Supporting information

Stepping stones in CO$_2$ utilization: Optimizing the formate to oxalate coupling reaction using response-surface modeling

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Number of pages: 67

Number of figures: 34

Number of tables: 32
Experimental

General

All chemicals (potassium formate, potassium oxalate, potassium carbonate, potassium hydroxide, silica, carbon (Norit SX Plus 1G), iron powder, nickel powder, NaCl) were obtained from commercial suppliers (Sigma-Aldrich®). For the reaction it is crucial that no water is present in the chemicals and they are stored in a dry environment.

Preparation reaction mixtures

Potassium formate was dried in a vacuum oven at 135 °C for 24 hours and transferred to the glovebox. All other chemicals were pre-heated in an oven at 200 °C to remove the water and then transferred to the glovebox with an atmosphere of argon.

Batch preparations

Design 1: Catalysts

For the first design, different catalysts were tested for their influence on the FOCR. Reaction mixtures of 1.500 g of dry potassium formate and 5% wt. (0.075 g) catalyst were mixed and ground
in a mortar to receive a homogeneous mixture. Portions of 300 mg were transferred to a glass vial with a plastic septum cap.

**Design 2: Poisons**

For the second design different poisons were tested with one of the most commercial used catalyst (KOH). Therefore, reaction mixtures of 1.5000 g of dry potassium formate, 5% wt. (0.0750 g) KOH and 5% wt. (0.0750 g) possible poisons were mixed and ground in a mortar to receive a homogeneous mixture. Portions of 300 mg were transferred to a glass vial with a plastic septum cap.

**Design 3: Atmosphere**

For the third design different atmospheres were tested to analyse which is the best atmosphere for the FOCR with catalyst KOH. For this, reaction mixtures with 1.5000 g of dry potassium formate and 5% wt. (0.0750 g) KOH were mixed and ground in a mortar to receive a homogeneous mixture. Portions of 300 mg were transferred to a glass vial with a plastic septum cap.

**Response Surface Models**
For the RSM, large batches with different amounts of catalyst (KOH) were prepared. The different amounts of KOH in the sample are 2.25%, 3.5%, 6%, 8.5% and 9.75% wt. Portions of 300 mg were transferred to a glass vial with a plastic septum cap.

Reactions

Glass vials of 7.0 mL were used for the reaction. These vials were pre-dried overnight in an oven at 200 °C and transferred in the glove box. Then the vials were filled with 300 mg of the batch mixtures. The reaction vials were transferred outside the glove box. During the reaction the flows were measured by a Brooksmite Purgemeter using the tube R-2-15-AA with a glass ball and the heating was regulated with a high-power heating element connected controlled via PID.

For the first three designs, several numerical factors were unchanged, but the categorical factors were varied. The numerical factors for these designs were temperature (400° C), flow rate (25 mL/min), catalyst loading (5 % wt.), reaction time (8 minutes) and heating rate (150° C). The reaction vials for the designs were placed in the heating element for 11 minutes to allow reaction at 400°C for 8 minutes given the heating rate for the mixture is then 150 °C/min. Afterwards, the
reactor was removed from the heating element, the gas lines were disconnected, and the vial was cooled rapidly.

For the RSM models the numerical factors were varied and the categorical factors remained unchanged for all the reactions. The numerical factors that were varied were reaction temperature, reaction time, catalyst loading and flowrate (volume exchange per minute). All experiments were performed in random order.

**IR characterization**

The products were analysed using IR spectroscopy. The solid mixtures obtained during the reaction were dissolved in 3.0 mL deionized water with the use of a sonicator. We used a liquid transmission IR cell and measure absorbance. After each measurement the cell was flushed with deionized water to flush out all the previous sample and then the next sample was measured.

In an IR spectrum the peaks of carbonate, formate and oxalate overlap, see Figure S1. Therefore an IR estimation method was developed which is based on the Lambert-Beer law and the fact that the analyte concentration depends on the linearity of the absorbance intensity. Even though the peaks in the IR spectra overlap, the absorption patterns differ for all compositions. For this reason,
the combined spectrum can be deconvoluted into its individual components and the molar concentrations of the species can be evaluated. The spectra were examined in the 1250 – 1400 cm\(^{-1}\) wavenumber range and then fitted with simulated spectrum. The algorithm that was used for the analysis method is based on a Limited-memory BFGS algorithm which is also used for parameter estimation in computational learning.

Figure S1: IR spectra of the main components of the FOCR.
Calculations

The conversion of formate consumed during the reaction is calculated from the formate remaining in the obtained solid after reaction. Oxalate yield is a measure combining the conversion of formate and the selectivity towards the production of oxalate in the reaction. It is calculated from the molar fraction of oxalate and the remaining formate in the solid obtained in the reaction. Carbonate yield expresses the same as oxalate yield but for the most common side-product carbonate. The carbon balance serves as an indication of whether any carbon is lost during the reaction in the form of gaseous or non-soluble elemental carbon contained in the solid obtained in the reaction.

In the IR estimation method, the molarity of the sample for oxalate, carbonate and formate were obtained. Conversion was calculated using Eq. S1.

\[
Conversion = \frac{N(\text{formate}_\text{start}) - N(\text{formate}_\text{unreacted})}{N(\text{formate}_\text{start})}
\]  
(Eq. S1)

The calculations for the selectivity of the conversion on oxalate, carbonate or others are described in Eq. S2 to Eq. S4.
Selectivity oxalate = \frac{N(\text{oxalate})}{\frac{1}{2}(N(\text{formate}_\text{start}) - N(\text{formate}_\text{unreacted}))} \quad (\text{Eq. S2})

Selectivity carbonate = \frac{N(\text{carbonate})}{N(\text{formate}_\text{start}) - N(\text{formate}_\text{unreacted})} \quad (\text{Eq. S3})

Selectivity_{\text{others}} = \frac{N(\text{formate}_\text{start}) - N(\text{formate}_\text{unreacted}) - 2 \times N(\text{oxalate}) - N(\text{α})}{N(\text{formate}_\text{start}) - N(\text{formate}_\text{unreacted})} \quad (\text{Eq. S4})

The conversion multiplied times the selectivity will lead to the yield of the product as in Eq. S5.

