Homogeneous Catalysis

DOI: 10.1002/anie.201000533

State-of-the-Art Catalysts for Hydrogenation of Carbon Dioxide

*Christopher Federsel, Ralf Jackstell, and Matthias Beller**

atmospheric chemistry · carbon dioxide fixation ·
homogeneous catalysis · hydrogenation · reduction

With around 300 billion tons, carbon dioxide gas (CO_2) is the most abundant carbon source of the Earth's atmosphere. It has been present throughout most of geological time and is a natural, fluctuating constituent.[1] It constitutes the primary carbon feedstock for the production of biomass, and thus life on earth. However, since the industrial revolution the concentration of CO_2 has risen significantly from around 280 to more than 380 parts per million in 2009 (Figure 1).[2]

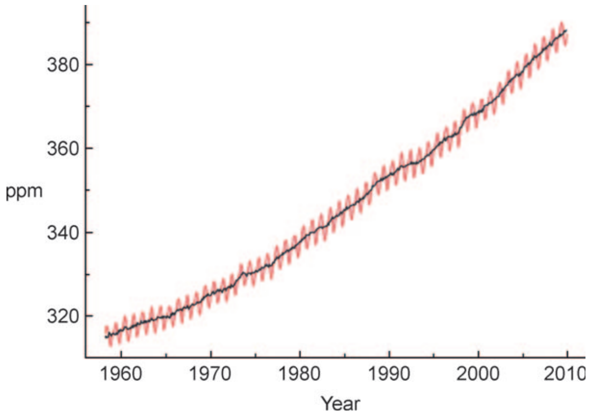


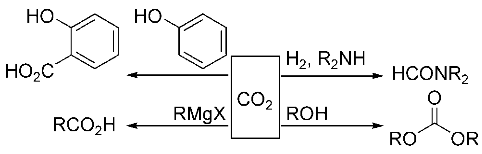
Figure 1. Trends in atmospheric CO_2 in the last 50 years. Atmospheric CO_2 at Mauna Lao observatory, Scripps Institution of Oceanography NOAA Earth System Research Laboratory (January 2010).

Most of this increase is attributed to the burning of carbon-rich fossil fuels—coal, natural gas, and oil—, which currently represent 80–85 % of the world's energy sources. There is no doubt that these still relatively inexpensive energy carriers will continue to play a major role at least in the next decades. Hence, a further steady increase of CO_2 concentration by 50–100 % is envisaged by the year 2030.[3]

The increased concentration of CO_2 contributes to increased trapping of heat radiating from the Earth's surface, which leads in turn to the so called greenhouse effect. Despite numerous debates it is widely accepted that this is the main reason for global warming and will result in climate changes. Hence, there is major political and scientific interest in preventing CO_2 formation and lowering its concentration in the atmosphere.[4] The obvious solution for this problem is to increase the efficiency of known energy technologies and convert as fast as possible to energy sources that do not generate CO_2, for example, solar and wind power. Unfortunately, switching to alternative energy sources will be a gradual process. Hence, all kinds of new technologies are needed that allow for commercially viable sustainable energy technologies, such as improving the efficient removal and use of CO_2 from today's fossil-fueled industries, and replacing oil and coal by less carbon-intensive natural gas. In this respect chemistry (in general) and catalysis (in particular) constitute key technologies to achieve these goals. However, it is obvious that utilization of CO_2 to generate chemical products can not solve the greenhouse effect. At present more than 110 million tons of CO_2 are used to produce chemicals. This corresponds to only 1 % of the net annual anthropogenic release (13 000 million tons) of CO_2 to the atmosphere. Even so, the increased exploitation of CO_2 as starting material in the chemical industry is desirable, because it is an abundant, cheap, and nontoxic C_1 source.

At the moment, the toxic carbon monoxide (CO) is the main competing feedstock to CO_2 in many industrial processes. In general, CO_2 is less reactive than CO and a larger energy input is needed when using CO_2 as raw material.[5] Nevertheless, in industry around 105 million tons of CO_2 are used for the production of urea. In addition, salicylic acid (90 000 tons), cyclic carbonates (80 000 tons), and polypropylenecarbonate (70 000 tons) are produced on industrial scale and a number of academic examples applying CO_2 in organic synthesis are known (Scheme 1).[1,6]

Taking thermodynamics into account carbonates, urethanes, and urea are the most attractive products from CO_2

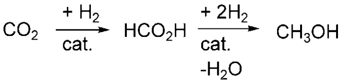


Scheme 1. Representative examples of utilization of CO_2 in organic synthesis.

