous, mechanically rigid and easy-to-handle CTF-based spheres prepared by a phase inversion method using the polyimide Matrimid® as a binder. After obtaining the spheres, Ir(III)Cp* was coordinated to bipyridine moieties of CTF in order to obtain efficient catalytic functionality. This sphere-based catalyst was shown to be a highly and easily recyclable catalyst in the hydrogenation of CO₂.

Results and Discussion

In order to shape CTF-based catalysts whilst maintaining porosity, we used Matrimid 5218 as binder, for it is highly stable, compatible with the CTF, inexpensive and (in contrast to the CTF) highly soluble in most common organic solvents.^[10] Additional experiments were performed using polylactic acid as binder, but the resulting pellets collapsed upon mild temperature treatments (up to 160 °C).

Home-made mesoporous copolymer meso-CTF was embedded within the Matrimid matrix to render shaped, hard-body spheres of CTF, of which the outer skin is denser than that of the inner part. The molecular catalyst, shown within the magnifier (Figure 1C), was successfully obtained on spheres-CTF using the protocol reported earlier by our group^[3]. Notably, SEM/EDX analysis of Ir@spheres-CTF composite shows that most of the iridium is located in the outer shell of the spheres, therefore providing a good accessibility (Fig. S11). Iridium's oxidation state of 3⁺ was confirmed by XPS analysis (Fig. 1D). **When iridium was coordinated to the meso-CTF powder prior to the shaping step, no porosity in the final composite material was preserved.**

Tests in determining the chemical stability of the obtained spheres towards organic solvents were performed by leaving them overnight in acetonitrile and hexane at 60 °C under vigorous stirring (1000 rpm). **Stability tests at different temperatures in water (up to 100 °C) showed that the composite material is highly stable in aqueous media.**

The CTF powder immersed within the spheres (which consist of 60% CTF) preserves its meso-porosity and displays a BET surface of 465 m²g⁻¹ (Figure 2), **meaning that roughly 43%**

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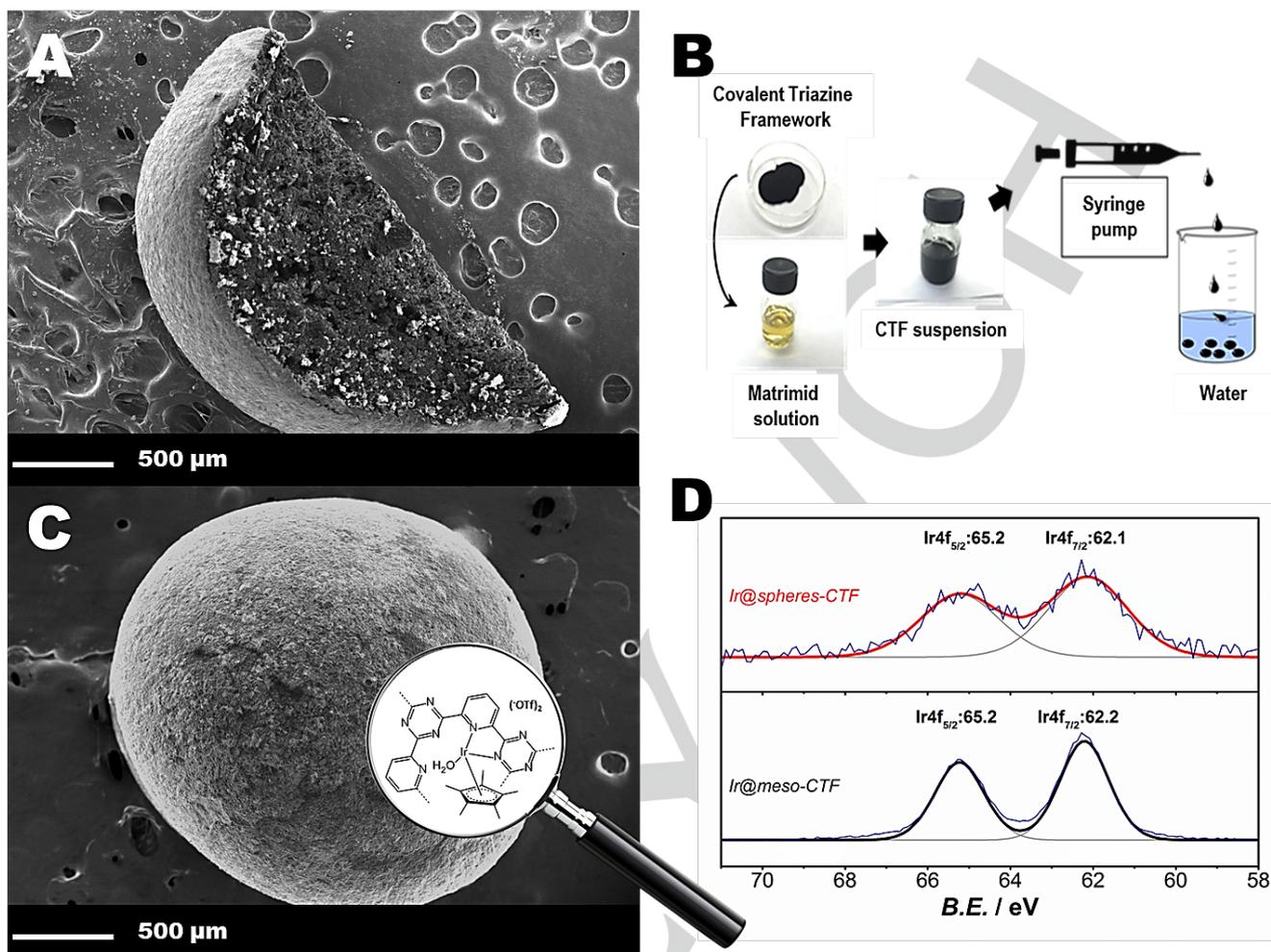


