View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Coufourier, S. gaillard, G. Clet, C. Serre, M. Daturi and J. Renaud, *Chem. Commun.*, 2019, DOI: 10.1039/C8CC09771B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Journal Name



Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 02 April 2019. Downloaded by UNIVERSITE PARIS SUD on 4/2/2019 1:58:18 PM

MOF-Assisted Phosphine Free Bifunctional Iron Complex for the Hydrogenation of Carbon Dioxide, Sodium Bicarbonate and Carbonate to Formate.

Sébastien Coufourier,^a Sylvain Gaillard,^a Guillaume Clet,^b Christian Serre,^c Marco Daturi,^{b*} Jean-Luc Renaud^{a*}

Abstract: Hydrogenation of carbon dioxide into formic acid (FA) with Earth-abundant metals is a vibrant research area, because FA is an attractive molecule for hydrogen storage. We report a cyclopentadienyl iron tricarbonyl complex that provides up to 3000 turnover numbers for carbon dioxide hydrogenation when combined with a catalytic amount of the chromium dicarboxylate MOF MIL-53(Cr). To date, this is the highest turnover number reported in the presence of a phosphine free iron complex.

Fossil fuels represent a large part of the global energy. Due to the depletion of these fossil resources and in the context of global warming, it is crucial to develop alternative processes. Hydrogen gas is a potential clean energy vector to replace fossil fuels, when synthesised via sustainable sources of energy. However, its storage and its transport remain a problematic issue. Dehydrogenation of formic acid (4.4 wt. % H₂) or methanol (12.6 wt. % H₂) has been proposed as an alternative solution for hydrogen storage. The current synthesis of formic acid and methanol is based on the use of nonrenewable feedstocks.¹ Carbon dioxide is, in sharp contrast, an abundant, non-toxic and inexpensive C1 carbon source.² Its hydrogenation can deliver, in the presence of a catalyst, formic acid and/or methanol, moreover decreasing the carbon fingerprint of related processes. Some organometallic complexes, mainly based on platinum metals, have been already designed and applied to these applications in the last decades.³⁻⁴ Despite its great interest on industrial scale and the exciting challenge, due to the lower electrophilic character of the carbonyl function, the hydrogenation of carbon dioxide with Earth-abundant metals is still underdeveloped.5-13 Laurenczy and Beller,10 Milstein,11 and

This journal is © The Royal Society of Chemistry 20xx

Gonsalvi12 disclosed recently well-defined iron hydride complexes for the reduction of carbon dioxide into formates or formamides. Bernskoetter and Hazari have described the most impressive results with a Turnover number (TON) of up to 60000 over 24h with a [Fe(H)(BH₄)(PNP)(CO)] complex and in the presence of DBU and LiOTf, with a 7.5 : 1 loading ratio, in THF at 80 °C.¹³ However, replacing noble metals by inexpensive, more abundant and biocompatible iron complexes to perform hydrogenation is not the unique criterion for industrial applications. Even if these complexes paved the way to new reactivities in iron chemistry, they contain electron-rich, air- and moisture sensitive and expensive phosphorous ligands. In our ongoing work on reduction and alkylation using phosphine free iron complexes, we have synthesized an iron tricarbonyl complex bearing an electron rich cyclopentadienone ligand (complex Fe1, Figure 1), which is more active than the well known Knölker's complex (Fe2, Figure 1).14-15 We and others have also demonstrated that these complexes could reduce sodium carbonate.^{15a-16} TON up to 1200 were reached with complex Fe1. We considered that our new cyclopentadienone iron tricarbonyl complex could be an alternative solution for the hydrogenation of carbon dioxide.



Figure 1. Cyclopentadienone iron tricarbonyl complexes.

To initiate this work, a rapid screening of solvents has been carried out at 80 °C for 20 h under 20 bar of CO_2 and 40 bar of H_2 in the presence of triethylamine as base (see the ESI). A 1:1 mixture of DMSO and water provided the best result with a TON of 82. Without any base or iron complex, no reaction was observed (Table 1, entry 1). Several bases were then evaluated and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) led to the highest TON (Table 1, entries 2-6). High concentration (Table 1, entries 3 and 7) and addition of Me₃NO to activate the iron

^{a.} Normandie Univ., LCMT, ENSICAEN, UNICAEN, CNRS, 6 boulevard du Maréchal Juin, 14000 Caen, France.

