Lithium-promoted hydrogenation of carbon dioxide to formates by heterobimetallic hydridozinc alkoxide clusters†

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The remarkably distinct reactivity of hydridozinc heterobimetallic cubanes [$(HZnO^tBu)_{4-n}(thf\cdot LiO^tBu)_n$] 1a–1d towards CO_2 is reported—the hydride transfer from Zn–H to CO_2 is drastically accelerated in the presence of Li ions in 1b–1d which led to the respective metal formate hydrates; the systems are inspiring models for the selective conversion of water gas into formates on lithium-promoted ZnO supports.

Carbon dioxide (CO_2) is an abundant yet low-value carbon source of enormous impact in Nature. However, the extraordinarily high stability of CO_2 has hampered its utilization as efficient C_1-building block for large-scale industrial syntheses of useful organic compounds. Thus, current efforts in developing efficient catalytic processes that exploit CO_2 as a source for valuable organic products belong to one of the most ambiguous challenges in industrial chemistry.[1] Of particular interest is the reductive transformation of CO_2 in the presence of H_2 into renewable sources such as methanol (MeOH).[2] The world demand for MeOH is currently enormously increasing because of its role as a precursor for many useful organic chemicals (*e.g.*, formaldehyde, acetic acid) and as a substitute for fuels.[3] This can only be managed by an efficient large-scale industrial process. In fact, MeOH synthesis is very efficiently achieved by the heterogeneously catalyzed conversion of syngas (CO, H_2) and water gas (CO_2, H_2), respectively, on heterometal-promoted ZnO carriers. Accordingly, the most commonly commercialized unit for the production of MeOH is the low-temperature ICI process, which converts a high-pressure gas mixture of CO, CO_2 and H_2 into MeOH at 250–300 °C, using Cu-promoted ZnO which is dispersed on alumina.[4] As expected, the mechanisms of the heterogeneously catalyzed reduction of carbon oxides depends sensitively on the nature of the support material (*i.e.*, composition, particle size, structure, defects) and the presence of promoters (*e.g.*, Cu). Notably, also Cu-free pure ZnO model systems show considerable catalytic activities in methanol synthesis under particular circumstances. The catalytic activity of pure ZnO supports does not increase linearly with increasing BET surface area but requires the presence of polar ZnO facets[5] and oxygen-vacancies as particularly important active sites.[6] Recently, it has also been shown that the catalytic activity of pure ZnO supports for using feed gas mixtures containing CO and H_2 correlate with the amount of oxygen-vacancies, whereas CO_2 has a poisoning effect presumably because it quenches oxygen defect sites.[7] Apparently, the exothermic conversion of CO_2 with H_2 (water gas) to methanol on ZnO supports, according to eqn (1), requires a different mechanism.

$$CO_2 + 3H_2 \rightarrow H_3COH + H_2O \quad \Delta_R H = -40.9 \text{ kJ mol}^{-1} \tag{1}$$

In line with that, five reactions on ZnO surfaces (eqn (2)–(6)) have been proposed in the literature, which play a crucial role for the conversion of water gas to methanol.[8]