The yield of carbonate was calculated with the same formula.

\text{Yield Oxalate} = \text{Conversion} \times \text{Selectivity}_{\text{oxalate}} \quad (\text{Eq. S5})

The carbon balance explains how much of the carbon is lost during the reaction. If carbon is lost during the reaction. The calculations for the carbon balance are presented in Eq. S7.

\text{Carbon balance}_{\text{total}} = \frac{2M(\text{oxalate}) + N(\text{carbonate}) + N(\text{formate}_\text{unreacted})}{N(\text{formate}_\text{start})} \quad (\text{Eq. S7})
Categorial design 1 – catalysts

Oxalate yield, carbon balance, conversion and selectivity for the test of different catalysts are shown in figure S2. Each catalyst test was performed in duplicates and random order to ensure statistically relevant results. For each catalyst 5 weight % loading was used to convert potassium formate in a nitrogen atmosphere with a flow of 25 mL/min (corresponding to 3.5 reactor volume exchanges per minute) at a temperature of 400 °C for 8 minutes.

The oxalate yield without any catalyst is below twenty percent due to an overall low conversion. Water as a catalyst entirely stops the FCR and the conversion into other chemicals. Even when the formate is converted with water as a catalyst, the selectivity is mainly towards carbonate. The carbon balance is also low for water, meaning that carbon atoms are converted into something else that we did not analyse and is considered undesirable. For the other catalyst (glass, SiO$_2$, iron, nickel, carbon, potassium carbonate, potassium oxalate and NaCl) used in this experiment, the conversion of formate is low. The selectivity towards oxalate is below 50% for all of them, leading to low oxalate yields below 20%. We conclude, that amongst the proposed catalyst, KOH is the
most suitable catalyst for the FCR. It favours high conversion with good selectivity towards oxalate. Hence, we decided to use KOH as a catalyst for the rest of the project.

Figure S2: Results of design 1 Catalysts, where a) oxalate yield, b) carbon balance, c) conversion, and d) selectivity.

Categorial design 2 – poisons

The effect of potential poisons reported for in literature for the formate coupling reaction on oxalate yield, carbon balance, conversion and selectivity are shown in figure S3. Each poison test

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was performed in duplicates and random order to ensure statistically relevant results. KOH was used as catalyst with a 5 weight % loading to convert potassium formate in a nitrogen atmosphere with a flow of 25 mL/min (corresponding to 3.5 reactor volume exchanges per minute) at a temperature of 400 °C for 8 minutes. Each potential poison was added at 5 weight % loading.

We observe that water, silica and carbon significant influence on the oxalate yield. The conversion and selectivity towards oxalate as well as the oxalate yield are decreased. The addition of water and silica strongly affects the conversion whilst the addition of carbon causes both the decrease in conversion and shift towards carbonate instead of oxalate formation. We suggest an influence of the morphology of the material which in the case of SiO$_2$ and Carbon is a puffy powder and a therefor good insulator. The supply of heat is hindered and therefor the apparent reaction temperature is decreased causing a lower conversion. Potassium carbonate and potassium oxalate have a significantly small negative influence on the FCR with KOH. The conversion for these two is similar but the selectivity towards oxalate decreased slightly. NaCl, glass, iron or nickel do not influence the selectivity of the FCR with KOH. For NaCl and glass, the same can be observed for the conversion of formate in the reaction. However, iron and nickel do increase the conversion of
formate and therefore lead to a higher oxalate yield. The carbon balance of all the poisons is high and an only minor amount of carbon is lost during the reaction. We conclude that water, silica and carbon have a poisonous effect on FCR.

Figure S3: Results of design 2 Poisons, where a) oxalate yield, b) carbon balance, c) conversion, and d) selectivity.

Categorial design 3 – Atmosphere

Various atmospheres including carbon dioxide, carbon monoxide, nitrogen, argon, hydrogen, air and steam have been proposed as either suitable or detrimental to the reaction performance. Each
atmosphere test was performed in duplicates and random order to ensure statistically relevant results. KOH was used as catalyst with a 5 weight % loading to convert potassium formate at a gas flow of 25 mL/min (corresponding to 3.5 reactor volume exchanges per minute) at a temperature of 400 °C for 8 minutes. The effects of the tested atmospheres on oxalate yield, carbon balance, conversion and selectivity are shown in figure S4.

We observe that CO₂ prevents conversion almost fully and only carbonate is formed. In carbon monoxide the conversion is still low but the selectivity towards oxalate is higher. This is in line with the observations of Górski et al. for carbon monoxide, yet they did observe oxalate formation at lower levels using CO₂.² Air and hydrogen behave similarly as the inert gases, argon and nitrogen. Other than suggested in literature, the oxygen in air did not react with the intermediate. A possible explanation for this effect can be that the air which is used is dry and therefore the moisture in air was really the poison in previous experiments. Dry air is still not desirable as an atmosphere because there was hydrogen produced during the reaction, which is highly valuable but cannot easily be subtracted from air and forms explosive mixtures with the oxygen contained in air. Nitrogen atmospheres lead to the highest conversions with high selectivity to oxalate. Formate
conversion in hydrogen shows high conversion, the highest selectivity towards oxalate and no selectivity to carbonate. During the reaction hydrogen is produced. Hence using hydrogen as purge gas allows for a separation free product harvest. We concluded that nitrogen and hydrogen are the most suitable atmospheres.

Figure S4: Results of design 3 Atmosphere, where a) oxalate yield, b) carbon balance, c) conversion, and d) selectivity.

Numerical factor – Purging and the effect of Volume exchange
Due to the scarcity of information of purging rates used in literature we first established a range in which to test the effect of purging in the response surface models. The chosen parameter limits were mainly determined by the available reactor configuration. We kept the remaining reaction conditions constant at 400 °C, 30 minutes reaction time and a catalyst loading of 6 weight percent. In figure S5A we can see that purging has a positive effect on the oxalate yield which is pronounced especially for lower purging rates. This improvement of oxalate yields coincides with the increase in conversion and the slight decrease of carbonate production with increasing purging. The levelling out of the improvement on oxalate yield in the chosen range indicates that the initially chosen range should be sufficient to estimate the overall effect and importance of purging in the formate coupling reaction. We conclude that purging the reaction benefits the oxalate yield with increasing gas-flow but the incremental improvements level-off.
Figure S5: Test of influence and appropriate purging range for formate coupling in nitrogen atmosphere. The effect of purging is expressed in exchanges of the full reactor volume per minute. The figure shows the influence of purging on the four responses oxalate yield (A), carbonate yield (B), conversion (C), and selectivity (D).

