Supporting information

Towards a continuous formic acid synthesis: a two-step carbon dioxide hydrogenation in flow

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Selection of methyl formate synthesis catalyst

A parallel study co-feeding methanol in a molar feed composition of $CO_2:H_2:MeOH = 4:4:1$ singled out Ag/Al_2O_3 as most promising catalyst for methyl formate synthesis. Out of nine catalysts evaluating three coinage metals Ag, Au, and Cu with three metal oxide supports SiO_2 , CeO_2 , and Al_2O_3 , the latter combined highest methanol conversion up to 8 % and a selectivity to methyl formate approaching 100 % at 200 °C and 300 bar (GHSV = 9000 h⁻¹). Shifting to excess from CO_2 -derived methanol over $Cu/ZnO/Al_2O_3$, the study attested the need for two consecutive packed-beds, rather than a physical admixture of both, to achieve highest methyl formate productivity. The reason for two separate reactors originated from the contrasting optimal temperatures for methanol synthesis on Cu (> 230 °C) and methyl formate synthesis on Ag (< 200 °C).

CO_2 hydrogenation efficiency

Helium factor

A helium factor f'_{He} is introduced based on the inert internal standard He premixed to the H₂ gas, in order to correct for the absence of water in the GC analysis.

$$n_{\mathrm{He},0} = n_{\mathrm{He}}$$

Dividing by the total amount of moles in the feed before reaction,

$$\frac{n_{\mathrm{He},0}}{n_{tot,0}} = \frac{n_{\mathrm{He}}}{n_{tot,0}} \cdot \frac{n_{tot}'}{n_{tot}'}$$

where n'_{tot} accounts for the reduction in total mole number stemming from the loss of water in analysis.

$$n'_{tot} = n_{tot} - n_{\rm H_2O}$$

 $x_{{\rm He},0} = x'_{\rm He} \cdot \frac{n'_{tot}}{n_{tot,0}}$

The helium factor $f_{\rm He}^{\prime}$ is obtained by reformulating,

$$f'_{\rm He} = \frac{n'_{tot}}{n_{tot,0}} = \frac{x_{\rm He,0}}{x_{\rm He}}$$

Conversion

The conversion X_i of a component *i* defines the fraction of the converted amount of component *i* in relation to the total amount of component *i* fed to the reaction at time t = 0. The conversion is calculated for the reactants of CO₂ and H₂ in terms of molar fractions x_i obtained from GC chromatograms.

$$X_{i} = \frac{x_{i,0} - x'_{i} \cdot f'_{\text{He}}}{x_{i,0}}$$

where $x_{i,0}$ is the mole fraction in the feed at room temperature, x_i the steady-state mole fraction at reaction temperature.

Selectivity

In case of multiple products formed in the reactive process, the selectivity S defines the amount of a specific product species p formed relative to the total amount of reactant i consumed.

$$S_{p,i} = \frac{x_p - x_{p,0}}{x_{i,0} - x_i} \frac{|\nu_i|}{|\nu_p|}$$

Because the water formed during hydrogenation is not quantified by GC, only the selectivities of the carbon-containing products are evaluated on the basis of the amount of carbon converted X_C .

$$X_C = f'_{\text{He}}(\sum_{j}^{N} x'_{p,j} \cdot r_{p,j})$$

where r_p stands for the number of carbon atoms contained in a molecule of product j.

The carbon-selectivity reads then

$$S_{p,C} = \frac{x'_p \cdot r_p \cdot f'_{He}}{X_C}$$

Space time yield

The space time yield Y is used as measure to quantify and compare the amount of a product p produced normalised per amount of catalyst and per unit of time. It is calculated on the basis of the CO₂ conversion and selectivities, and considers the mass of catalyst used as well as the residence time in the reactor.

$$Y_p = \frac{\dot{n}_{\rm CO_2,0} \cdot X_C \cdot S_{p,C}}{m_{cat}} \qquad \left[\frac{\rm mmol}{\rm g \cdot h}\right]$$

GC chromatograms of reaction effluent

The chromatograms of the FID and TCD channels of a typical reaction effluent are represented below with the identified products labelled and the new carbonated product labelled as unidentified.



Figure 1: Chromatogram of the FID channel with enlarged sections to amplify the features originating from the products in comparison to the large peak of CO_2 . DME, methanol and methyl formate are calibrated products while the weak peak labelled as unidentified represents the new carbonated product, which we believe originated from the decomposition of CO_2 -derived formic acid.

NMR spectrum of reaction effluent

The 1H-NMR analysis was measured with a Bruker Advance III 300 MHz (7.0 T) spectrometer. All proton chemical shifts are referenced to the residual solvent resonance of dimethyl sulfoxide-d₆ ($\delta = 2.50 \, ppm$). Data are reported as chemical shifts. Two characteristic peaks were observed in d-DMSO. One represents methanol ($\delta = 3.16 \, ppm$) while the other represents formates originating either from methyl formate or from formic acid ($\delta = 8.48 \, ppm$) reacting in KOH. Although the time span between sampling and actual NMR analysis was kept as short as possible, it could not be reduced sufficiently to reliably rule out the



Figure 2: Chromatogram of the TCD channel with enlarged sections to amplify the features originating from CO in comparison to the large peaks of H_2 and the internal standard He.

contribution from methyl formate.



Figure 3: 1H-NMR spectrum of the gaseous reactor effluent was bubbled in a 1 M KOH(aq) solution.