^{b.} Normandie Univ., ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France.

^c Institut des Matériaux Poreux de Paris, UMR 8004 CNRS, Ecole Normale Supérieure, Ecole Supérieure de Physique et des Chimie Industrielles de Paris, PSL Research University, 75005 Paris, France

Electronic Supplementary Information (ESI) available: Preparation details, optimzation conditions, NMR spectra and characterization of MIL-53(Cr). See DOI: 10.1039/x0xx00000x

COMMUNICATION

complex (Table 1, entries 7-8) enhanced also the overall activity. A temperature threshold was also required to reach a high conversion and, at 80 or 100 °C, full conversion and a TON of 500 were obtained (Table 1, entries 8-10). Any variation of the CO_2/H_2 ratio led to TON depletion (see ESI). To elucidate the optimum performance, the catalyst loading was lowered to 0.02 mol % (Table 1, entries 11-15). A turnover of 1466 to formate was finally obtained. Finally, in a last trial, DBU, the most encountered, but expensive, base in reduction of CO_2 , was replaced by an amidine analogue, namely 1,1,3,3-tetramethylguanidine (TMG, Table 1, entry 16). Gratifyingly, a TON of 1772 to formate was obtained. Even if these results are moderate compared to the most active iron complex,¹³ they are the highest reported so far with an iron complex without any air-sensitive pincer ligand or polydentate phosphine ligand.

Table1. Hydrogenation of carbon dioxide.

	CO ₂ + H ₂ + ba	se Fe1 (DMS temp.	x mol %} 30/H_0 (°C), 20 h	HCO ₂ H.base	
Entry	Fe1	Base	Temp.	Yield	TON⁵
	(mol %)		(°C)	(%) ^a	
1 ^c	0.2	-	80	-	-
2 ^c	0.2	NEt_3	80	16.3	82
3°	0.2	DBU	80	24	120
4 ^c	0.2	DABCO	80	8.4	42
5 ^{c,d}	0.2	TEOA	80	10.6	53
6 ^c	0.2	NH₃aq.	80	3.6	18
7 ^{c,e}	0.2	DBU	80	59.3	297
8 ^c	0.2	DBU	80	100	500
9°	0.2	DBU	100	100	500
10 ^f	0.2	DBU	60	34.3	172
11 ^f	0.1	DBU	80	51.9	519
12 ^f	0.1	DBU	100	59.5	595
13 ^f	0.05	DBU	80	27.1	542
14 ^f	0.05	DBU	100	39.4	788
15 ^f	0.02	DBU	100	29.3	1466
16 ^f	0.02	TMG	100	34.5	1772

^a Yield were determined by ¹H-NMR spectroscopy using DMF as internal standard. ^b Mol of sodium formate per mol of catalyst. ^c CO₂ (20 bar), H₂ (40 bar), base (2.5 mmol), **Fe1** in DMSO/H₂O 1/1 (5 mL) for 20 hours. ^d TEOA: triethanolamine. ^e with Me₃NO (0.2 mol%). ^f CO₂ (20 bar), H₂ (40 bar), base (5 mmol), **Fe1** (x mol %) and Me₃NO (x mol %) in DMSO/H₂O 1/1 (5 mL) for 20 hours.

To enhance the reactivity of our catalytic system, we thought to combine our system with particles of Metal Organic Frameworks (MOFs). MOFs are a recent class of 3D crystalline hybrid micro-/mesoporous materials constructed from inorganic nodes (clusters, chains, layers...) interconnected with multi-dentate organic linkers (carboxylates, phosphonates, azolates...).¹⁸ Their unprecedented chemical and structural diversity led so far to the development of numerous applications with these materials.¹⁹ MOFs, for example, are particularly suitable for carbon dioxide capture and sequestration²⁰, or for photocatalytic CO₂ reduction.²¹ Moreover, their Lewis or Brønsted acid sites, provided by the inorganic building units, might allow the CO₂ activation. So these materials might assist / cooperate with the iron complex