Figure 1. A: SEM of cut CTF sphere; B: Scheme of spheres-CTF formation; C): SEM of CTF based sphere with the molecular structure of the catalyst EDX analysis of Ir@spheres-CTF catalyst; D) XPS analysis of iridium in the powder and shaped Ir@CTF catalysts.

of the original surface area of the CTF was preserved. It is important to note that the polymer binder does not contribute to this BET area. Figures S12 & S13 show a similar pore size distribution for both the shaped and unshaped catalysts along with a reduction on the total porosity upon shaping. These results indicate that part of the CTF porosity is used to host polymer chains: partial penetration of the CTF porosity by the polymer occurs, leading to totally blocked pores and polymer free ones. In the latter, no pore size modification is observed.

The coordination of 2 wt% Ir on powder-based CTF results in a decrease of the accessible surface area of the material (Fig. 2). In contrast, the nitrogen uptake for Ir@spheres-CTF is slightly higher than that for the original spheres. This could be rationalized by the fact that DMF was used during iridium coordination, resulting in the partial leaching of some binder without affecting the integrity of the spheres. Indeed, spheres that were treated overnight in acetonitrile, like DMF a highly polar non-protic solvent, were seen to partially leach out binder, whilst the spheres after treatment in apolar hexane remained entirely intact.

In addition to 2 wt% Ir@CTF, catalysts containing a lower amount of active phase were prepared. It must hereby be noted that “wt%” refers to the amount of Ir with respect to the entire sphere. This amounts to only 43% of the porosity available for the coordination to Ir. Using this definition, the samples are henceforth referred to as 1, 0.5, and 0.2 wt% and correspond to an Ir loading per accessible CTF of 2.3, 1.2, and 0.46 wt%, respectively.

Tables 1 and 2 display the performance of the Ir@meso-CTF and Ir@spheres-CTF catalysts in basic aqueous media. In contrast to the triphenyl-phosphine based catalysts and most homogeneous catalysts in literature, the herein reported Ir@meso-CTF does not require operation under an oxygen-free atmosphere during catalyst handling. Experiments with potassium bicarbonate as base showed a better performance than those with potassium hydroxide, suggesting that the hydrogenation mechanism proceeds via bicarbonates^[11].

