# **Supporting Information for**

# Base-free hydrogen generation from methanol using a bi-catalytic system

## Angèle Monney, Enrico Barsch, Peter Sponholz, Henrik Junge, Ralf Ludwig and Matthias **Beller**\*

Leibniz-Institut für Katalyse e.V. and der Universität Rostock, Albert-Einstein-Strasse 29a, 18059 Rostock, Germany. Fax: 0049 381 1281 51113; Tel: 0049 381 1281 113; E-mail: matthias.beller@catalysis.de

## **General methods**

Compounds A2-A3,<sup>1</sup> A5,<sup>2</sup> B1-B5,<sup>3</sup> and B6<sup>4</sup> were synthesised according to literature procedures and stored under argon atmosphere. All other compounds were purchased from fine chemical companies, used as received and stored under argon atmosphere. Methanol, water and triglyme were degassed by bubbling argon for 3 hours.

All experiments were carried out under an argon atmosphere with the exclusion of air. The amount of hydrogen generated was measured by manual gas burette (100 mL and 2000 mL). The gas purity was established by GC analysis. Typically, only hydrogen, carbon dioxide and argon were observed, though trace amounts of carbon monoxide may occasionally be detected.

In a typical experiment methanol, water and triglyme were heated at strong reflux ( $T_{set} = 93.5$  °C) under an argon atmosphere. Catalysts A and B were quickly added and this marked the beginning of the gas evolution measurements. The turnover number (TON) was calculated from the amount of hydrogen produced. The volume of hydrogen gas generated corresponds to 75% of the total volume of gas measured. Every H<sub>2</sub> molecule represents one catalyst turnover. The gas volumes were corrected by blank values which were obtained from the same reaction conditions in the absence of catalyst and which include traces of solvent. The TON values were calculated using the following

Equation 1:

$$TON = \frac{V_{obs} - V_{blank}}{V_{m,H_2,25 \circ C} \cdot n_{cat}} * 0.75$$

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Vobs: measured gas volume from gas burette [mL] V<sub>blank</sub>: blank volume [mL]  $V_{m,H_{2,25}}$  · C [mL·mmol<sup>-1</sup>] c molar gas volume of H<sub>2</sub> at 25 °C [mL·mmol<sup>-1</sup>]  $n_{cat}$ : amount of catalyst [mmol] (in the case of a bi-catalytic system:  $n_{cat} = n_{catA} + n_{catB}$ )

#### **Supplementary Equation 1**

The molar gas volume was calculated using Van der Waals Equation 2:

$$V_{m,H_{2,25}} = \frac{RT}{p} + b - \frac{a}{RT} = 24.49 \ mL \cdot mmol^{-1}$$

$$R = 8.3145 \ m^{3} \cdot Pa \cdot mol^{-1} \cdot K^{-1}$$

$$T = 298.15 \ K$$

$$P = 101325 \ Pa$$

$$a = 2.49 \cdot 10^{-10} \ Pa \cdot m^{6} \cdot mol^{-2}$$

$$b = 26.7 \cdot 10^{-6} \ m^{3} \cdot mol^{-1}$$

#### **Supplementary Equation 2**

The turnover frequency (TOF) at a specified time was calculated from the TON after x hours divided by x hours.

For example, in Table 2, entry 1,  $TON_{1h} = 239$ ,  $TON_{3h} = 413$  and  $TON_{7h} = 578$ , therefore  $TOF_{1h} = TON_{1h}/(1 h) = 239 h^{-1}$ ,  $TOF_{3h} = TON_{3h}/(3 h) = 138 h^{-1}$  and  $TOF_{7h} = TON_{7h}/(7 h) = 83 h^{-1}$ .

The catalytic runs were performed between one and four times and the error was obtained using the following Equation 3:

 $error = \frac{standard\ deviation}{mean} * 100$ 

**Supplementary Equation 3** 

### Screening of reaction conditions

The combination of catalyst A1 (5  $\mu$ mol) and catalyst B1 (5  $\mu$ mol) was used to screen the reaction conditions (Supplementary Figure 1). The methanol-water ratio was varied in the absence of solvent from a 1:1 molar ratio (6.9 mL MeOH / 3.1 mL H<sub>2</sub>O) to neat methanol. The best results were obtained with a 9:1 volume ratio MeOH/H<sub>2</sub>O. Anhydrous methanol was initially dehydrogenated with the highest rate, but the gas generation completely stopped after about 1 hour. The lack of water does not allow the reaction to proceed to formic acid and further (see Scheme 1).