$$H_2(g) \rightarrow 2\,H\,(ad) \tag{2}$$

$$CO_2(g) \rightarrow CO_2\,(ad) \tag{3}$$

$$CO_2(ad) + H(ad) \rightarrow HCO_2(ad) \tag{4}$$

$$HCO_2(ad) + 4H(ad) \rightarrow H_3CO(ad) + H_2O \tag{5}$$

$$H_3CO(ad) + H(ad) \rightarrow H_3COH(ad) \rightarrow H_3COH(g) \tag{6}$$

The initial step of the catalytic process is the hydrogenation of ZnO, leading to surface-terminated ZnH and OH sites[9] which indicate the heterolytic fission of dihydrogen. It has also been shown for a few cases that alkali metals can promote the catalytic performance of ZnO.[10] On the molecular level, however, little is known about the consecutive mechanism of chemisorption and reduction steps. This lack of knowledge could be partially overcome by using hydridozinc alkoxides as molecular models which resemble some electronic features of hydrogenated ZnO. Additionally, the promoting influence of heterometals could be mimicked by using heterobimetallic hydridozinc clusters (*e.g.*, mixed lithium hydridozinc alkoxides). Recently, we reported the synthesis and structure of a series of well-defined homo- and heterobimetallic hydridozinc *tert*-butoxide clusters of the formula [$(HZnOtBu)_{4-n}(LiOtBu)_n$] **1a–1d**[11] (Scheme 1) which could be useful to study Zn–H assisted and heterometal promoted hydrogenation of CO_2.

Here we report the remarkably different reactivity of the lithium-free *vs.* lithium-containing hydridozinc heterocubane-like clusters **1a** *vs.* **1b–1d**. The latter show the pivotal role of lithium ions for an accelerated reduction of CO_2 at Zn–H sites at ambient

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$(HZnO^tBu)_4$	**1a**
$(HZnO^tBu)_3(thf{\cdot}LiO^tBu)$	**1b**
$(HZnO^tBu)_2(thf{\cdot}LiO^tBu)_2$	**1c**
$(HZnO^tBu)\ (thf{\cdot}LiO^tBu)_3$	**1d**

Scheme 1 The homometallic cubane **1a** *vs.* heterobimetallic lithium zinc *tert*-butoxide cubanes **1a–1d**.

temperature and atmospheric pressure to give selectively zinc formate.

The reaction progress for the consumption of CO_2 has been monitored by *in situ* IR measurements. In contrast to ZnH_2 which remains unchanged even after one day in a pure CO_2 atmosphere, the powdered hydridozinc heterocubane cluster **1a** reacts slowly with CO_2 to give additional vibrational bands in the region of 1330, 1600–1650, 1798–1813 and 2700–2800 cm^{-1} in the IR spectrum which can be assigned to the formate ion in different coordination modes.[12] The consumption of **1a** is complete after *ca.* three days. The formation of formate is similar to the process of insertion of CO_2 into the Zn–H bond of a hydridozinc tris(pyrazole)borate described by Parkin *et al.* which enabled the isolation of an η^1-formate zinc complex.[13] Interestingly, the insertion of CO_2 into the Zn–H bond is drastically accelerated in the presence of Li ions in the heterocubane framework: thus, powders of **1b** react immediately with CO_2 as shown by IR measurements (Fig. 1).

The characteristic Zn–H vibrational mode of **1b** at 1769 cm^{-1} decreases gradually during the reaction progress. Concomitantly, an additional band at 1805 cm^{-1} is growing in and additional new bands appear at 1336, 1630–1674, and 2700–2800 cm^{-1}. Furthermore, the appearance of a broad OH stretching vibration in the region of 3200–3500 cm^{-1} suggests the formation of water which is coordinated to zinc and/or lithium formate. In fact, the vibrational modes can be unequivocally assigned to zinc formate–hydrate species based on characteristic reference data[13] and

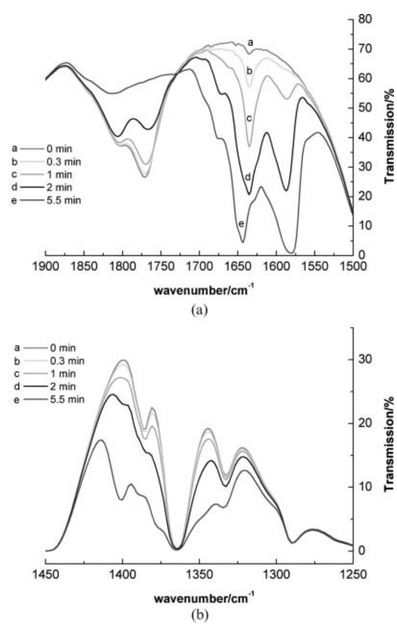

Fig. 1 ***In situ*** IR spectra of the gradual conversion of **1b** with CO_2. (a) Vibrational bands between 1900 and 1500 cm^{-1}. (b) Vibrational modes between 1450 and 1250 cm^{-1}.

