DOI: 10.1002/anie.200906054

Production of HCOOH/NEt$_3$ Adducts by CO$_2$/H$_2$ Incorporation into Neat NEt$_3$**

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Research efforts are currently devoted to hydrogen storage in CO_2 as formic acid derivatives, a thirty-year old idea[1] not yet implemented. A chemical loop is conceivable based on a formate intermediate which can be produced in a pure and storable form under moderately high CO_2 and H_2 pressures and which can release gases at atmospheric pressure on demand when in contact with an appropriate catalyst. The catalytic decomposition of HCOOH itself has received renewed attention.[2] Remarkably, M. Beller and co-workers have demonstrated that HCOOH/NEt$_3$ adducts can also be catalytically decomposed at 40 °C to H_2 free of CO, albeit diluted by CO_2.[3] However, a procedure for the production of either HCOOH or HCOOH/NEt$_3$ adducts from CO_2 and H_2 is still lacking. The formation of HCOOH by CO_2 hydrogenation is hampered by unfavorable thermodynamics ($\Delta G^{o}_{298} = +33\,\text{kJ}\,\text{mol}^{-1}$ for the reaction $H_{2(g)} + CO_{2(g)} \rightarrow HCOOH_{(l)}$). The HCOOH/NEt$_3$ adducts are reportedly formed under moderate CO_2/H_2 pressures, with a molar acid/amine ratio (AAR) in the range of 1.3–1.8, by employing a variety of Ru^{II} and Rh^{I} homogeneous precursors. High turnover numbers and frequencies (TOF) have been achieved in supercritical carbon dioxide (scCO$_2$) or organic solvents,[4] but the large amounts of scCO$_2$ or organic solvents that are needed render these methods unsuitable for industrial application. Moreover, separation of the adduct from the reaction medium and of the homogeneous catalyst from the adduct has been achieved only in the case of scCO$_2$[5] by employing $[RuH_2(PMe_3)_4]$ as homogeneous catalyst. Under these conditions, removal of gases at the end of the reaction can be performed without product entrainment, and the catalyst contaminating the adduct can be deactivated by exposure to air. The use of a heterogeneous catalyst for CO_2 hydrogenation in the presence of NEt$_3$[6] would make catalyst removal easy.

We report here the quantitative conversion of NEt$_3$ to pure and storable HCOOH/NEt$_3$ adducts by incorporation of CO_2/H_2 into neat NEt$_3$, without foreign solvents or additives.

Catalyst removal and recycling apart, pure adducts could be straightforwardly formed by carrying out CO_2 hydrogenation in neat NEt$_3$, provided the reaction can be driven to completion. As far as we know, only three reports mention hydrogenation reactions in neat NEt$_3$: both Rh^{I} with a bidentate phosphane ligand[7] and $[RuCl(O_2CMe)(PMe_3)_4]$,[8] which promote the reaction in DMSO/NEt$_3$, were found to be inactive in neat amine. More encouragingly, a third paper reports[9] that $[RuCl(O_2CMe)(PMe_3)_4]$ promotes CO_2 hydrogenation in neat NEt$_3$, but the reaction was stopped by freezing when only 15 % of NEt$_3$ had reacted. For better understanding and planning of CO_2/H_2 incorporation into NEt$_3$ it must be borne in mind that addition of HCOOH to an excess of amine leads to a biphasic system[10] constituted by NEt$_3$ and an adduct with AAR = 1.33, whose composition remains unchanged upon addition of HCOOH until free amine is present (see Supporting Information). The chemical and physical properties of the amine are completely different from those of the immiscible adduct. For instance, the dielectric constant of the amine is 2.4, while that of the 1.33 adduct is so high that cannot be determined by classical methods and it has been evaluated to be 86.6.[10] The IR spectra of the two equilibrated phases (amine and the 1.33 adduct) show that the amine contains only traces of undissociated HCOOH ($\tilde{\nu}_{CO} = 1706\,\text{cm}^{-1}$), while the 1.33 adduct is basically a $[NEt_3H]^+[HCOO]^-$ ($\tilde{\nu}_{CO} = 1598\,\text{cm}^{-1}$) ionic liquid with some oligomeric $(HCOOH)_n$ ($\tilde{\nu}_{CO} = 1710\,\text{cm}^{-1}$; see Supporting Information). An intriguing hypothesis is that CO_2/H_2 incorporation occurs in the separate phase of the 1.33 adduct rather than in NEt$_3$ itself, and that the amine merely converts the richer adduct back to the 1.33 adduct. Under these conditions, the presence of a separate phase of the 1.33 adduct would be essential to start the reaction, which would be autocatalytic. This is what we observed: with $[RuCl_2(PMe_3)_4]$ (**1**) as promoter, a long induction period occurred in neat NEt$_3$, but the incorporation reaction promptly started if the 1.33 adduct was present as a separate phase. Therefore, in order to circumvent the induction period, we invariably employed NEt$_3$ in the presence of a separate phase of the 1.33 adduct, that is, we always added 2 wt % HCOOH to the amine already charged into the reactor. For a systematic investigation of the incorporation it was necessary to avoid changes in the gas-phase composition with progress of the reaction. Therefore, **1**-promoted formation of adducts was investigated by feeding the reactor with an equimolar CO_2/H_2 mixture prepared in a separate high-pressure reservoir. The amounts of gaseous mixture fed into the reactor were determined by weighing the reactor or the reservoir. The reaction order with respect to CO_2 or H_2 has not yet been investigated.