---

[*] C. Federsel, Dr. R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock (LIKAT)
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de
Homepage: http://www.catalysis.de

because no additional reduction step is needed. However, formates and especially methanol represent interesting chemical product options when the required hydrogen or reduction equivalents are generated from renewable energy, e.g. hydrogen from electrolysis of water powered by photovoltaics or wind energy (Scheme 2).



$$CO_2 \xrightarrow[\text{cat.}]{+ H_2} HCO_2H \xrightarrow[\text{cat.}\ -H_2O]{+ 2H_2} CH_3OH$$

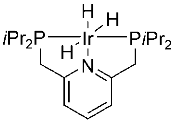
Scheme 2. Hydrogenation of CO_2 to formic acid and methanol.

In the last decades excellent reviews by Jessop and Leitner have summarized the field of homogeneously catalyzed hydrogenation of CO_2.[7] Advances that have been made since then include: the discovery of new highly active catalysts for the production of formic acid and formates, the direct reduction of CO_2 with silanes to methanol at ambient conditions,[8] and the development of the concept to use CO_2 as hydrogen storage material by combining CO_2 hydrogenation with selective formic acid decomposition.[9]

In this Highlight we point out the recent achievements by Nozaki and co-workers for the reduction of CO_2 in the presence of iridium catalysts.[10] Since the beginning of the 90s there has been an increasing interest in catalytic hydrogenations of CO_2 towards formic acid, alkyl formates, and formic acid amides. Hence, improvements with respect to catalyst productivity and activity have been continuously accomplished. Compared to heterogeneously catalyzed reductions of CO_2,[11] hydrogenation towards formic acid derivatives in the presence of organometallic complexes proceeds at comparably low temperature (<100 °C) and sometimes low pressure.

As shown in Table 1, to date high turnover numbers (TON) have been achieved in the hydrogenation of CO_2 using transition-metal catalysts based on rhodium,[12–15] ruthenium,[16–18] and iridium.[19,20]

In 1992 Graf and Leitner already reported a benchmark TON up to 3400 by using various Rh–phosphine complexes as catalysts at room temperature with low H_2/CO_2 pressure.[13,14] Shortly afterwards, further improvement was disclosed by Noyori and co-workers who used Ru^{II} catalysts in supercritical CO_2 ($scCO_2$) and obtained a TON of 7200.[16,17] The increased catalyst efficiency was believed to be a result of the higher miscibility of H_2 in $scCO_2$ compared with other previously used solvents. Later on, Jessop and co-workers achieved TON values of up to 28500 and turnover frequencies (TOF) of up to 95000 h^{-1} by using $[RuCl_2(OAc)(PMe_3)_4]$, which is highly soluble in $scCO_2$.[18] The next milestone was disclosed in 2007, when Himeda et al. reported excellent catalyst productivity (TON = 222000) for the formation of formic acid in the presence of a cationic $[Ir^{III}Cp^*]$ catalyst with phenanthroline derivates as ligands.[19] Most recently, a significant breakthrough in catalyst efficiency for hydrogenation of CO_2 was achieved by Nozaki and co-workers.[10] As active catalyst they used a defined iridium–pincer trihydride complex $[Ir^{III}PNP]$ **1** containing two diisopropylphosphino substituents (Scheme 3). Excellent TON values of 3500000 and TOF values of 150000 h^{-1} were obtained in aqueous KOH generating potassium formate (HCOOK).



1

Scheme 3. Highly active Ir^{III}-pincer complex **1** in hydrogenation of CO_2.

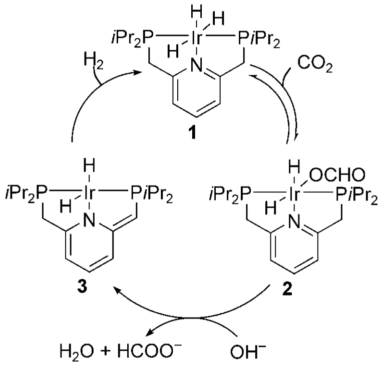
This catalyst efficiency opens up new possibilities for the industrial production of formic acid and related formates. Formic acid itself is an important chemical preservative for winter feed for cattle and an antibacterial product in the poultry industry.[20] In addition, it is used for the production of solvents and synthetic building blocks. So far, the annual production (>500000 ton-scale) is based on base-catalyzed reaction of carbon monoxide with methanol and subsequent hydrolysis. Comparing the hydrogenation of CO_2 with this established route it is clear that hydrogen is the cost-determining factor in the latter process. Depending on the future pricing of CO_2, the hydrogenation of CO_2 might become an economically viable route. From an environmental point of view the required hydrogen should be produced without concomitant formation of CO_2.[21]

In Scheme 4 the proposed catalytic cycle for the hydrogenation of CO_2 using the iridium–trihydride complex **1** is shown. The resulting formate complex **2** is believed to react with hydroxide to give the amidoiridium dihydride species **3**, which has been independently prepared by addition of $CsOH{\cdot}H_2O$ to the corresponding chloroiridium dihydride complex. Notably, **3** converts into **1** in the presence of molecular hydrogen, thus closing the catalytic cycle.

