

CO₂ Hydroboration

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The use of CO₂ as C1 building block for chemical synthesis is receiving growing attention, due to the potential of this simple molecule as abundant and cheap renewable feedstock. Among the possible reductants used in the literature to bring about CO₂ reduction to C1 derivatives, hydroboranes have found various applications, in the presence of suitable homogenous catalysts. The main results obtained since 2016 in the synthetic design of main group, first and second row transition metals for use as catalysts for CO₂ hydroboration are summarized.

carbon dioxide conversion

hydroboration

metal complexes

selectivity

1. Introduction

In recent years, the accumulation of greenhouse gases in the atmosphere has steadily increased due to human activity ^[1]. The combustion of fossil fuels for the production of energy is the largest source of greenhouse gas emissions ^[2]. CO₂ is a by-product of fuel combustion, representing the most abundant greenhouse gas (81.3%) of the global anthropogenic emissions (Figure 1). A significant increase of CO₂ in the atmosphere is expected in view of growing demand for energy ^[3]. These reasons, combined with the need for sustainable, fossil-free routes to chemicals and fuels, fostered a new impetus in the use of CO₂ as a C1 building block for chemical synthesis ^[1].

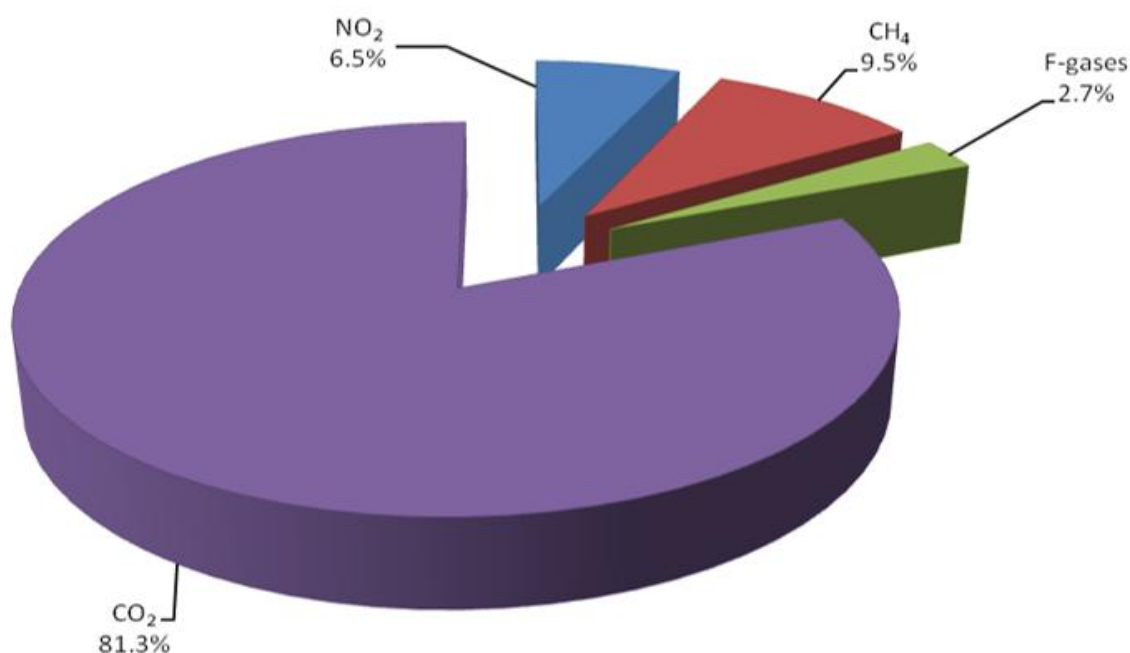


Figure 1. Global greenhouse gas emission per type of gas in 2018 [1].