Page 2 of 5

Initially, we used the same reaction conditions as those reported previously above (Table 1, entries 15-16), but in the presence of MIL-53(Cr) (0.05 mol %). To our delight, whatever the base (DBU or TMG), the activities were higher (Table 2, entries 1-2). Again, TMG, as base, gave better results than DBU and TON's up to 3006 were reached. By comparison with the sole iron-catalyzed reduction of CO₂, a two-fold higher TON was reached through this cooperative catalysis. Variation of the catalytic amount of MOF led to lower TONs (Table 2, entry 3). When a simple chromium salt such as Cr(acetate)₃ was introduced as Lewis acid, a low TON of 99 was obtained, -highlighting the role of the hybrid material in this hydrogenation and not simply of the Cr presence (Table 2, entry 4). MIL-53(Cr) alone or the absence of base led to no reduction of CO₂ (Table 2, entries 5-6). All components are therefore required to deliver the formate in such a high TON. Finally, a decrease of the CO_2 / H₂ pressure led to a lower activity and a TON of 86 (Table 2, entry 7).

Having demonstrated that a combination of a MOF and a cyclopentadienone iron tricarbonyl complex could enhance the catalytic activity, we scrutinized the nature of the metal centre and the organic linker. MIL-53(Fe) and MIL-53(Al) were then evaluated, but both MOFs led only to moderate activities (Table 2, entries 8-9). These results might be due, not to the nature of the metal centre (Cr³⁺, Al³⁺ and Fe³⁺ are all good Lewis acids), but to the stability of the MOF. Indeed, compared to MIL-53(Cr), Huang et al. showed that the MIL-53(AI) was poorly stable in basic aqueous medium at 100 °C.²² Regarding the MIL-53(Fe), the lower activity might also be due to its structural configuration in the reaction conditions. While the pores are completely opened under high CO2 pressure with the MIL-53(Cr), they are partially opened in the MIL-53(Fe). The absorption ability of the latter is then lower under the reaction conditions and this might explain its lack of activity.

Table2. MOF-assisted iron complex for	the hydrogenation of carbon dioxide. ^a
---------------------------------------	---

	Fe1 (0.02 mol %) MOF (0.05 mol %)
+ Dase	DMSO/H ₂ O 100 °C, 20 h

CO2 + H2

HCO₂H.base

Journal Name

Entry	Additive	Base	Yield (%) ^b	TON ^c
1	MIL-53(Cr)	DBU	43.5	2173
2	MIL-53(Cr)	TMG	60.1	3006
3 ^d	MIL-53(Cr)	DBU	38	1900
4	Cr(OAc)₃	TMG	2	99
5 ^e	MIL-53(Cr)	TMG	N.R.	N.R.
6	MIL-53(Cr)	-	N.R.	N.R.
7 ^f	MIL-53(Cr)	TMG	1.7	86
8	MIL-53(Fe)	TMG	12	599
9	MIL-53(AI)	TMG	20.5	1026
10	MIL-100(Cr)	TMG	4.5	224
11	MIL-101(Cr)	TMG	25.3	1265

^a CO₂ (20 bar), H₂ (40 bar), base (5 mmol), MOF (0.05 mol %), **Fe1** (0.02 mol %) and Me₃NO (0.02 mol %) in DMSO/H₂O 1/1 (5 mL) for 20 hours. ^b Yield were determined by ¹H-NMR spectroscopy using DMF as internal standard. ^c Mol of sodium formate per mol of catalyst. ^d MIL-53(Cr) (0.02 mol %). ^e without **Fe1**. ^f CO₂ (10 bar), H₂ (20 bar),

We extended this work to the hydrogenation of sodium bicarbonate and carbonate. TON of 1246 was achieved with the iron complex for the reduction of sodium bicarbonate into formate, while a slight increase to 1525 was obtained in the presence of both iron complex and MIL-53(Cr) (Scheme 1). Moreover, in contrast to CO₂ hydrogenation, the amount of MOF has a little influence on the activity (Scheme 1). When Na₂CO₃ was employed under the same conditions, the conversion was much lower with a TON of 26, but higher than in the sole presence of the iron complex (TON of 17, Scheme 1). This result represents also the highest TON reached with an Earth abundant metal based-complex.¹¹

Fe1 (0.01 mol %) Fe1 (0.2 mol %) H₂ (50 bar) H₂ (50 bar) NaHCO₂ NaO₂CH Na₂CO₃ DMSO/H₂O DMSO/H-O 100 °C, 20 h 100 °C, 2ồ h w/o MIL-53(Cr) TON = 1246 w/o MIL-53(Cr) TON = 17 MIL-53(Cr) (0.05 mol %) TON = 1525 MIL-53(Cr) (0.5 mol %) TON = 26 MIL-53(Cr) (0.01 mol %) TON = 1307 MIL-53(Cr) (0.2 mol %) TON = 14

Scheme 1. Hydrogenation of sodium bicarbonate and sodium carbonate.