The rationale behind the improved catalytic behavior of this type of pincer complex is the formation of strong

Table 1: Catalytic hydrogenation of CO_2 to formic acid.

Catalyst precursor	Solvent	Additives	p_{H_2/CO_2} [bar]	T [°C]	t [h]	TON	TOF [h^{-1}]	Ref.
$[RhCl(PPh_3)_3]$	MeOH	$PPh_3 + NEt_3$	20/40	25	20	2700	125	[12]
$[\{RhCl(cod)\}_2]$	DMSO	NEt_3 + dppb	20/20	RT	22	1150	52	[13]
$[RhCl(tppts)_3]$	H_2O	$NHMe_2$	20/20	RT	12	3439	287	[14]
[(dcpb)Rh(acac)]	DMSO	NEt_3	20/20	RT	0.2	267	1335	[15]
$[RuCl_2\{P(CH_3)_3\}_4]$	$scCO_2$	NEt_3 + dppb	85/120	50	47	7200	150	[16]
$[RuH_2\{P(CH_3)_3\}_4]$	$scCO_2$	CH_3OH	80/120	50	0.5	2000	4000	[17]
$[RuCl_2(OAc)(PMe_3)_4]$	$scCO_2$	NEt_3, C_6F_5OH	70/120	50	0.3	28500	95000	[18]
[Cp*Ir(phen)Cl]Cl	H_2O	KOH	30/30	120	48	222000	33000	[19]
$[Ir^{III}PNP]$	H_2O	KOH	30/30	120	48	3500000	73000	[10]



Scheme 4. Proposed mechanism for the hydrogenation of CO_2 to formic acid.[10]

coordination between the metal and the tridentate ligand, thus preventing the latter from being easily removed from the metal center and the interesting redox chemistry of the ligand, which has also been observed in other catalytic reactions.[22]

What are the remaining challenges for the hydrogenation of CO_2? Obviously, using a modular approach it is feasible to optimize Nozaki's state-of-the-art pincer complexes further.[23] However, more crucial for practical applications will be efficient catalysis with industrially available feedstocks enriched with CO_2, for example, CO_2 streams directly from power plants or large industrial plants. However, it should be noted that the availability and use of inexpensive "green" hydrogen[24] or alternative reduction equivalents is a prerequisite for such large-scale applications.

In addition, for the future it might be also important to investigate more closely the efficient hydrogenation of carbonates (CO_3^{2-}) or bicarbonates (HCO_3^-)[25] because of their easy availability and handling. From a scientific standpoint, efficient catalysis with inexpensive biorelevant metals such as iron complexes constitutes an interesting academic challenge. Finally, the development of more energy efficient reduction processes of CO_2, or more likely of CO_2-enriched synthesis gas mixtures (CO/H_2), to methanol at lower temperature or with the aid of visible light is of major importance to industrial and society. We are convinced that organometallic catalysis will contribute further on to develop solutions for these vital questions.

