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Iron Catalyzed Hydrogenation and Electrochemical Reduction of CO_2: The Role of Functional Ligands

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Dedicated to Prof. Dr. Dr. h.c. mult. W. A. Herrmann on the occasion of his 70th birthday

Abstract

The reduction of CO_2 is an attractive route to utilize the green-house gas as a C_1 building block. In recent years, the scientific progress that could be obtained for CO_2 hydrogenation to formate and electrochemical reduction mainly to CO was strongly driven by the development of molecular iron catalysts with high activities and selectivities. However, these advances are also associated with the utilization of functional ligands that facilitate, e.g. H_2 heterolysis in thermal hydrogenation or the storage of redox-equivalents in electrochemical transformations. In this review the use of such cooperating and redox non-innocent ligands in iron catalyzed CO_2 transformations is discussed with the aim at providing some guidelines for catalyst design and improvement.

Keywords: carbon dioxide, iron, catalysis, hydrogenation, electrochemistry, functional ligands

1 Introduction

Chemical industry, which heavily relies on carbon sources like methane and ethylene, needs a new, post-fossil energy and feedstock basis.[1] CO_2 is an attractive C_1 building block for chemical synthesis, due to its abundance and low cost. The free enthalpy of formation ($\Delta_f G^0$ = -394.38 kJ/mol) indicates high thermochemical stability of CO_2.[2] But the formation of strong O–H and C–H bonds can counterbalance the enthalpic cost of reduction, making several products from CO_2 hydrogenation thermochemically accessible (Table 1). The C–O bond polarity generally renders CO_2 kinetically susceptible to *C*-centered nucleophilic attack. In fact, chemical transformations (without reduction) using strong *N*- and *O*-nucleophiles, such as the formation of urea or co-polymerization with epoxides to (poly)carbonates,[3–11] are industrially well established. However, the nucleophilic activation of CO_2 requires considerable structural rearrangement due to bending of the linear molecule. Hence, CO_2