Based on these results, the following mechanism might be proposed. After oxidative release of one CO ligand (intermediate I, Scheme 2), coordination and activation of hydrogen would lead to the hydride intermediate II (Scheme 2). In basic conditions, the hydroxyl group on the cyclopentadienyl ancillary ligand would be deprotonated leading to III.^{15b-e} The MIL-53(Cr) might have two roles in this catalytic reduction. It might first uptake CO₂ from the gas phase into the solution and increase the amount of CO₂ in the medium and second activate the CO₂ via the OH groups from the 1D inorganic chains (Scheme 2). After the hydride transfer, the formate would be released as a guanidinium formate regenerating the catalytic species I.



Scheme 2. Proposed mechanism.

In conclusion, we have demonstrated that a simple combination of our cyclopentadienone iron tricarbonyl complex and the Cr dicarboxylate MOF MIL-53(Cr) is able to hydrogenate carbon dioxide in turnover numbers up to 3006. In contrast to previously reported iron complexes, this is the first example of a phosphine free iron complex with such a high activity. This simple combination is competitive with some of the currently reported phosphine-based iron complexes.⁵⁻¹¹ These results are also 10 fold higher than the indirect method previously reported in the presence of Knölker's complex (Fe3),16 highlighting the potential of such combination. Because MOFs can combine a wide range of functionalized organic linkers and metal centre, they offer a broad variety of acidity character, of cationic polarization, of pore size, of surfaces. Their physical and chemical properties can be modulated and adjusted. Further work will then be dedicated first to extend this work to the synthesis/use of various functionalized MOFs and their application in such reduction to draw a structure/activity relationship. Second, our work will focus into the mechanism understanding and the activation of other small molecules.

Conflicts of interest

"There are no conflicts to declare".

We gratefully acknowledge financial support from the "Ministère de la Recherche et des Nouvelles Technologies", Normandie Université, CNRS, Région Normandie, Ademe Agency and the LABEX SynOrg (ANR-11-LABX-0029).

Notes and references

- 1 *Transformation and Utilization of Carbon Dioxide*, ed. B. M. Bhanage and M. Arai, Springer, 2014.
- For some recent selected reviews on CO₂ valorization, see: (a) A. Tlili, X. Frogneux, E. Blondiaux, T. Cantat, *Angew Chem. Int. Ed.* 2014, 53, 2543-2545. (d) A. Goeppert, M. Czaun, J.-P. Jones, G. K. S. Prakash, G. A. Olah, *Chem. Soc. Rev.* 2014, 43, 7995-8048. (e) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* 2018, 118, 434-504. (f) Y. Li, X. Cui, K. Dong, K. Junge, M. Beller, *ACS Catal.* 2017, 7, 1077-1086.