Carbon dioxide can be used to make added value products, by reactions such as copolymerization [4], hydrogenation [5][6], biochemical approaches [7], and electrochemical reduction [7][8]. Recently, there has been an increase in interest in the homogeneous reduction of CO₂ using hydrogen [9][10][11], hydrosilanes [12][13][14][15] and hydroborates [16][17]. Reductive approaches allow to obtain simple C1 molecules such as formic acid (HCO₂H), formaldehyde (HCHO), methanol (CH₃OH), dimethyl ether (CH₃OCH₃), methane (CH₄) or higher hydrocarbons, that find many applications in chemistry, manufacturing and industry [18][19][20][21][22][23]. CO₂ hydrogenation (i.e., reduction under a pressure of hydrogen gas) is, in principle, the most atom-efficient method, but has safety risks connected with the use of flammable, pressurized gas. Alternative reductants such as hydrosilanes and hydroboranes have been successfully applied to replace H₂, as they are liquid at room temperature, hence easier and safer to handle and store. They can bring about CO₂ reduction to different products under mild reaction conditions, due to the fact that E–H bonds (E = Si, B) are weaker than the H–H bond, and that the formation of stronger E–O bonds constitutes a driving force for the reaction. It has been demonstrated that CO₂ can be reduced by a hydroborane (Scheme 1) to give formoxyborane (A), bis(boryl)acetal (B), methoxyborane (C) and bis(boryl)ether (D), and that the choice of appropriate homogeneous catalysts can drive the selectivity of the process to the desired products, further than promoting the overall reaction rate [16]. Although precious transition metals play a dominant role as catalysts for CO₂ reduction, various studies demonstrated the possible use of earth-abundant metals and p-block elements [24][25]. An excellent, comprehensive review on this chemistry was published by Bontemps in 2016 [16].

**Scheme 1.** General reaction and product distribution for CO₂ hydroboration.

2. Main Group Metal Catalysts for CO₂ Hydroboration

Main group metal (Li, Na, K, Mg) and non-metal (Si) compounds and adducts showed a modest degree of activity for CO₂ hydroboration, using hydroboranes such as pinacolborane (HBpin), catecholborane (HBcat) and 9-BBN, under mild reaction conditions. Whereas alkali metals did not play a role in either borane or CO₂ activation, the role of the Mg(II) centers in the activation mechanism likely depended on the nature of the complex, and in some cases, borane activation seems to take place first. On the other hand, Si(II)-NHC hydrido adducts were proposed to activate preferentially CO₂, which then reacts with HBpin in an outer-sphere fashion, to give formoxyborane as product. The process selectivity varied from formoxy- to methoxyborane products, and the latter are generally obtained at higher temperature (90–100 °C, Table 1).

3. First-row transition metal catalysts for CO₂ hydroboration

Different first-row transition metal (Mn, Fe, Co, Ni, Cu, Zn) complexes showed to be competent catalysts for CO₂ hydroboration at different reductions levels. A wide variety of stabilizing ligands, ranging from simple bidentate bis(phosphines) such as dmpe, to tripodal triphos-type phosphine and phosphinite ligands forcing facial coordination to metal, to PNP, PCP, POCOP pincer-type, meridional ligands were applied, together with ancillary ligand-free catalytic protocols, as in the case of Co(acac)₃ [26]. Moderate to very good conversions, yields, TONs and TOFs were obtained in the different cases, with remarkable selectivities to multi-electron reductions up to the methoxy level [27][28] and to the challenging acetal level [29][30]. Although not all studies have reported mechanistic details, the presence of metal-hydrido bonds in the active catalysts were often invoked to explain three-step reduction pathways, starting with insertion of CO₂ into the M-H bond. The major effects in driving the selectivity of the process to a specific product were demonstrated to be more due to the steric and electronic properties of the hydroborane and to the choice of temperature and solvent rather than on the nature of the catalyst.

4. Second-row transition metal catalysts for CO₂ hydroboration

The recent contributions describing second-row transition metal (Ru, Pd, Ir) catalyzed CO₂ hydroboration are focused mainly on the application of pincer-type complexes. Mechanistic details were achieved in various cases, showing for example [31] that it is possible to drive the process selectivity by tuning the reaction conditions, such as solvent, temperature and use of additives, to bring about selectivity switch from 2-electrons to 6-electrons reduction of CO₂.

5. Conclusions

In conclusion, remarkable results have been described in the period 2016-2020 both with first-row and second-row transition metals, in particular Mn, Fe, Ni and Pd, setting a new state-of-the-art for the conversion of CO₂ to added value products such as HCOOH, HCHO and MeOH by hydroboration processes. The advantage of such an approach was confirmed as the possibility to use very mild conditions of temperature (in general favoring 2-electrons reduction), small amounts of catalysts and different hydroboranes. Under this point of view, the recent studies confirmed that the less sterically hindered HBcat favors in general 6-electron reduction to methoxyboranes. Noteworthy, recent results showed that also the challenging 4-electrons reduction to bis(boryl)acetals can be achieved with high selectivity. In our view, this can be considered as one of the most likely targets for future research in the field of CO₂ hydroboration, due to the possible synthetic applications of such molecules as efficient methylene transfer reagents in organic synthesis.

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