Runs were carried out at 40 and 50 °C, in a magnetically driven 320 mL Parr autoclave modified to 190 mL by a home-made Teflon filling, equipped with an internal temperature

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[**] This research was supported by Chimet SpA, Badia Al Pino, Italy. We thank Prof. F. Calderazzo for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200906054.

sensor, heater, and cooler and charged with 80 mL (58 g, 568 mmol) of amine "doped" with 21 wt% HCOOH and with 3 mM (**1**). The autoclave was pressurized with various weighed amounts of the CO_2/H_2 equimolar mixture ($CO_2/H_2:NEt_3 < 1.33$); for each run, an indication of the reaction rate at various stages can be derived from the pressure changes with time (Figure 1).

The sigmoidal pressure–time curves, together with the induction period, confirm that the reaction is autocatalytic and support that the 1.33 adduct incorporates CO_2/H_2. Remarkably, the pressure leveled off at 41 ± 1 bar at 40°C and at 61 ± 1 bar at 50°C regardless of the amount of equimolar CO_2/H_2 mixture which had been introduced into the reactor. Such a one-to-one correspondence between temperature and equilibrating pressure was confirmed by employing **1** as promoter for the decomposition reaction of the 1.33 adduct. In the same reactor at 40 and 50°C, the pressure built up by the decomposition reaction leveled off at the same values as those for the formation reaction (Figure 1). In the equilibrated mixtures two separate liquid phases are present: an upper layer of NEt_3, and a lower layer of 1.33 adduct (see mass balances in the Supporting Information). The one-to-one correspondence between temperature and pressure is a prominent feature of the equilibrium between CO_2/H_2 (1/1), NEt_3, and the 1.33 $HCOOH/NEt_3$ adduct. The Gibbs phase rule ($F = C - P + 2$) establishes a single degree of freedom of the intensive properties temperature and pressure for a system with two components (C) and three phases (P). Indeed, due to the constant CO_2/H_2 molar ratio of 1/1 and the working equilibrium, only two independent components are present, while the three phases are a consequence of the immiscibility between the amine and the 1.33 adduct. In principle, therefore, it is expected that the 1.33 adduct is quantitatively formed or decomposed, respectively, at CO_2/H_2 pressures just above or just below the equilibrium value at a given temperature. However, for complete conversion of amine to adducts, kinetic reasons, that is, concurrent catalyst deactivation, compelled us to avoid temperatures higher than 40°C and to use working pressures considerably higher than that of equilibrium (41 bar). Figure 2 shows that, under 120 bar pressure at 40°C, the incorporation reaction proceeds beyond AAR = 1.33 up to AAR = 1.78. Both under lower pressure and at higher temperature the incorporation reaction fades before amine conversion is complete, that is, before the incorporated number of moles of CO_2/H_2 per mole of NEt_3 reaches a value of 1.33.