All carbon dioxide hydrogenation experiments were performed in duplo. Although both the shaped and the powder catalysts could be recycled, experiments with the powder

catalyst resulted in a 25% deviation, as the sample tends to stick to the reactor walls (at all stirring rates).

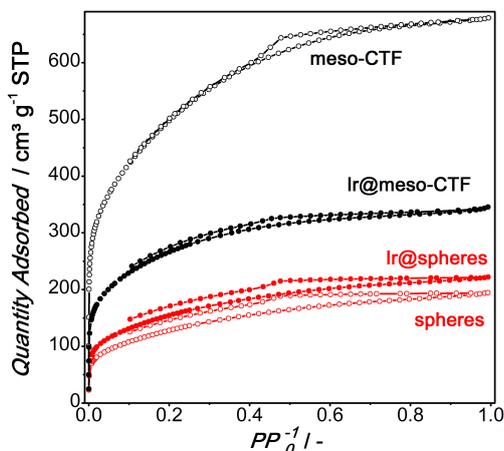


Figure 2. N_2 adsorption isotherms of meso-CTF (open black) BET $1800 \text{ m}^2 \text{ g}^{-1}$, CTF based spheres (open red) BET $465 \text{ m}^2 \text{ g}^{-1}$, Ir@meso-CTF catalysts with 2.4 wt% Ir (solid black) BET $970 \text{ m}^2 \text{ g}^{-1}$, Ir@spheres-CTF catalyst with 2wt% Ir (solid red) BET $560 \text{ m}^2 \text{ g}^{-1}$.

In contrast, when Ir@CTF spheres are used, differences less than 5% are found within the duplicate experimental range. In comparing the performance of the shaped and powder solids on a total Ir wt% basis, an overall loss in catalytic activity of circa 80 % is observed in case of the spheres (see table 1 entry 10.1 and 10.2 vs. Table 2 entries 2.1 to 2.4). However, taking into consideration the amount of accessible CTF within the spheres, the activity loss for the samples with an effectively comparable Ir loading (table 1 entry 10.1. and 10.2 vs. Table 2 entry 3) is approximately 40% of that of the CTF powder.

Table 1. Carbon dioxide hydrogenation with Ir@meso-CTF catalyst. Iridium content is 2.4 w%^a

	base	$T / ^\circ\text{C}$	TON ^{b,c}
1	no	90	-
2	KOH	50	29
3	KOH	70	66
4	KOH	90	83
5	KHCO_3 1M	50	167
6	KHCO_3 1M	70	194
7	KHCO_3 1M	90	358
8	KHCO_3 0.5M	50	155
9	KHCO_3 0.5M	70	173
10.1	KHCO_3 0.5M	90	302 (1 st run)
10.2	KHCO_3 0.5M	90	330 (2 nd run)

[a] Reactions were carried out at 20 bar with an equimolar H_2/CO_2 mixture and 50 mg catalyst. [b] TON obtained from UPLC analysis after 2 h reaction. [c] Presented as average of two experiments with a reproducibility of $\pm 25\%$.

Table 2. Carbon dioxide hydrogenation with Ir@CTF spheres catalyst^a

	Ir loading/ wt%	$T / ^\circ\text{C}$	TON ^{b,c}
1	2	50	15
2.1 ^d	2	90	54
2.2	2	90	62
2.3	2	90	57
2.4	2	90	57
3	1	90	120
4	0.5	90	175
5	0.2	90	219

[a] Reactions were carried out at 20 bar with an equimolar H_2/CO_2 mixture using 0.5M KHCO_3 as a base and 50 mg catalyst. [b] TON obtained via UPLC analysis after 2 hours of reaction. [c] Presented as average of two experiments with a reproducibility of $\pm 5\%$. [d] Four catalytic runs with the recycled catalyst.