confirmed by quantum chemical calculations.[14] From the literature it is known that the formate ligand can adopt the η^1- and η^2-coordination mode, respectively. We considered in our DFT calculations three different coordination modes for the formate ligand: the η^1-, symmetric η^2- and asymmetric η^2-coordination modes, respectively. As expected, the η^2-coordination modes are favoured with a slight preference for the asymmetric one. Our calculations suggest that both coordination modes contribute to the vibrational spectra of the formate species obtained by the reaction of **1b** and CO_2. This is in accordance with the MAS ^{13}C-NMR spectrum of the product which shows two resonances for the HCO_2 moiety at $\delta = 168$ and 169 ppm. Furthermore, powder-XRD studies confirm the presence of $Zn(HCO_2)_2$ and $Li(HCO_2)$ hydrates as microcrystalline components of the reaction mixture. Other hydrogenated products of CO_2 such as formaldehyde and methanol or CO could not be detected (IR, NMR, MS). The experiments have been performed under rigorous anhydrous and anaerobic conditions. Accordingly, using the deuterated isotopomer of **1b**, $[(DZnO^tBu)_3(thf{\cdot}LiO^tBu)]$, leads to $[Zn(DCO_2)_2{\cdot}2D_2O]$ as proven by IR. Remarkably, contamination of CO_2 with water vapour (0.05–0.1%) *prevents* hydrogenation of CO_2 and leads merely to partial hydrolysis of Zn–H bonds in **1b** and sorption of CO_2 to give carbonates exclusively. The water molecules of $[Zn(HCO_2)_2{\cdot}2H_2O]$ are presumably formed by secondary reduction of formate to give as yet unidentified reduction products. Apparently, the formation of water necessitates the presence of lithium ions, since the Li-free cluster **1a** leads exclusively to anhydrous zinc formate. The formation of water during the hydrogenation of CO_2 on ZnO supports has previously been discussed by Bailey *et al.*.[15] In the latter case, however, formate species are also formed as initial products at elevated temperature *via* hydride transfer apart from other hydrogenation products (*e.g.*, methanolate) and water. Interestingly, the formation of $Zn(HCO_2)_2$ and $Li(HCO_2)$ hydrates occurs also in solution. Thus, clear solutions of **1b** in thf react with CO_2 leading immediately to precipitation of $[Zn(HCO_2)_2{\cdot}2H_2O]$ which has been characterized by IR, ^1H- and ^{13}C-NMR spectroscopy. Crystals of the latter have been characterized by a single-crystal X-ray diffraction analysis (Fig. 2). The crystal structure[16] consists of a coordination polymer with two octahedrally coordinated Zn ions linked by a formate anion as a bridging bidentate ligand.[17]

The two Zn ions are in different environments and lie on independent inversion centres: while Zn1 is coordinated to six formate ligands, Zn2 is surrounded by two formate ligands and four water molecules. As proven by ^1H-NMR spectroscopy of the filtrate, compound **1b** has been completely consumed and neither another Zn–H compound nor formate species remain in solution. Instead, resonance signals of as yet unknown metal *tert*-butoxide

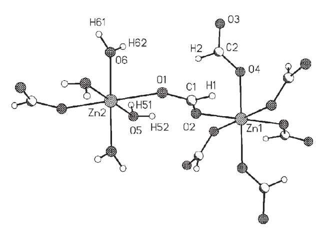

Fig. 2 Structural unit of polymeric $[Zn(HCO_2)_2{\cdot}2H_2O]$ in the crystal. The Zn2-atom coordinates four water molecules.