COMMUNICATION

- For some reviews on CO₂ hydrogenation in formic acid, see: (a) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, E. Fujita, *Chem. Rev.* 2015, **115**, 12936-12973. (b) J. Klankermayer, S. Wesselbaum, K. Beydoun, W. Leitner, *Angew. Chem. Int. Ed.* 2016, **55**, 7296-7343. (c) N. Onishi, G. Laurenczy, M. Beller, Y. Himeda, *Coord. Chem. Rev.* 2018, **373**, 317-332. (d) K. Sordakis, C. Tang, L. K. Vogt, H. Junge, P. J. Dyson, M. Beller, G. Laurenczy, *Chem. Rev.* 2018, **118**, 372-433.
- For some selected reviews on CO₂ hydrogenation in methanol, see:
 (a) P. Gao, S. Li, X. Bu, S. Dang, Z. Liu, H. Wang, L. Zhong, M. Qiu, C. Yang, J. Cai, W; Wei, Y. Sun, *Nature Chem*. 2017, **9**, 1019-1024. (b) A. Álvarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* 2017, **117**, 9804-9838. (c) S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez, P. Liu, *Science* 2017, **355**, 1296-1299. (d) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, E. Fujita, *Chem. Rev.* 2015, **115**, 12936-12973.
- [Co]: (a) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, *Chem. Eur. J.* 2012, **18**, 72-75. (b) Y. M. Badiei, W.-H. Wang, J. F. Hull, D. J. Szalda, J. T. Muckerman, Y. Himeda, E. Fujita, *Inorg. Chem.* 2013, **52**, 12576-12586. (c) M. S. Jeletic, M. T. Mock, A. M. Appel, J. C. Linehan, *J. Am. Chem. Soc.* 2013, **135**, 11533-11536. (d) A. Z. Spentzos, C. L. Barnes, W. H. Bernskoetter, *Inorg. Chem.* 2016, **55**, 8225-8233.
- 6 [Mn]: (a) A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi, J. R. Khusnutdinova, *ACS Catal.* 2017, **7**, 3864-3868. (b) F. Bertini, M. Glatz, N. Gorgas, B. Stöger, M. Peruzzini, L. F. Veiros, K. Kirchner, L. Gonsalvi, *Chem. Sci.* 2017, **8**, 5024-5029.
- [Cu]: (a) C. M. Zall, J. C. Linehan, A. M. Appel, J. Am. Chem. Soc. 2016, 138, 9968-9977. (b) C. M. Zall, J. C. Linehan, A. M. Appel, ACS Catal. 2015, 5, 5301-5305.
- [Ni]: (a) S. A. Burgess, A. J. Kendall, D. R. Tyler, J. C. Linehan, A. M. Appel, ACS Catal. 2017, 7, 3089-3096. (b) S. Enthaler, A. Brück, A. Kammer, H. Junge, E. Irran, S. Gülak, ChemCatChem 2015, 7, 65-69. (c)
- 9 (a) W. H. Bernskoetter, N. Hazari, Acc. Chem. Res. 2017, 50, 1049-1058. (b) D. S. Mérel, M.-L. Tran Do, S. Gaillard, P. Dupau, J.-L. Renaud. Coord. Chem. Rev. 2015, 288, 50-68. (c) A. Glüer, S. Schneider, J. Organomet. Chem. 2018, 861, 159-173.
- (a) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem. Int. Ed.* 2010, 49, 9777-9780. (b) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 2012, 134, 20701-20704.
- R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, Y. Ben-David, D. Milstein, Angew. Chem. Int. Ed. 2011, 50, 9948-9952.
- (a) F. Bertini, I. Mellone, A. Ienco, M. Peruzzini, L. Gonsalvi, *ACS Catal.* 2015, **5**, 1254-1265. (b) F. Bertini, N. Gorgas, B. Stöger, M. Peruzzini,
 L. F. Veiros, K. Kirchner, L. Gonsalvi, *ACS Catal.* 2016, **6**, 2889-2893.
- Y. Zhang, A. D. MacIntosh, J. L. Wong, E. A. Bielinski, P. G. Williard, B. Q. Mercado, N. Hazari, W. H. Bernskoetter, *Chem. Sci.* 2015, 6, 4291-4299.
- (a) A. Pagnoux-Ozherelyeva, N. Pannetier, D. M. Mbaye, S. Gaillard, J. L. Renaud, *Angew. Chem. Int. Ed.* 2012, **51**, 4976-4980. (b) S. Moulin,

H. Dentel, A. Pagnoux-Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J.-F. Lohier, J.-L. Renaud, *Chem. Eur. J.* 2013 (19:1788) (2:890) (0) S. Mérel, M. Elie, J.-F. Lohier, S. Gaillard and J.-L. Renaud, *ChemCatChem* 2013, **5**, 2939-2945. (d) D. S. Merel, S. Gaillard, T. R. Ward, J.-L. Renaud, *Catal. Lett.* 2016, **146**, 564-596.