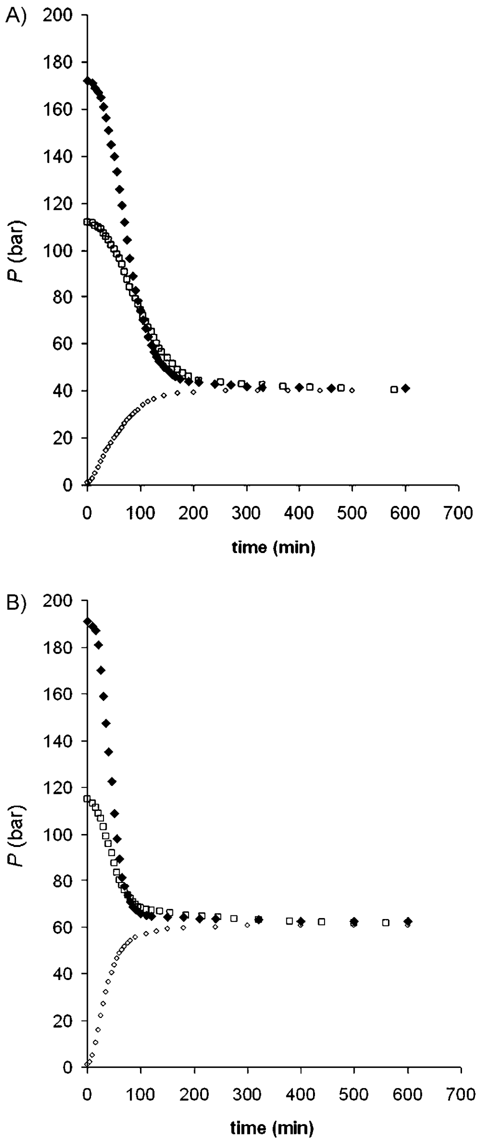

Figure 1. Time course of pressure during **1**-promoted equilibration between the 1.33 $HCOOH/NEt_3$ adduct and NEt_3 under different CO_2/H_2 (1/1) initial pressures. Reactor volume = 190 mL; liquid-phase volume = 80 mL; weighed amounts of the introduced gas are given in the inset. A) $T = 40$°C. B) $T = 50$°C. ◆: $CO_2/H_2 = 23.2$ g; □: $CO_2/H_2 = 15.6$ g; ◇: 1.33 AAR decomposition.

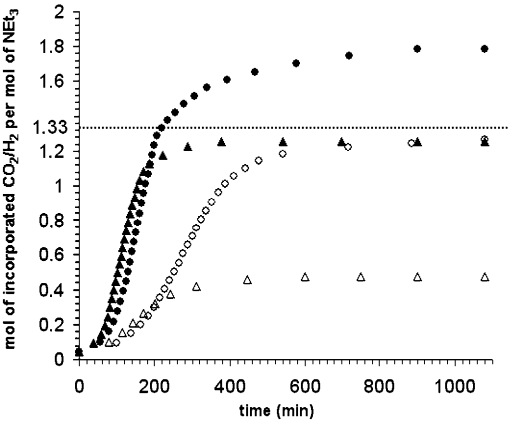

Figure 2. Moles of incorporated CO_2/H_2 equimolar mixture per mole of NEt_3 at various times, under constant pressures of 80 or 120 bar at 40 or 50°C, respectively. 190 mL reactor charged with 70.5 mL (51 g, 0.5 mol) of NEt_3 "doped" with 2 wt% HCOOH and 3 mM **1**. ●: $T = 40$°C, $P = 120$ bar; ○: $T = 40$°C, $P = 80$ bar; ▲: $T = 50$°C, $P = 120$ bar; △: $T = 50$°C, $P = 80$ bar.

Such behavior is due to catalyst deactivation competing with CO_2/H_2 incorporation. At a given temperature, increasing pressure favors incorporation but does not affect catalyst deactivation. Under a given pressure, a higher temperature accelerates catalyst decomposition more than incorporation, presumably due to a larger positive activation enthalpy of the former.

The incorporation reaction is exothermic, and under favorable conditions for which a TOF of 1600 h^{-1} is reached (Figure 3), effective cooling is needed to avoid an undesirable rise in temperature and catalyst deactivation.

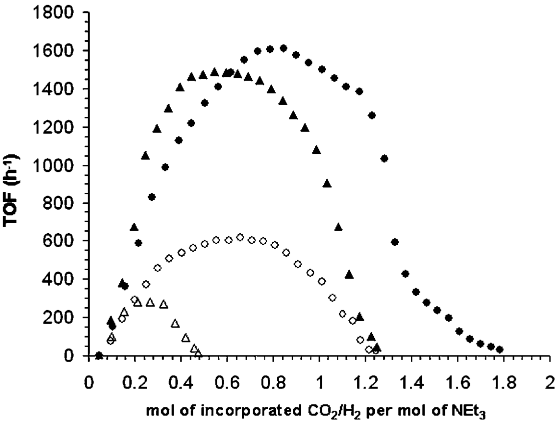

Figure 3. TOFs for incorporation of equimolar CO_2/H_2 mixture at various P and T with [**1**] = 3 mM. ●: $T = 40$ °C, $P = 120$ bar; ○: $T = 40$ °C, $P = 80$ bar; ▲: $T = 50$ °C, $P = 120$ bar; △: $T = 50$ °C, $P = 80$ bar.