Response surface model 1 – Nitrogen as atmosphere

For our response surface model (RSM), we use a central composite design. This allows the development of quadratic models including linear, quadratic and two-factor interaction terms. Each datapoint was collected in duplicate and for the central point six replicates were performed. All experiments were performed in total random order without using blocks. Overall, this leads to 53
individual experiments for the whole model. We use an alpha of 1.5 to allow for even numbers for
each parameter. In total we included four factors (A-D) in the model all of which are numeric
continuous types. The design space for temperatures (A) was 300 to 500°C, when using a model
with $a = 1.5$ this leads to a minimum value of 250 °C and a maximum value of 550 °C. The details
for remaining parameters purging (B), catalyst loading (C) and reaction time (D) and are listed in
Table S2. As responses we consider the conversion of formate, oxalate yield, carbonate yield and
the overall carbon balance calculated using the formulas described above. All responses are
measured are reported as a fraction of 1. The minimum, maximum and mean values are reported
in Table S3.

To analyse the RSM we use Design-Expert software supplied by Stat-Ease Inc. The Design-
Expert software by default performs regression computations using the coded scale where the low
setting for each factor is set to -1 and the high set to +1. This allows to interpret and compare the
influence of each model term similarly as the reported coefficient estimates are obtained using the
same scale.\textsuperscript{3}
As a measure of trustworthiness and quality of the model we present here mainly R² value and discuss agreement between predicted and adjusted R². Another measure we use and discuss is adequate Precision which is a signal-to-noise ratio. It compares the range of the predicted values at the design points to the average prediction error. During the model-building process we check cook-distances, DFFITS and DFBETA to ensure a high-quality model but decided not to present these results here in sight of concision. For detailed explanations of the used terms refer to the textbook ‘Response Surface Methodology’. ³

For the analysis, we first fitted a model with the full quadratic models including linear, two-factor interactions and quadratic terms. We did not transform the acquired data prior to the model-building. We excluded the presence of higher-order factors and non-gaussian data distribution by comparing non-transformed model results with a square-root pre-processed model. To improve the model and extract the true influential model parameters we reduced the model by performing a backward exclusion using the p-value as discriminating criterium. Only model parameters with a p-value lower than 0.01 ware considered in the reduced model. This corresponds to a strict confidence interval of 99%. For all four models we observe an improved overall F-value, and better
agreement between the calculated and adjusted $R^2$ value whilst expectedly reducing the apparent $R^2$ value due to reduced overfitting by exclusion of non-significant parameters.

Table S1: Overview of build information for the response surface model with nitrogen atmosphere

| Study Type          | Randomized Response Surface |
|---------------------|-----------------------------|
| Design Type         | Central Composite           |
| Design Model        | Quadratic                   |
| Runs                | 53 runs, no blocks          |

Table S2: Numerical continuous factors used in the RSM with nitrogen as atmosphere

| Factor               | Units                     | Minimum | Maximum  | Coded Low | Coded High | Mean  | Std. Dev. |
|----------------------|---------------------------|---------|----------|-----------|------------|-------|-----------|
| Temperature (A)      | °C                        | 250.00  | 550.00   | -1 ↔ 300.00 | +1 ↔ 500.00 | 400.00| 88.80     |
| Purging (B)          | ml/min (vol. ex. /min)   | 1 (0.15)| 25 (3.5) | -1 ↔ 5.00  | +1 ↔ 21.00  | 13.00| 7.10      |
| Catalyst loading (C) | wt.%                      | 2.25    | 9.75     | -1 ↔ 3.50  | +1 ↔ 8.50   | 6.00 | 2.22      |
| Reaction time (D)    | min                       | 1.00    | 60.00    | -1 ↔ 10.00 | +1 ↔ 50.00  | 30.50| 17.46     |
Table S3 Responses and their obtained values in the RSM in nitrogen atmosphere:

| Response             | Units | Observations | Minimum | Maximum | Mean  | Std. Dev. | Ratio  |
|----------------------|-------|--------------|---------|---------|-------|-----------|--------|
| Conversion           | %     | 53.00        | 0.063   | 1       | 0.73  | 0.34      | 15.75  |
| Oxalate yield        | %     | 53.00        | 0.014   | 0.847   | 0.49  | 0.23      | 62.65  |
| Carbonate yield      | %     | 53.00        | 0.011   | 0.380   | 0.13  | 0.09      | 34.17  |
| Carbon balance       | %     | 53.00        | 0.674   | 1.009   | 0.89  | 0.08      | 1.50   |

Analysis: Conversion in nitrogen atmosphere

The results we receive for the conversion of formate in nitrogen atmosphere are shown for the range of each factor in figure S6 below. Note, that due to the nature of the central composite design the values for the three remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in figure S6A, has the clearest trend of all factors and the conversion increases with increasing temperature. For the reaction time (figure S6B) and purging (figure S6D), expressed as volume exchange, the conversion rate seems separated in two of lower and higher conversion regimes. This indicates the presence of interactions between two factors. Generally, the conversion appears to be increasing with long reaction times and higher purging rates. The conversion appears independent of catalyst
loading as the achieved conversions are equally spread through the design space. The potential presence of interacting factors justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each term's influence can be estimated.

Figure S6 Shows the raw data obtained for conversion relative to all four factors temperature (A), reaction time (B), catalyst loading (C) and purging (D).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high R² value of
0.97 meaning that 97% of the results can be explained with the variables offered in our experiments.

This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the conversion. The Predicted $R^2$ of 0.9370 is in reasonable agreement with the Adjusted $R^2$ of 0.9551 and adequate precision measures 26.49 indicating that this model can be used to navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in figure S7A.