In order to explore whether this decrease in activity also occurs in the reversed reaction, namely the dehydrogenation of formic acid, we performed additional experiments using the shaped Ir@spheres-CTF with 2w% Ir loading (corresponding to 4.6 w% Ir of accessible CTF) in a 3M aqueous solution of formic acid at 80°C . TOFs of 800 h^{-1} were obtained. Though this value is still far from the outstanding performance of the powder version (21300 h^{-1} , 2 w% Ir)^[3], it shows that the catalyst still outperforms systems based on nanoparticles^[12] and has a similar activity to the Ru immobilised complex reported by Laurency^[13].

The catalytic performance of Ir@spheres-CTF in both direct and reverse reactions demonstrate that active, stable and readily shaped catalysts for reversible hydrogen storage can be manufactured using the method here reported. Moreover, utilization of shaped particles carry the advantage of facile catalyst recycling and improved reproducibility.

Conclusions

Covalent Triazine Frameworks can be shaped to a spherical form without losing their properties. CTF spheres show high thermal stability, porosity, and the possibility of coordinating metal clusters. In contrast to the powder, the spheres-based catalyst is more easily handled, whilst fully recyclable without loss of material through at least four consecutive runs. A highly efficient organometallic complex such as IrCp^* is immobilized via coordination within the CTF spheres to render a molecular yet heterogeneous, stable catalyst which is easy to handle and recycle in the carbon dioxide hydrogenation to formic acid.

The development of methods for the facile shaping of new catalytic materials is of high interest in order to further

demonstrate catalyst stability and recyclability, two key features for perspective application.^[14] We believe that the results here reported further highlight the promise that CTF-based materials hold in application.

Experimental Section

Materials

All reagents and solvents were purchased from Sigma-Aldrich and used as received.

Meso-CTF synthesis

The following procedure is carried out for the preparation of the polymer: a quartz ampoule was loaded with 2,6-pyridinedicarbonitrile (0.41 g, 3.2 mmol), 4,4'-biphenyldicarbonitrile (1.31 g, 6.40 mmol), and anhydrous ZnCl₂ (6.64 g, 0.048 mol), in a glovebox. The ampoule was flame sealed and subjected to the following temperature programme: temperature is brought to 500 °C via a heating rate of 60 °C h⁻¹, kept at this temperature for 48 h, then cooled to room temperature at a rate of 10 °C h⁻¹. The product was crushed in a mortar, then subsequently refluxed in 5M HCl (150 mL) at 100 °C, 6M NH₄OH at 60 °C, H₂O (150 mL) at 100 °C, and THF at 60 °C. Every washing step was performed overnight. Activation of the material was performed by drying it under vacuum at 200 °C for 24 h. After all required filtrations, a fully amorphous powder was obtained with a final yield of at least 90% on molar basis. The washing steps might seem excessive and are more severe than those described in literature, but were required, as we found, to remove ZnCl₂.

Spheres production

A Matrimid 5218 solution was prepared by dissolving 0.4 g polymer in a mixture of 3.6 ml THF and 1.8 ml NMP. Then 0.6 g meso-CTF were added and the mixture was stirred at room temperature for one hour. Afterwards, the slurry mixture was pumped to a vessel filled with water using a syringe pump (inner diameter of a syringe tip is around 1 mm) at a flow rate of 0.2 ml/min. The solid spheres precipitated immediately. They were kept in water overnight and subsequently activated at 350 °C (heating rate of 1 °C/min) under nitrogen flow (100 ml/min) for 8 h.

Spheres stability test

In order to check stability of the spheres in different solvents, the spheres were placed in a flask filled with a solvent under vigorous stirring (1000 rpm) at elevated temperatures (60-100 °C). The spheres were called stable if they did not undergo any decomposition and preserved their structure.

Ir@meso-CTF catalyst synthesis

A mixture of 480 mg meso-CTF polymer and 40 mg [Cp*Ir(Cl)₂]₂ was placed in a Schlenk flask in a glovebox. Outside of the glovebox, degassed water (40 ml) was added with a syringe to the flask under a continuous Ar flow. The mixture was stirred overnight and filtered. The powder was further washed in a mixture of triflic acid (HOTf) (300 mg) and a 1:1 DMF/water mixture (50 ml) to remove the chloride ions. Finally, the powder

was stirred in water at 50 °C for another 12 h, before being filtered and dried under vacuum at 50 °C.