On the basis of these findings, the adducts, rather than the amine itself, seem to be the active species incorporating CO_2/H_2. In fact, it was shown above (Figure 1) that **1**-promoted incorporation into NEt_3 is autocatalytic and depends on the amount of 1.33 adduct. On the other hand, the capability of adducts to incorporate CO_2/H_2 in the absence of free amine is demonstrated by formation of the 1.78 adduct.

To evaluate how high an AAR can be reached under reasonable pressures, that is, how much H_2 can be directly stored in the $HCOOH/NEt_3$ adducts, we investigated the relationship between equilibrating pressure and AAR > 1.33 at 40 °C. We assumed that the equilibrating pressure is that which leveled off at the end of either incorporation or decomposition reactions. The equilibrating pressure increases exponentially with increasing AAR (Figure 4), and AAR > 2.0 seems unattainable in spite of the low temperature of 40 °C. For instance, decomposition of a richer adduct at 40 °C in a homemade rocking stainless steel autoclave was stopped, for safety reasons, at 300 bar: under this pressure, presumably lower than that of equilibrium, the residual adduct still had AAR = 2.3 (see Supporting Information).

Finally, by distillation at 68 °C under reduced pressure, the 1.78 adduct was quantitatively converted to recyclable amine and an azeotrope with AAR = 2.35. To avoid the reverse decomposition reaction of the adduct, it was necessary to completely deactivate the ruthenium species before distillation. This was achieved by treating the ruthenium-contaminated 1.78 adduct with KCN in an Ru/CN^{-1} molar ratio of 6/1 soon after venting the gas at room temperature. Quantitative ruthenium recycling and de-cyanidation were carried out by treating the colorless distillation residue with alkaline hypochlorite (**Caution**: alkali must be in excess, otherwise toxic and explosive RuO_4 is formed; see Supporting Information).

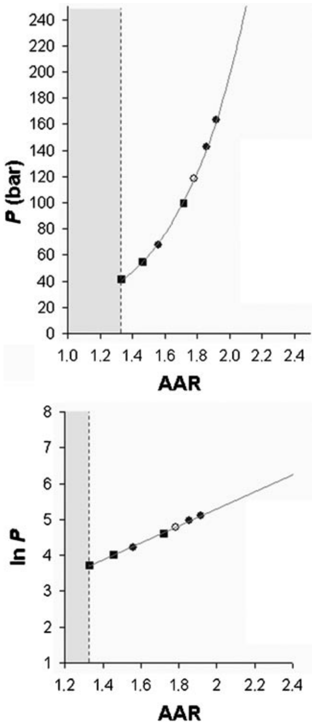

Figure 4. Relationship between equilibrating pressure and AAR > 1.33 at 40 °C. Equilibrating pressures were obtained from incorporation or decomposition reaction. ●: incorporation; ■: decomposition; ○: incorporation, $T = 40$ °C, $P = 120$ bar.

To summarize, for the first time a pure formic acid derivative has been isolated in substantial amounts by employing CO_2 rather than CO as raw material. At 40 °C under 120 bar CO_2/H_2, NEt_3 is quantitatively converted within hours to a 1.78 adduct whose distillation, after catalyst deactivation, yielded a pure and stable azeotrope with AAR = 2.35 without CO_2 or H_2 loss. Catalyst removal and recycling are easily accomplished by means of limited amounts of cheap reagents. No foreign solvents or additives are necessary.

In conclusion, the process reported here could be economically carried out even on an industrial scale. The present findings make hydrogen storage in CO_2 more realistic. Under reasonable pressures, direct incorporation of CO_2/H_2 into NEt_3 can afford adducts with a maximum AAR of 2. However, adduct decomposition gives back H_2/CO_2 (1/1), and the mixture cannot be employed to feed a fuel cell, in which the accumulation of the inert gas would occur. To circumvent this problem, it has been proposed that the gas stream flow through a fuel-cell stack.[3b] The profitability of such a strategy has still to be ascertained. On the other hand, $HCOOH/NEt_3$ adducts are widely employed in organic chemistry as selective hydrogen-transfer reagents, [11] for which the here-reported production of adducts could be economically viable.

Received: October 28, 2009
Revised: January 13, 2010

Keywords: amines · carbon dioxide · hydrogen · hydrogen storage · hydrogenation

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