Since the solubility of the catalysts in the methanol-water mixture was low, a solvent was added. Even though the reaction rate was improve by the addition of 1,4-dioxane, the latter was ruled out because of its lower boiling point and therefore the higher error it may induce. Propylene carbonate (PC) seemed at first to be an ideal solvent for this reaction. However the gas produced was composed almost exclusively of  $CO_2$  with only traces of H<sub>2</sub>, meaning that our catalytic system was decomposing the solvent before the substrate. Finally, diglyme (diethylene glycol dimethyl ether) and triglyme (triethylene glycol dimethyl ether) were found to be suitable solvents for the dehydrogenation of methanol with triglyme leading to the highest rate. A volume of 4.0 mL of triglyme was optimal for this reaction.



Supplementary Figure 1 Screening of reaction conditions.

## **Screening of catalysts**

The combination of catalyst A1 and catalyst B2 showed the highest activity, surpassing that of A1 + B1 after about 5.5 hours as clearly visible on the following Supplementary Figure 2:



Supplementary Figure 2 Screening of catalysts.

## Screening of catalysts' ratios and quantities

The ratios and the quantities of catalysts A1 and B2 were investigated (Supplementary Figure 3). The gas evolution was greater when the quantity of A1 was increased from 5  $\mu$ mol to 20  $\mu$ mol, 45  $\mu$ mol and finally 95  $\mu$ mol. On the other hand, the quantity of catalyst B2 did not matter and the same gas evolution was obtained with 5  $\mu$ mol, 20  $\mu$ mol and 45  $\mu$ mol. Of note, B2 was not completely soluble in the reaction mixture at 20  $\mu$ mol and 45  $\mu$ mol catalyst loadings. When combined, A1 and B2 interacted in a synergistic manner and produced more gas. This synergy however decreased at higher catalyst loading from 5  $\mu$ mol / 5  $\mu$ mol (A1/B2) to 20  $\mu$ mol / 5  $\mu$ mol, 45  $\mu$ mol / 5  $\mu$ mol and 95  $\mu$ mol / 5  $\mu$ mol. The synergistic effect could not be recovered by increasing the quantity of catalyst B2 (45  $\mu$ mol / 45  $\mu$ mol (A1/B2) or 95  $\mu$ mol / 20  $\mu$ mol), probably because of the low solubility of B2 at higher concentrations.



Supplementary Figure 3 Screening of catalysts' ratios and quantities.

## **Formic acid addition**

In order to assess the role of formic acid in this methanol reforming process, HCOOH (0.5 mL) was added to the reaction mixture. Supplementary Figure 4 shows the gas evolution following formic acid addition catalysed by A1 (5  $\mu$ mol, pale blue line), A1 (45  $\mu$ mol, deep blue line), B2 (5  $\mu$ mol, red line) and by the combination of A1 (5  $\mu$ mol) and B2 (5  $\mu$ mol) (green line).



Supplementary Figure 4 Formic acid addition.

## Long term experiment

A long term experiment was performed using the following conditions:

MeOH 9.0 mL, H<sub>2</sub>O 1.0 mL, triglyme 4.0 mL, A1 5 µmol, B2 5 µmol, T<sub>set</sub> = 93.5 °C

The reaction was left to run for 10 days using a 2000 mL burette for the accumulation of the produced gas. The gas evolution was constant for about 24 hours and then slowly decreased to finally stop after 8 days. A total gas volume of 1400 mL was produced, corresponding to a turnover number of 4286.



Supplementary Figure 5 Long term experiment.

### **IR spectroscopy**

FTIR measurements were carried out on a Bruker Matrix spectrometer equipped with an MCT detector. The optics were purged and the reaction was carried out under inert gas atmosphere. The reaction solution was continuously circulated through a demountable IR cell maintained at 90.0  $^{\circ}$ C by a micro gear pump. The window material was CaF<sub>2</sub> and the optical path length was 0.1 mm. The following reaction conditions were used:

MeOH 19.0 mL, H<sub>2</sub>O 1.0 mL, triglyme 8.0 mL, A1 10 µmol, B2 10 µmol, T<sub>set</sub> = 90.0 °C

#### 1. Relevant section of the IR spectrum

The reaction was followed by *in situ* IR spectroscopy and the relevant section of the spectrum is shown in Supplementary Figure 6. When the two catalysts were added to the reaction mixture, a vibration band at  $1730 \text{ cm}^{-1}$  appeared and continuously increased until it reached a steady-state. The appearance of this band was accompanied by a negative contribution at  $1650 \text{ cm}^{-1}$  which we attributed to the consumption of water.

Of note, the strong reflux conditions used for this reaction allowed for an efficient degassing of the solution. The presence of  $CO_2$  in the IR spectrum was observed only for a short time when formic acid was directly added to the reaction mixture and its fast decomposition produced a large quantity of carbon dioxide.