![Figure S7: Predicted versus actual values for conversion in the DoE with nitrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.](image)

The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for formate conversion in nitrogen atmosphere are shown in Table S4. For the full quadratic model, it becomes apparent that catalyst loading has no significant influence on the conversion. Only interactions between temperature and purging as well as reaction times are significant
interacting terms. Quadratic terms of temperature and reaction time are significant. All of which exhibit p-values higher than 0.01. Using this cut-off, we can realize that A, B, D, AB, AD, A², D² are significant model terms. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for formate conversion in nitrogen atmosphere are shown in Table S5. The overall model F-value of 79.96 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 150.48 is greatly improved compared to the full quadratic model implies the model is significant. The improved reduced model containing only the most significant factors has a lower R² value and only 95.9% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.9527) and Predicted R² (0.9425) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 26.5 to 33.7. Compared to the full quadratic model, the actual vs. predicted values have moved closer to the convergence line as shown in figure XB.

*Table S4: Full results of full quadratic RSM for formate conversion in nitrogen atmosphere*

| Source  | Sum of Squares | df | Mean Square | F-value | p-value |
|---------|----------------|----|-------------|---------|---------|
| Model   | 5.71           | 14 | 0.4077      | 79.96   | < 0.0001 |
| Factor               | Coefficient | DF | Coefficient | Sum of Squares |
|----------------------|-------------|----|-------------|----------------|
| A-Temperature        | 4.06        | 1  | 4.06        | 796.66         | < 0.0001       |
| B-Purging            | 0.1013      | 1  | 0.1013      | 19.88          | < 0.0001       |
| C-Catalyst loading   | 0.0015      | 1  | 0.0015      | 0.30           | 0.5861         |
| D-Reaction time      | 0.4644      | 1  | 0.4644      | 91.09          | < 0.0001       |
| A*B                  | 0.0620      | 1  | 0.0620      | 12.15          | 0.0013         |
| A*C                  | 0.0023      | 1  | 0.0023      | 0.45           | 0.5061         |
| A*D                  | 0.2673      | 1  | 0.2673      | 52.44          | < 0.0001       |
| B*C                  | 0.0065      | 1  | 0.0065      | 1.28           | 0.2656         |
| B*D                  | 0.0029      | 1  | 0.0029      | 0.57           | 0.4549         |
| C*D                  | 0.0016      | 1  | 0.0016      | 0.30           | 0.5813         |
| A²                   | 0.5391      | 1  | 0.5391      | 105.75         | < 0.0001       |
| B²                   | 0.0240      | 1  | 0.0240      | 4.72           | 0.0362         |
| C²                   | 0.0096      | 1  | 0.0096      | 1.88           | 0.1788         |
| D²                   | 0.1534      | 1  | 0.1534      | 30.10          | < 0.0001       |
| Residual             | 0.1937      | 38 | 0.0051      |                |                |
| Lack of Fit          | 0.1425      | 10 | 0.0142      | 7.78           | < 0.0001       |
| Pure Error           | 0.0513      | 28 | 0.0018      |                |                |
| Cor Total            | 5.90        | 52 |             |                |                |
Table S5: Full results of improved RSM for formate conversion in nitrogen atmosphere

| Source       | Sum of Squares | df | Mean Square | F-value | p-value |
|--------------|----------------|----|-------------|---------|---------|
| Model        | 5.66           | 7  | 0.8084      | 150.48  | < 0.0001|
| A-Temperature| 4.06           | 1  | 4.06        | 755.96  | < 0.0001|
| B-Purging    | 0.1013         | 1  | 0.1013      | 18.86   | < 0.0001|
| D-Reaction time | 0.4644       | 1  | 0.4644      | 86.44   | < 0.0001|
| AB           | 0.0620         | 1  | 0.0620      | 11.53   | 0.0014  |
| AD           | 0.2673         | 1  | 0.2673      | 49.76   | < 0.0001|
| A²           | 0.5404         | 1  | 0.5404      | 100.59  | < 0.0001|
| D²           | 0.1541         | 1  | 0.1541      | 28.68   | < 0.0001|
| Residual     | 0.2418         | 45 | 0.0054      |         |         |
| Lack of Fit  | 0.1905         | 17 | 0.0112      | 6.12    | < 0.0001|
| Pure Error   | 0.0513         | 28 | 0.0018      |         |         |
| Cor Total    | 5.90           | 52 |             |         |         |

The coefficient estimate listed in Table S6 is a measure of how each of the terms effect the formate conversion when the terms value is changed. A positive value means the conversion increases with increasing term values vice-versa is the case for negative coefficients. As we use coded variables, their impact can be directly compared within the design-space. The combined
effect of each factor including their linear and quadratic terms are shown in figure S8. In the case of formate conversion in nitrogen atmosphere can see, that the linear term of temperature has the biggest effect on formate conversion, but the overall effect of temperature is dampened by its quadratic term and interaction with purging and reaction time. Longer reaction times and higher purging rates benefit the conversion too. All two-factor interactions and quadratic terms act as dampening terms towards higher values. From a chemical point of view, the increase of conversion with the increase of the factor values make sense as higher temperatures, longer reaction times and better removal of side-products by purging drive the reaction. Temperature is the main driver for the reaction to occur, and we observe a saturation of influence of temperature at higher values due to the high overall conversion which can only reach a maximum of 1. A longer time at given temperature increases the likeliness of the conversion. This effect is pronounced at lower reaction temperatures and the model reflects as can be seen in figure S8D. The effect of purging follows a linear development and positively contributes to higher conversions. The lack of benefit from higher catalyst loadings is unexpected as the presence of more catalytic species should have an impact on conversion especially at lower reaction times and lower temperatures.
Table S6: Estimated model coefficients for significant factors describing the model for formate conversion in nitrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor          | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF  |
|-----------------|----------------------|----|----------------|------------|-------------|------|
| Intercept       | 0.9195               | 1  | 0.0203         | 0.8787     | 0.9603      |      |
| A-Temperature   | 0.3147               | 1  | 0.0114         | 0.2917     | 0.3378      | 1.0000 |
| B-Purging       | 0.0497               | 1  | 0.0114         | 0.0267     | 0.0728      | 1.0000 |
| D-Reaction time | 0.1064               | 1  | 0.0114         | 0.0834     | 0.1295      | 1.0000 |
| AB              | -0.0440              | 1  | 0.0130         | -0.0701    | -0.0179     | 1.0000 |
| AD              | -0.0914              | 1  | 0.0130         | -0.1175    | -0.0653     | 1.0000 |
| A²              | -0.1623              | 1  | 0.0162         | -0.1948    | -0.1297     | 1.00 |
| D²              | -0.0866              | 1  | 0.0162         | -0.1192    | -0.0541     | 1.00 |