- (a) T.-T. Thai, D. S. Mérel, A. Poater, S. Gaillard, J.-L. Renaud, *Chem. Eur. J.* 2015, **21**, 7066-7070. (b) C. Seck, M. D. Mbaye, S. Coufourier, A. Lator, J.-F. Lohier, A. Poater, T. R. Ward, S. Gaillard, J.-L. Renaud, *ChemCatChem* 2017, **9**, 4410-4416. (c) A. Lator, S. Gaillard, A. Poater, J.-L. Renaud, *Chem. Eur. J.* 2018, **24**, 5770-5774. (d) A. Lator, S. Gaillard, A. Poater, J.-L. Renaud, *Org. Lett.* 2018, **20**, 5985-5990. (e) C. Seck, M. D. Mbaye, S. Gaillard, J.-L. Renaud, *Adv. Synth. Catal.* 2018, **360**, 4640-4645.
- 16 F. Zhu, L. Zhu-Ge, G. Yang, S. Zhou, ChemSusChem 2015, 8, 609-612.
- 17 The hydrogenation reported in reference 16 was, in practice, a two step-one pot reduction.
- (a) G. Maurin, C. Serre, A. Cooper, G. Férey, *Chem. Soc. Rev.* 2017, 46, 3104-3107. (b) W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch, H.-C. Zhou, *Chem. Soc. Rev.* 2014, 43, 5561-5593. (c) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* 2013, 341, 1230444.
- For some reviews, see: (a) Y.-B. Huang, J. Liang, X.-S. Wang, R. Cao *Chem. Soc. Rev.*, 2017, **46**, 126-157. (b) T. L. Easun, F. Moreau, Y. Yan, S. Yang, M. Schröder *Chem. Soc. Rev.*, 2017, **46**, 239-274. (c) S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepulveda-Escribano, A. Vimont, G. Clet, P. Bazin, F Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck, J. Gascon, *Chem. Soc. Rev.* 2017, **46**, 3134-3184. (d) Y. Cui, B. Li, H. He, W. Zhou, B. Chen, G. Qian, *Acc. Chem. Res.* 2016, **49**, 483-493. (e) T. Simon-Yarza, A. Mielcarek, P. Couvreur, C. Serre, *Adv. Mater.*, 2018, **30**, 1707365.
- (a) N. S. Bobbitt, M. L. Mendonca, A. J. Howarth, T. Islamoglu, J. T. Hupp, O. K. Farha, R. Q. Snurr, *Chem. Soc. Rev.*, 2017, 46, 3357-3385.
 (b) C. A. Trickett, A. Helal, B. A. Al-Maythalony, Z. H. Yamani, K. E. Cordova, O. M. Yaghi, *Nature Reviews Materials* 2017, 2, 17045-17061.
 (c) J. Qian, Q. Li, L. Liang, T. Li, Y. Hu, S. Huang, *Dalton Trans.* 2017, 46, 14102-14106.
 (d) Z. J. Zhang, Z. Z. Yao, S. C. Xiang, B. L. Chen, *Energy Environ. Sci.* 2014, 7, 2868-2899.
 (e) C. Serre, S. Bourrelly, A. Vimont, N. Ramsahye, G. Maurin, P.L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, *Adv. Mater.*, 2007, 19, 2246-2251.
 (f) P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. K. Hwang, S. H. Jhung, G. Férey, *Langmuir* 2008, 24, 7245-7250.
 (g) C. Serre, F. Millange, C. Thouvenot, M. Nogues, G. Marsolier, D. Loüer, G. Férey *J. Am. Chem. Soc.*, 2002, 124, 13519-13526.
- (a) Y. Chen, D. Wang, X. Deng, Z. Li *Catal. Sci. Technol.* 2017, 7, 4893-4904 and references cited therein. (b) J. L. Wang, C. Wang, W. B. Lin, *ACS Catal.* 2012, 2, 2630-2640. (c) Y. B. Huang, J. Liang, X. S. Wang, R. Cao, *Chem. Soc. Rev.* 2017, 46, 126-157.
- 22 X. Qian, B. Yadian, R. Wu, Y. Long, K. Zhou, B. Zhu, Y. Huang, Int. J. Hydrog. Energy 2013, 38, 16710-16715.

Page 4 of 5

0

MIL-53(Cr)



Iron complex

TONs up to 3000

View Article Online DOI: 10.1039/C8CC09771B

A catalytic combination of a phosphine-free iron complex and a MOF allowed the hydrogenation of carbonic derivatives into formate with TON up to 3000.