Ir@spheres-CTF catalyst synthesis

Sphere shaped iridium catalyst Ir@CTF spheres was prepared following the same procedure as Ir@meso-CTF, but with altered loadings: for the coordination at 480 mg CTF-spheres, 145 mg [Cp*Ir(Cl)₂]₂ was used.

Carbon dioxide hydrogenation

Hydrogenation experiments were performed in a Parr 5000 Multi Reactor Stirrer System under pressure using an equimolar mixture of gases H₂:CO₂ (batch condition). The reaction vessels (autoclaves) had a volume of 45 cm³ and were stirred with suspended magnetic bars. Autoclaves were filled with 30 cm³ of water as solvent, KHCO₃, and 40mg of Ir@CTF catalyst. The gas mixture was then introduced in the autoclaves until 20 bar pressure was reached. The autoclaves were heated to the desired temperature with a heating rate of 2 °C min⁻¹ and kept at this temperature for 2 h. Subsequently, the autoclaves were immediately depressurized, the gas mixture was replaced by flushing the system with He, and the vessels were cooled down to ambient temperature. Liquid samples were taken and analyzed by UPLC. The UPLC analysis was carried with column Shodex KC-811 and Rspak KC-G guard column with 0.1% of H₃PO₄ in water as a mobile phase with a rate of 0.70 ml/min. The formic acid product was detected with a UV detector at a wavelength of 210 nm.

The recycling procedure was identical for both Ir@meso-CTF and Ir@spheres-CTF. Spent catalyst was filtered from the reaction mixture, suspended in water at 50 °C overnight and activated at 50 °C under vacuum for 12 h.

Characterization

Nitrogen adsorption measurements were done using a Tristar II 3020 Micromeritics instrument employing N₂ gas (99.999 %). Argon adsorption was performed on a Micromeritics ASAP 2010 gas-adsorption analyzer (stainless-steel version) at 88 K. For the DFT calculations, a Slit Pores N₂@77 on Carbon NLDFT model with a regularization factor of 0.003160 was used.

XPS measurements were performed on a K-alpha Thermo Fisher Scientific spectrometer using a monochromatic Al K α X-ray source. The measurements were performed by scanning three spots per sample at ambient temperature and chamber pressure of about 10⁻⁷ mbar. A flood gun was used for charge compensation. All measured spectra were corrected by setting the reference binding energy of carbon (C1s) at 285.0 ± 0.025 eV. Spectra were analyzed using the Thermo Avantage software package, background subtraction is done using the setting "SMART".

For elemental analysis, the samples were analyzed by Mikroanalytisches Laboratorium KOLBE, (Mülheim an der Ruhr, Germany).

SEM images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart-Thornley detector. X-ray microanalysis (SEM/EDX) confirmed the elemental composition in the sample by the scanning electron

microscopy (SEM) coupled with a dispersive X-ray microanalysis system (EDX) with a Silicon-drift detector.

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Keywords: Covalent Triazine Framework • catalyst shaping • carbon dioxide hydrogenation • formic acid

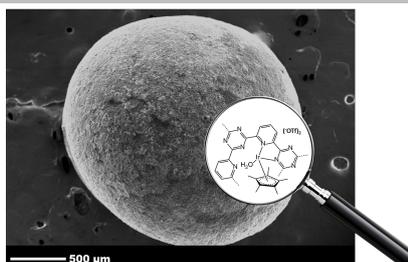
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Shaping Covalent Triazine

Framework: A facile one-step method to shape Covalent Triazine Frameworks into composite spheres with accessible porosity, high mechanical, and thermal stability is reported. The fabricated spheres were used to host organometallic complexes and the obtained catalyst Ir@speres-CTF is active and fully recyclable in the direct hydrogenation of carbon dioxide into formic acid.



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