Figure S8: Influence of (A) Temperature, (B) Purging, (C) Catalyst loading and (D) Reaction time on the conversion of formate at medium values for the remaining factors in the reduced quadratic model. Note that catalyst loading is no-longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.
**Analysis Oxalate yield in nitrogen atmosphere**

The obtained oxalate yield from formate conversion in nitrogen atmosphere are shown for the full range of each factor in figure S10 below. Note, that due to the nature of the central composite design the values for the three remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in figure S10A, has the clearest trend of all factors and the oxalate yield appears to first increase until a reaction temperature of 400 °C after which it decreases again. For the reaction time (figure S10B)
and purging (figure S10D), expressed as volume exchange, the conversion rate seems separated in two of lower and higher oxalate yield regimes. This indicates the presence of interactions between two factors. Generally, the average oxalate yields appear to be increasing with long reaction times and higher purging rates. For increasing catalyst loading however no increase of average values is visible in figure S10C as the achieved conversions are equally spread through the design space. The potential presence of interacting factors and non-linear behaviour of oxalate yield justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.
Figure S10 Shows the raw data obtained for oxalate yield relative to all four factors temperature (A), reaction time (B), catalyst loading (C) and purging (D).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.93 meaning that 93% of the results can be explained with the variables offered in our experiments. This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the conversion. The Predicted $R^2$ of 0.8848 is in reasonable agreement with the Adjusted $R^2$ of 0.9123 and adequate precision measures 21.03 indicating that this model can be used to
navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in figure S11A.

The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for oxalate yields in nitrogen atmosphere are shown in Table S7. For the full quadratic model, it becomes apparent that catalyst loading has no significant influence on the oxalate yield. Only interactions between temperature and purging as well as reaction times are significant interacting terms. Quadratic terms of temperature and catalyst loading are significant. All of which exhibit p-values higher than 0.01. Using this cut-off, we can realize that A, B, D, AB, AD, BD, A², C² are significant model terms. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for oxalate yields in nitrogen atmosphere are shown in Table S8.
The overall model F-value of 39.64 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. As the linear terms for catalyst loading is clearly not significant, we do not include any other terms involving catalyst loading in the improved model. Hence, the quadratic term is not considered. With the improved model the overall model F-value of 75.00 is greatly improved compared to the full quadratic model. The improved reduced model containing only the most significant factors has a lower R² value and only 90.7% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.895) and Predicted R² (0.880) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 21.03 to 28.08. Compared to the full quadratic model, the actual vs. predicted values have moved closer to the convergence line as shown in figure S11B.

Table S7: Full results of full quadratic RSM for oxalate yield in nitrogen atmosphere

| Source           | Sum of Squares | df | Mean Square | F-value | p-value |
|------------------|----------------|----|-------------|---------|---------|
| Model            | 2.22           | 14 | 0.1586      | 39.64   | < 0.0001|
| A-Temperature    | 0.8605         | 1  | 0.8605      | 215.12  | < 0.0001|
| B-Purging        | 0.0991         | 1  | 0.0991      | 24.77   | < 0.0001|
| C-Catalyst loading| 0.0065        | 1  | 0.0065      | 1.63    | 0.2093  |
|                      |        | 1 |      |      |        |
|----------------------|--------|---|------|------|--------|
| D-Reaction time      | 0.2078 |   | 0.2078 | 51.94 | < 0.0001 |
| AB                   | 0.0721 |   | 0.0721 | 18.03 | 0.0001 |
| AC                   | 0.0002 |   | 0.0002 | 0.0496 | 0.8250 |
| AD                   | 0.3210 |   | 0.3210 | 80.25 | < 0.0001 |
| BC                   | 0.0000 |   | 0.0000 | 0.0063 | 0.9369 |
| BD                   | 0.0236 |   | 0.0236 | 5.89  | 0.0201 |
| CD                   | 0.0008 |   | 0.0008 | 0.1998 | 0.6574 |
| A²                   | 0.5942 |   | 0.5942 | 148.54 | < 0.0001 |
| B²                   | 0.0013 |   | 0.0013 | 0.3284 | 0.5700 |
| C²                   | 0.0319 |   | 0.0319 | 7.97  | 0.0075 |
| D²                   | 0.0038 |   | 0.0038 | 0.9535 | 0.3350 |
| Residual             | 0.1520 | 38 | 0.0040 |      |        |
| Lack of Fit          | 0.0894 | 10 | 0.0089 | 4.00  | 0.0018 |
| Pure Error           | 0.0626 | 28 | 0.0022 |      |        |
| Cor Total            | 2.37   | 52 |      |      |        |
Table S8: Full results of improved RSM for oxalate yield in nitrogen atmosphere

| Source      | Sum of Squares | df | Mean Square | F-value | p-value |
|-------------|----------------|----|-------------|---------|---------|
| Model       | 2.15           | 6  | 0.3586      | 75.00   | < 0.0001|
| A-Temperature| 0.8605        | 1  | 0.8605      | 179.97  | < 0.0001|
| B-Purging   | 0.0991         | 1  | 0.0991      | 20.72   | < 0.0001|
| D-Reaction time | 0.2078     | 1  | 0.2078      | 43.45   | < 0.0001|
| AB          | 0.0721         | 1  | 0.0721      | 15.08   | 0.0003  |
| AD          | 0.3210         | 1  | 0.3210      | 67.14   | < 0.0001|
| A²          | 0.5913         | 1  | 0.5913      | 123.65  | < 0.0001|
| Residual    | 0.2199         | 46 | 0.0048      |         |         |
| Lack of Fit | 0.1573         | 18 | 0.0087      | 3.91    | 0.0006  |
| Pure Error  | 0.0626         | 28 | 0.0022      |         |         |
| Cor Total   | 2.37           | 52 |             |         |         |