Received: January 29, 2010

---

[1] For general reviews on CO_2, see: a) *Carbon Dioxide as Chemical Feedstock* (Ed.: M. Aresta), Wiley-VCH, Weinheim, **2010**; b) M. Maroto-Valer, *Carbon Dioxide Capture and Storage*, Woodhead Publishing Limited, Abington Hall, Granta Park, Cambridge, **2009**; c) G. Centi, S. Perathoner, *Catal. Today* **2009**, *148*, 191–205; d) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063–2095; e) *Carbon Dioxide as a Source of Carbon* (Eds.: M. Aresta, G. Forti), Kluwer, Dordrecht, **1987**, ; f) A. Behr, *Carbon Dioxide Activation by Metal Complexes*, Wiley-VCH, Weinheim, **1988**.
[2] P. Tans, NOAA/ESRL (www.esrl.noaa.gov/gmd/ccgg/trends).
[3] Department of Energy (US), International Energy Agency Report, 0484, **2008**.
[4] a) J. Tollefson, *Nature* **2009**, DOI: 10.1038/news.2009.1125; b) J. Tollefson, *Nature* **2009**, DOI: 10.1038/news.2009.1156; c) J. Tollefson, *Nature* **2009**, *462*, 966–967.
[5] T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387.
[6] Carbon Dioxide Recovery and Utilization (A summary report of the EU Project BRITE-EURAM 1998 BBRT-CT98–5089) (Ed.: M. Aresta), **2003**, p. 407.
[7] a) P. G. Jessop in *Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 489–511; b) P. G. Jessop, F. Joó, C.-C. Tai, *Coord. Chem. Rev.* **2004**, *248*, 2425–2442; c) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1995**, *95*, 259–272; d) W. Leitner, *Angew. Chem.* **1995**, *107*, 2391–2405; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207–2221.
[8] S. N. Riduan, Y. Zhang, J. Y. Ying, *Angew. Chem.* **2009**, *121*, 3372–3375; *Angew. Chem. Int. Ed.* **2009**, *48*, 3322–3325.
[9] For reviews, see: a) C. T. Johnson, M. Morris, M. Wills, *Chem. Soc. Rev.* **2010**, *39*, 81–88; b) S. Enthaler, *ChemSusChem* **2008**, *1*, 801–804; c) F. Joó, *ChemSusChem* **2008**, *1*, 805–808; for selected recent examples, see: d) B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026–4029; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962–3965; e) C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem.* **2008**, *120*, 4030–4032; *Angew. Chem. Int. Ed.* **2008**, *47*, 3966–3968; f) S. Fukuzumi, T. Kobayashi, T. Suenobu, *ChemSusChem* **2008**, *1*, 827–834; g) A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751–758; h) H. Junge, A. Boddien, F. Capitta, B. Loges, J. R. Noyes, S. Gladiali, M. Beller, *Tetrahedron Lett.* **2009**, *50*, 1603–1606; i) C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, *Chem. Eur. J.* **2009**, *15*, 3752–3760; j) R. Williams, R. S. Crandall, A. Bloom, *Appl. Phys. Lett.* **1978**, *33*, 381–383; k) M. Halmann, M. Ulman, B. Aurian-Blajeni, *Solar Energy* **1983**, *31*, 429–431; l) B. Zaidman, H. Wiener, Y. Sasson, *Int. J. Hydrogen Energy* **1986**, *11*, 341–347.
[10] R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169.
[11] For selected examples of heterogeneously catalyzed reductions of CO_2, see: a) A. Kruse, H. Vogel, *Chem. Eng. Technol.* **2008**, *31*, 23–32; b) U. Kestel, G. Fröhlich, D. Borgmann, G. Wedler, *Chem. Eng. Technol.* **1994**, *17*, 390–396; c) A. Baiker, *Appl. Organomet. Chem.* **2000**, *14*, 751–762; d) H. Sakurai, M. Haruta, *Appl. Catal. A* **1995**, *127*, 93–105.
[12] N. N. Ezhova, N. V. Kolesnichenko, A. V. Bulygin, E. V. Slivinskii, S. Han, *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 2165–2169.
[13] E. Graf, W. Leitner, *J. Chem. Soc. Chem. Commun.* **1992**, 623–624.
[14] F. Gassner, W. Leitner, *J. Chem. Soc. Chem. Commun.* **1993**, 1465–1466.
[15] K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, *Chem. Eur. J.* **1997**, *3*, 755–764.
[16] P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **1994**, *368*, 231–233.
[17] a) P. G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 344–355; for more recent work on Ru catalysts, see: b) A. Urakawa, F. Jutz, G. Laurenczy, A. Baiker, *Chem. Eur. J.* **2007**, *13*, 3886–3899.
[18] P. Munshi, A. D. Main, J. C. Linehan, C. C. Tai, P. G. Jessop, *J. Am. Chem. Soc.* **2002**, *124*, 7963–7971.
[19] Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, *Organometallics* **2007**, *26*, 702–712.
[20] W. Reutemann, H. Kieczka "Formic Acid" in *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed., Wiley-VCH, Weinheim, **2009**.
[21] Currently, 4% of the industrially produced hydrogen comes from electrolysis of water. Combining this electrolysis with renewable energy allows for the production of so-called "green

hydrogen". Other hydrogen productions such as coal gasification and steam reforming produce hydrogen and carbon dioxide.

[22] a) S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74–77; b) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841; c) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792; d) E. Ben-Ari, G. Leitus, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 15390–15391; e) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; f) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, *131*, 3146–3147.

[23] For reviews on pincer complexes, see: a) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; b) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; c) *The Chemistry of Pincer Compounds* (Eds.: D. Morales-Morales, C. M. Jensen), Elsevier, Amsterdam, **2007**.

[24] "Green hydrogen" is here defined as hydrogen, which is produced without concomitant production of carbon dioxide.

[25] J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó, *Appl.Catal. A* **2003**, *255*, 59–67.