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A Breakthrough in Sustainable Production of Formate Salts: Combined Catalytic Methanol Dehydrogenation and Bicarbonate Hydrogenation

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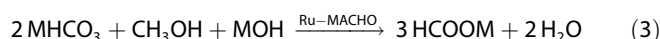
Large-scale catalytic transformation of carbon dioxide to useful products is the focus of intensive research for several important reasons. Carbon dioxide is a building block for polymers and fine chemicals.^[1] Similarly, it is the starting material or an intermediate in industrial synthesis of methanol, which is one of the most versatile platform chemicals. Whether the industrial consumption of carbon dioxide can contribute to the mitigation of the greenhouse effect to a reasonable extent remains to be seen, however, environmental considerations do also drive research on carbon dioxide utilization. Since the seminal work of Beller^[2] and Laurenczy^[3] on homogeneous catalytic decomposition of formic acid to carbon monoxide-free hydrogen, research into the practical use of formic acid for reversible hydrogen storage has greatly accelerated and brought new breakthroughs both in hydrogenation of carbon dioxide^[4] and dehydrogenation of formic acid and formates.^[5] In addition to hydrogen, silanes^[6] and alcohols such as methanol^[7] and 2-propanol^[8] have also been used for reduction of carbon dioxide. Catalysts applicable to the generation of hydrogen from alcohols, an example of which is shown in Equation (1), or from components of biomass^[9] have also been studied and several highly active catalysts discovered. An interesting example is hydrogen generation from aqueous formaldehyde by $[\{\text{RuCl}_2(p\text{-cymene})_2\}_2]$ [Eq. (2)].^[10]



In some cases, hydrogen generation was coupled to a reductive transformation, such as the alkoxy-carbonylation of alkenes.^[11]

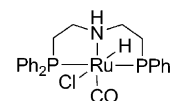
Beller and co-workers have brought a new idea onto the scene that could dramatically change the production of formate salts.^[12] Formates have many large-scale applications. For example, sodium formate is used in drilling fluids and potassium formate applied as a deicing agent. At present, industrial production of sodium formate is based on the reaction of toxic

and flammable carbon monoxide with dry sodium hydroxide at 160 °C. Beller et al. found that in the presence of a suitable ruthenium(II) pincer catalyst and alkali, reaction of bicarbonates with methanol leads to formates and water [Eq. (3)].



in which $\text{M} = \text{Na}$ or K and $\text{Ru-MACHO} = [\text{RuHCl}(\text{CO})(\text{HN}(\text{C}_2\text{H}_4\text{PPh}_2)_2)]$.

Of the several catalysts screened, the ruthenium–MACHO complex was found most effective (its structure is shown in Scheme 1) and potassium bicarbonate was more reactive than sodium bicarbonate. The rate of the reaction was a sensitive function of temperature and the best results were obtained at 130–150 °C. Under optimized conditions in $\text{MeOH}/\text{H}_2\text{O}$ 25:5 (v/v), 92% conversion of potassium bicarbonate to potassium formate was achieved in 20 h, which corresponded to a turnover number of 18422. In the first 4 h of the reaction, the average turnover frequency was 1346 h^{-1} . Other ruthenium(II) pincer complexes showed lower catalytic activity, whereas the phosphine complexes $[\{\text{RuCl}_2(\text{benzene})_2\}_2]/1,1\text{-bis}(\text{diphenylphosphino})\text{methane}$ and $[\text{RuH}(\text{OAc})(\text{PPh}_3)_3]$ did not catalyze the reaction.



Scheme 1. Ruthenium–MACHO, the most active catalyst for bicarbonate reduction with methanol.

Notably, the reaction rate largely depends on the pH of the reaction mixture and, while formates can also be obtained directly from carbon dioxide, high pressures of carbon dioxide (leading to low concentration of free potassium hydroxide) completely stop the reaction (a similar effect is observed at low $[\text{KOH}]/[\text{KHCO}_3]$ ratios). A remarkable feature of the ruthenium–MACHO catalyst is its high activity in dehydrogenation of methanol in the absence of bicarbonate; in the presence of sodium hydroxide or potassium hydroxide the reaction yields the corresponding formate salts.^[7b] For example, in 20 h at 150 °C a large amount (20 mmol) of potassium hydroxide was converted to potassium formate in 68% yield (turnover number 10882) with no added potassium bicarbonate as hydrogen acceptor.

The observed effects of reaction parameters allow some conclusions on the reaction mechanism. During the reactions, considerable hydrogen pressure ($> 3 \text{ MPa}$) develops in the re-

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actor. This is not surprising, as the catalyst is highly active in dehydrogenation of methanol. Although the reaction of potassium formate and potassium hydroxide is known to create potassium carbonate and hydrogen, no carbonates are detected in these systems, that is, the reactions are completely selective to the production of formates. These two observations suggest that presence of hydrogen in the reactor suppresses carbonate formation and leads to high selectivity towards formate. Hydrogenation of bicarbonates to formates is well known^[13] (as is the hydrogenation of carbon dioxide in strongly alkaline solutions)^[4b,5b] and can easily proceed in this case, too, at the expense of hydrogen from methanol decomposition. However, from the available data the possibility of direct hydrogen transfer to bicarbonate cannot be excluded.

The reaction has several advantageous features. Methanol can be obtained from renewable sources such as biomass, or from hydrogenation of carbon dioxide from concentrated point sources. Handling of bicarbonates and aqueous methanol poses less hazards than work with high pressure carbon monoxide at high temperature. In many cases, the final conversions of direct hydrogenations of bicarbonate to formate do not approach 100% owing to the catalysts' ability to decompose formate even under relatively high hydrogen pressures. In contrast, over 90% conversions were obtained in most cases of the present work and no carbonates were detected in the final reaction mixtures. In addition to formate, the reaction generated hydrogen, which in principle can be utilized, for example in fuel cells.

Some critical remarks are also appropriate. As in similar processes, the price and stability of the catalyst can be prohibitive here. In general, pincer complexes are durable catalysts and Beller and co-workers have already achieved outstanding results in application of complexes of non-noble metals (such as cobalt^[4d] and iron^[4e]) in catalysis of carbon dioxide and bicarbonate hydrogenation. In the procedure described in the paper, the final reaction mixture in MeOH/H₂O/KOH was evaporated to dryness and the formate composition and absence of carbonate were determined by NMR spectroscopy. Purification of the product from the catalyst and recovery, reuse, and regeneration of the latter should be also solved. Furthermore, the catalytic decomposition of methanol and/or the use of the generated hydrogen also needs attention to avoid considerable loss of an important reagent. Nevertheless, these are problems which can be handled with a reasonable chance of success. Finally, it may deserve some interest, that a clean, non-catalytic, hydrothermal reduction of sodium bicarbonate with glycerol has also been reported, albeit under much harsher conditions (260–300 °C).^[14]

Altogether, this new process for manufacturing formate salts offers a greener alternative to the existing procedures. In addition, and perhaps more importantly, it leads to new ideas on the use of multistep reactions and their fine tuning.^[12] Notably, several solid (mainly palladium-based) catalysts have been found active in reactions that are or may be involved in the production of potassium formate from methanol, potassium bicarbonate, and potassium hydroxide, such as the decomposition of aqueous methanol to hydrogen and carbon dioxide

(through intermediate formation of formic acid),^[15] hydrogenation of aqueous bicarbonate to formate,^[16] and decomposition of formic acid and aqueous formate.^[17] This may lead to construction of similar systems based on heterogeneous catalysis.

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