The coefficient estimate listed in Table S9 is a measure of how each of the terms effect the oxalate yield and the combined effect of each factor including their linear and quadratic terms are shown in figure S12. The linear term of temperature has the biggest effect on oxalate yield, but the overall effect of temperature is dampened by its quadratic term and interaction with purging and reaction time. Longer reaction times and higher purging rates benefit the conversion too. All two-factor
interactions and quadratic terms act as dampening terms towards higher values. From a chemical point of view, the increase of oxalate yields with the increase of the factor values makes sense as higher temperatures, longer reaction times and better removal of side-products by purging drive the reaction. Yet, above a certain temperature and with prolonged reaction times the formed oxalate decomposes which explains the decreasing oxalate yields for high temperatures and reaction times visible in the plot of the two-factor interaction in figure S13B. The effect of purging follows a linear development and positively contributes to oxalate yields. The lack of benefit from higher catalyst loadings is unexpected as the presence of more hydroxide should increase the likeliness of formate and oxalate decomposition towards carbonates which was reported to be more favourable compared to the decomposition of oxalate itself without the presence of hydroxide by Gorski.\textsuperscript{2} This finding indicates that the dominating decomposition pathway is indeed the decomposition of formed oxalate caused by high reaction temperatures and helped by long residence times in the latter. Temperature is the main driver for the reaction to occur and different reaction pathways are available depending on the temperature region. Through the investigated temperature range oxalate is formed, above 430°C a competing reaction or subsequent decomposition of formate is present.
The decrease in oxalate yield with increasing reaction time at high temperature (Figure S12B) indicates at least the presence of a subsequent decomposition reaction. Competing side-reactions occurring in parallel would not require longer reaction times to occur more pronounced. Unfortunately, the model does not turn out to present us with a local or global maximum for the oxalate yield as figure S13 shows. A combination of a lower reaction temperature with a longer reaction time promises improvements in the achievable oxalate yield.
Table S9: Estimated model coefficients for significant factors describing the model for obtained oxalate yields in nitrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor     | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|------------|----------------------|----|----------------|------------|-------------|-----|
| Intercept  | 0.7952               | 1  | 0.0152         | 0.7647     | 0.8257      |     |
| A-Temperature | 0.1449            | 1  | 0.0108         | 0.1231     | 0.1666      | 1.0000 |
| B-Purging  | 0.0492               | 1  | 0.0108         | 0.0274     | 0.0709      | 1.0000 |
| D-Reaction time | 0.0712            | 1  | 0.0108         | 0.0494     | 0.0929      | 1.0000 |
| AB         | -0.0475              | 1  | 0.0122         | -0.0721    | -0.0229     | 1.0000 |
| AD         | -0.1002              | 1  | 0.0122         | -0.1248    | -0.0756     | 1.0000 |
| A²         | -0.1697              | 1  | 0.0153         | -0.2004    | -0.1390     | 1.0000 |
Figure S12: Influence of (A) Temperature, (B) Purging, (C) Catalyst loading and (D) Reaction time on the oxalate yield of formate at medium values for the remaining factors in the reduced quadratic model. Note that catalyst loading is no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.

Figure S13: Contour-plots for oxalate yields development depending on (A) Temperature and Purging and (B) Temperature and Reaction time with reduced quadratic design.

Analysis Carbonate yield in nitrogen atmosphere
Carbonate yields obtained in nitrogen atmosphere are shown for the full range of each factor in figure S14 below. Note, that due to the nature of the central composite design the values for the three remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in figure S15A, has the clearest trend of all factors and the carbonate yield increase with increasing temperatures. For reaction times the carbonate yield appears to find its maximum at thirty minutes and then decrease again, yet the average distribution does not follow a clear trend. For catalyst loading and purge flow the carbonate yields appear to be relatively equally distributed on average. The potential presence of interacting factors and non-linear behaviour of carbonate yield especially for the term reaction time and temperature justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.
Figure S14 Shows the raw data obtained for carbonate yield relative to all four factors temperature (A), reaction time (B), catalyst loading (C) and purging (D).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.92 meaning that 92% of the results can be explained with the variables offered in our experiments. This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the carbonate yield. The Predicted $R^2$ of 0.8431 is in reasonable agreement with the Adjusted $R^2$ of 0.8905 and adequate precision measures 18.07 indicating that this model can be used to navigate the design space. An equal and continuous distribution of the data through the
space and close correlation between predicted and actual values is achieved as shown in figure S15A.

Figure S15: Predicted versus actual values for carbonate yield in the DoE with nitrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.

The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for carbonate yield in nitrogen atmosphere are shown in Table S10. For the full quadratic model, it becomes apparent that catalyst loading, and purging have no significant influence on the carbonate yield. No interacting terms are present for the formation of carbonate. The Quadratic terms of temperature is significant. All of which exhibit p-values higher than 0.01. Using this cut-off, only A, D, D² are significant model terms. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for carbonate yield in nitrogen atmosphere are shown in Table S11. The overall model F-value of 31.20 implies the model is
significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With
the improved model the overall model F-value of 153.26 is greatly improved compared to the full
quadratic model. The improved reduced model containing only the most significant factors has a
similar $R^2$ value and 90.7% of the results can be explained with the variables offered in our
experiments. Yet, the closer resemblance between $R^2$, Adjusted $R^2$ (0.899) and Predicted $R^2$ (0.889)
indicates a higher quality prediction which is also apparent from the adequate Precision which
increased from 18.07 to 35.32. Compared to the full quadratic model, the actual vs. predicted values
have moved closer to the convergence line as shown in figure S15B.