Supplementary Figure 6 Relevant section of the IR spectrum.

## 2. Vibration band at 1730 $\text{cm}^{-1}$

In Supplementary Figure 7, the vibration band at 1730 cm<sup>-1</sup> detected during the catalytic reaction is compared with "free" formic acid, *i.e.* HCOOH in a MeOH-H<sub>2</sub>O-triglyme (9:1:8) mixture at 90 °C. The position and the shape of the bands are very similar, however not exactly identical. We tentatively attribute this difference to a slight interaction of HCOOH with the catalysts.



Supplementary Figure 7 Vibration band at 1730 cm<sup>-1</sup>.

### 3. Stepwise addition of the catalysts

The evolution of the vibration band at  $1730 \text{ cm}^{-1}$  was followed and the absorption *vs*. time is plotted in Supplementary Figure 8. When catalysts A1 and B2 were added together the absorption increased significantly for several hours before it reached a steady-state after about 20 hours (green line). The intensity of the absorption signal increased only slowly when the catalysts were used individually. The increase in absorption is triggered by the addition of B2 to A1 (blue line) or vice versa by the addition of A1 to B2 (red line). The same phenomenon was observed using gas evolution measurements (*cf.* text and Figure 1). However, the two graphs cannot be compared since they report different aspects of the catalysis. In Figure 1, the produced gas volume is reported as a function of time, while in Supplementary Figure 8, the evolution of the IR band corresponding to *in situ* formed formic acid as a function of time is shown.



Supplementary Figure 8 Stepwise addition of the catalysts followed by in situ IR spectroscopy.

## 4. Formic acid addition

The evolution of the vibration band at  $1730 \text{ cm}^{-1}$  was followed after the addition of 0.1 mL of formic acid (performed twice) and the absorption *vs*. time is plotted in Supplementary Figure 9. As expected, when formic acid was added to the reaction mixture, the intensity of the band was greatly increased. It then quickly decreased to reach again its previous state. The added formic acid was decomposed each time in about 10 minutes. This behaviour supports our attribution of this vibration band to HCOOH since its fast decomposition relates to our observations using gas evolution measurements (*cf* text).



Supplementary Figure 9 Formic acid addition followed by in situ IR spectroscopy.

### 5. Formaldehyde addition

The proposed reaction pathway of the methanol dehydrogenation involves the formation and consumption of formaldehyde.<sup>1</sup> To support this hypothesis, an aqueous solution of formaldehyde (37%, 0.1 mL) was added to the reaction mixture connected to the IR spectrometer. The evolution of the vibration band at 1730 cm<sup>-1</sup> was followed (Supplementary Figure 10) and the absorption *vs.* time is plotted in Supplementary Figure 11.

A direct detection of formaldehyde was not possible since its vibration frequency coincides with the frequency of the broad band corresponding to  $H_2O$  deformation whose intensity increase was also due to the added water. However, the addition of the formaldehyde solution triggered an immediate increase in intensity of the formic acid vibration band at 1730 cm<sup>-1</sup> which reached a maximum after about 18 min before decreasing again during the course of the reforming process. Even though this observation is only an indirect consequence of the addition of formaldehyde, it demonstrates that formaldehyde is converted into formic acid and then  $CO_2$  under catalytic dehydrogenation conditions. Due to the high complexity of our bi-catalytic system, it was however not possible to detect intermediate catalytic species.



Supplementary Figure 10 Formaldehyde addition followed by in situ IR spectroscopy.



Supplementary Figure 11 Formaldehyde addition followed by in situ IR spectroscopy (vs. time).

### 6. KOH addition

As another evidence of the band at 1730 cm<sup>-1</sup> corresponding to the vibration of formic acid, a small pellet of potassium hydroxide was added to the reaction mixture. Supplementary Figure 12 shows the relevant section of the IR spectrum. The HCOOH signal disappeared and a band attributed to a formate species appeared within 10 minutes. The intensity of the HCOO<sup>-</sup> band then slowly decreased and a new band attributed to a carbonate species appeared during the next 2 hours.



Supplementary Figure 12 KOH addition followed by in situ IR spectroscopy.

## References

- 1. M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali and M. Beller, *Nature*, 2013, **495**, 85-89.
- 2. D. Canseco-Gonzalez and M. Albrecht, *Dalton Trans.*, 2013, **42**, 7424-7432.
- 3. M. Khorasani-Motlagh, N. Safari, C. B. Pamplin, B. O. Patrick and B. R. James, *Inorg. Chim. Acta*, 2001, **320**, 184-189.
- 4. A. Bodien and M. Beller, unpublished results.