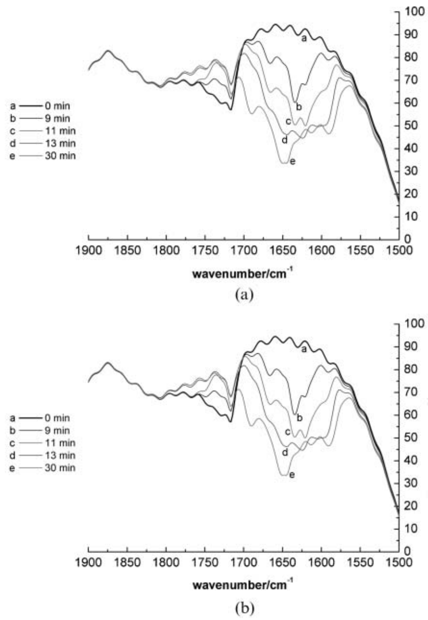

Fig. 3 *In situ* IR spectra of the gradual conversion of **1c** with CO_2. (a) Vibrational bands between 1250 and 1450 cm^{-1}. (b) Vibrational modes between 1500 and 1900 cm^{-1}.

aggregates and uncharacterized organic side-products can be observed.

The heterobimetallic cubanes **1c** (ratio Li : Zn = 2 : 2) and **1d** (ratio Li : Zn = 3 : 1) react also with CO_2 which has been monitored by *in situ* IR spectroscopy. Fig. 3 shows the changes of selected characteristic vibrational modes for the gradual conversion of **1c** which are practically identical with those of **1d**. However, reaction progress is significantly slower than that for the monolithium cluster **1b**. While the conversion of **1b** with CO_2 is complete after *ca.* 5 min, it takes *ca.* 30 min to consume the same molar quantity of **1c** and **1d**, respectively, affording $[Zn(HCO_2)_2{\cdot}2H_2O]$ and $Li(HCO_2)$ hydrates as major products.

The distinct reactivity of **1b** *vs.* **1c** and **1d** suggests that hydride transfer from the Zn–H bond to CO_2 is significantly reduced by increasing the molar ratio of Li : Zn. In line with that, the relatively low reactivity of **1a** indicates that the presence of at least one Li ion as a Lewis-acidic centre in proximity to the Zn–H moiety fosters the hydride transfer to CO_2.

On the other hand, increasing the Li : Zn ratio reduces the basicity of the Zn–H moiety due to a stronger O → Li *vs.* O → Zn coordination. In conclusion, our model systems demonstrate the pivotal role of Li ions for an accelerated reduction of CO_2 at Zn–H sites. Although, the mechanism for the accelerated reduction of CO_2 through the presence of Li ions is still unknown, our preliminary results on the model systems **1a–1d** suggest that the selective conversion of water gas (hydrogenation of CO_2) into formic acid derivatives (*e.g.*, formic acid methylester) could be strongly favoured by using lithium-promoted ZnO supports. In line with our previous results on synthesizing nanoscaled zinc oxide materials through the organometallic precursor approach,[18] **1b–1d** are promising molecular single-source precursors for the synthesis of Li-promoted, nanoscaled ZnO materials. Respective investigations on the synthesis and catalytic performance of Li-promoted ZnO nanoparticles for the selective catalytic conversion of water gas to formic acid derivatives are currently underway.

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16 Crystal data for $[Zn(HCO_2)_2{\cdot}2H_2O]$ see ESI.† Crystal data for $C_2H_6O_6Zn$, M_r = 191.44, monoclinic, space group $P2_1/c$ (No. 14), a = 8.6803(9), b = 7.1241(10), c = 9.3060(12) Å, β = 97.664(3)°, V = 570.3(1) $Å^3$, ρ_{calcd} = 2.229 g cm^{-3}, μ = 4.265 mm^{-1}, Z = 4, λ = 0.71073 Å, T = 213 K, 209 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(Θ range: 3.71 to 25.02], 926 independent (R_{int}=0.019) and 734 observed reflections [$I > 2\sigma(I)$], 110 refined parameters, R = 0.022, wR_2 = 0.062. CCDC 650772. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b714806b.

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