Table S10: Full results of full quadratic RSM for carbonate yield in nitrogen atmosphere

| Source           | Sum of Squares | df  | Mean Square | F-value | p-value |
|------------------|----------------|-----|-------------|---------|---------|
| Model            | 1.04           | 14  | 0.0742      | 31.20   | < 0.0001|
| A-Temperature    | 0.9313         | 1   | 0.9313      | 391.63  | < 0.0001|
| B-Purging        | 0.0002         | 1   | 0.0002      | 0.0910  | 0.7645  |
| C-Catalyst loading | 0.0012    | 1   | 0.0012      | 0.5035  | 0.4823  |
| D-Reaction time  | 0.0371         | 1   | 0.0371      | 15.61   | 0.0003  |
| AB               | 0.0010         | 1   | 0.0010      | 0.4044  | 0.5286  |
| AC               | 0.0042         | 1   | 0.0042      | 1.79    | 0.1893  |
| AD               | 5.773E-06      | 1   | 5.773E-06   | 0.0024  | 0.9610  |


|      |      |      |      |      |
|------|------|------|------|------|
| BC   | 0.0043 | 1 | 0.0043 | 1.81 | 0.1865 |
| BD   | 0.0003 | 1 | 0.0003 | 0.1066 | 0.7458 |
| CD   | 0.0008 | 1 | 0.0008 | 0.3405 | 0.5630 |
| A²   | 0.0038 | 1 | 0.0038 | 1.61 | 0.2120 |
| B²   | 0.0026 | 1 | 0.0026 | 1.10 | 0.3003 |
| C²   | 1.833E-06 | 1 | 1.833E-06 | 0.0008 | 0.9780 |
| D²   | 0.0517 | 1 | 0.0517 | 21.76 | < 0.0001 |
| Residual | 0.0904 | 38 | 0.0024 | |
| Lack of Fit | 0.0295 | 10 | 0.0030 | 1.36 | 0.2490 |
| Pure Error | 0.0608 | 28 | 0.0022 | |
| Cor Total | 1.13 | 52 | | |
Table S11: Full results of reduced RSM for carbonate yield in nitrogen atmosphere

| Source            | Sum of Squares | df | Mean Square | F-value | p-value |
|-------------------|----------------|----|-------------|---------|---------|
| Model             | 1.02           | 3  | 0.3401      | 153.26  | < 0.0001|
| A-Temperature     | 0.9313         | 1  | 0.9313      | 419.69  | < 0.0001|
| D-Reaction time   | 0.0371         | 1  | 0.0371      | 16.73   | 0.0002  |
| D²                | 0.0519         | 1  | 0.0519      | 23.37   | < 0.0001|
| Residual          | 0.1087         | 49 | 0.0022      |         |         |
| Lack of Fit       | 0.0479         | 21 | 0.0023      | 1.05    | 0.4450  |
| Pure Error        | 0.0608         | 28 | 0.0022      |         |         |
| Cor Total         | 1.13           | 52 |             |         |         |

The coefficient estimate listed in Table S12 is a measure of how each of the terms effect the carbonate yield and the combined effect of each factor including their linear and quadratic terms are shown in Figure S16. Only three terms have been found significant and the linear term of temperature has the biggest effect on carbonate yield. The catalyst loading Purge flow has no impact on the carbonate yield in this model. The role of reaction times has a linear and quadratic nature. The linear term benefits the formation of carbonate, yet the quadratic term, which has a higher coefficient, dampens the effect. This leads to a model in which an increasing reaction time,
the carbonate yield decreases. From a chemical point of view this is counter intuitive at first. As the formation at carbonate is mainly occurring at higher temperatures due to the decomposition. A longer residence time at these high temperatures should therefore benefit the decomposition to carbonate. However, carbonate itself can decompose further to elemental carbon and at high temperatures. In our design space this reaction only occurs at relatively low rates due to insufficient temperatures but is favoured by relatively long reaction times. Overall, our model does not describe the formation of carbonate in detail due to the choice of the design space chosen to find optimal conditions for high oxalate yields. Yet, chemically the results are sounds and point to the presence of a cascade of decomposition reactions of the formed oxalate first to carbonate and later to elemental carbon or gaseous carbonous substances do not present in the obtained solid after the reaction. The absence of a significant effect of catalyst loading indicates that the main pathway for oxalate or formate decomposition does not include a reaction where hydroxide is consumed as a reactant as suggested by Gorski.²

Table S12: Estimated model coefficients for significant factors describing the model for obtained carbonate yields in nitrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.
| Factor         | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|----------------|----------------------|----|----------------|------------|-------------|-----|
| Intercept      | 0.3647               | 1  | 0.0103         | 0.3439     | 0.3854      |     |
| A-Temperature  | 0.1507               | 1  | 0.0074         | 0.1359     | 0.1655      | 1.0000 |
| D-Reaction time| 0.0301               | 1  | 0.0074         | 0.0153     | 0.0449      | 1.0000 |
| D²             | -0.0503              | 1  | 0.0104         | -0.0711    | -0.0294     | 1.0000 |
Figure S16: Influence of (A) Temperature, (B) Purging, (C) Catalyst loading and (D) Reaction time on the Carbonate yield of formate at medium values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and purging are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.

Analysis Carbon balance in nitrogen atmosphere

The carbon balances obtained in nitrogen atmosphere are shown for the full range of each factor in Figure S17 below. Note, that due to the nature of the central composite design the values for the three remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in Figure S17A, has the only clear trend of all factors and the carbon balances decreases with increasing temperatures. For the remaining factors no trend of any influence on the carbon balance is visible as the date appears equally
distributed. The potential presence of non-linear behaviour of carbon balance and small linear factors invisible in the raw data especially for the term reaction time and temperature justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.

Figure S17 Shows the raw data obtained for carbonate yield relative to all four factors temperature (A), reaction time (B), catalyst loading (C) and purging (D).
The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.77 meaning that 77% of the results can be explained with the variables offered in our experiments. This indicates that there might be more factors, not considered or controlled in our experiments which influence the carbon balance. The Predicted $R^2$ of 0.5764 is in reasonable agreement with the Adjusted $R^2$ of 0.58332 and adequate precision measures 11.72 indicating that this model can be used to navigate the design space. Yet, the model for the carbon-balance is the worst out of the four models. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in Figure S18A.

Figure S18: Predicted versus actual values for carbon balance in the DoE with nitrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.
The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for carbon balance in nitrogen atmosphere are shown in Table S13. For the full quadratic model, it becomes apparent that catalyst loading, and purging have no significant influence on the carbon balance. No interacting terms affect the carbon balance. The quadratic term of temperature is significant. All of which exhibit p-values higher than 0.01. Using this cut-off, only Temperature (A) and reaction time (D) are significant model terms. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for the carbon balance in nitrogen atmosphere are shown in Table S14. The overall model F-value of 9.01 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 36.51 is greatly improved compared to the full quadratic model. The improved reduced model containing only the most significant factors has a similar R² value and 59.36% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.5773) and Predicted R² (0.5465) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 11.72 to 16.10. Compared to the full quadratic model, the actual vs. predicted
values have not moved closer to the convergence line as shown in Figure S19B due to the simplicity and potential missing influences on the carbon balance not considered in our model.

Table S13: Full results of full quadratic RSM for carbon balance in nitrogen atmosphere

| Source          | Sum of Squares | df | Mean Square | F-value | p-value |
|-----------------|----------------|----|-------------|---------|---------|
| Model           | 0.2512         | 14 | 0.0179      | 9.01    | < 0.0001|
| A-Temperature   | 0.1778         | 1  | 0.1778      | 89.29   | < 0.0001|
| B-Purging       | 0.0001         | 1  | 0.0001      | 0.0502  | 0.8240  |
| C-Catalyst loading | 0.0090      | 1  | 0.0090      | 4.51    | 0.0402  |
| D-Reaction time | 0.0162         | 1  | 0.0162      | 8.14    | 0.0070  |
| AB              | 0.0000         | 1  | 0.0000      | 0.0190  | 0.8912  |
| AC              | 0.0028         | 1  | 0.0028      | 1.39    | 0.2456  |
| AD              | 0.0017         | 1  | 0.0017      | 0.8487  | 0.3627  |
| BC              | 0.0020         | 1  | 0.0020      | 0.9845  | 0.3274  |
| BD              | 0.0009         | 1  | 0.0009      | 0.4491  | 0.5068  |
| CD              | 0.0008         | 1  | 0.0008      | 0.4040  | 0.5288  |
| A²              | 0.0013         | 1  | 0.0013      | 0.6327  | 0.4313  |
| B²              | 0.0249         | 1  | 0.0249      | 12.48   | 0.0011  |
| C²              | 0.0049         | 1  | 0.0049      | 2.44    | 0.1269  |
| D²              | 0.0084         | 1  | 0.0084      | 4.21    | 0.0472  |
Table S14: Full results of reduced RSM for carbonate yield in nitrogen atmosphere

| Source            | Sum of Squares | df | Mean Square | F-value | p-value |
|-------------------|----------------|----|-------------|---------|---------|
| Model             | 0.1940         | 2  | 0.0970      | 36.51   | < 0.0001|
| A-Temperature     | 0.1778         | 1  | 0.1778      | 66.92   | < 0.0001|
| D-Reaction time   | 0.0162         | 1  | 0.0162      | 6.10    | 0.0170  |
| Residual          | 0.1329         | 50 | 0.0027      |         |         |
| Lack of Fit       | 0.0787         | 22 | 0.0036      | 1.85    | 0.0626  |
| Pure Error        | 0.0542         | 28 | 0.0019      |         |         |
| Cor Total         | 0.3269         | 52 |             |         |         |

The reaction temperature by far has much larger impact on the carbon balance compared to the reaction time visible from the estimated coefficients for the factors shown in Table S15. Overall, we can see that the loss of carbon predominantly occurs at high temperatures and long reaction
times, which indicates a relatively slow decomposition of the formed products in these conditions. If the decomposition was faster, we would expect a higher influence of reaction time on the carbon balance. The fact that the decomposition and alteration of carbon balance only occurs in a relatively small part of the design-space explains the relatively poor model quality. In our case the goal was to study the influences on oxalate yield and not a precise description of the degradation of the formed oxalate. If this degradation was to be studied extensively, the design-space should be expanded towards higher temperatures and reaction times. Yet, as this expansion would decrease the prediction strengths of the model for oxalate yields, we did not incorporate higher reaction times and temperatures. For our purpose the insight in decomposition is sufficient.
Table S15: Estimated model coefficients for significant factors describing the model for carbon balance in nitrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor       | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|--------------|----------------------|----|----------------|------------|-------------|-----|
| Intercept    | 0.8860               | 1  | 0.0071         | 0.8718     | 0.9002      |     |
| A-Temperature| -0.0659              | 1  | 0.0081         | -0.0820    | -0.0497     | 1.0000 |
| D-Reaction time | -0.0199            | 1  | 0.0081         | -0.0361    | -0.0037     | 1.0000 |

Figure S19: Influence of (A) Temperature, (B) Purging, (C) Catalyst loading and (D) Reaction time on the carbon balance of formate at medium values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and purging are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.

Response surface model 2 – Hydrogen as atmosphere
For the second design with Hydrogen as atmosphere we use the same approach as described above for the design with Nitrogen as atmosphere. The only difference is the obliteration of purging rate as variable due to safety issues with high flows of hydrogen. We use a central composite design which allows the development of quadratic models including linear, quadratic and two-factor interaction terms. Each datapoint was collected in duplicate and for the central six replicates were performed, all experiments were performed in total random order without using blocks. Overall, this leads to 34 individual experiments for the whole model. We use an alpha of 1.5 to allow for even numbers for each parameter. In total we included three factors (A-C) in the model all of which are numeric continuous types. Temperatures (A) were varied from 300 to 500°C using a model with $a = 1.5$ this leads to a minimum value of 250 °C and a maximum value of 550 °C. The details for two remaining, reaction time (B) and catalyst loading (C) are listed in Table S17. As responses we consider the conversion of formate, oxalate yield, carbonate yield and the overall carbon balance. All responses are measured are reported as a fraction of 1. The minimum, maximum and mean values are reported in Table S18.

Table S16: Overview of build information for the response surface model in hydrogen atmosphere

| Study Type            | Randomized Response Surface |
|-----------------------|-----------------------------|

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| Design Type       | Central Composite |
|-------------------|--------------------|
| Design Model      | Quadratic          |
| Runs              | 34, no blocks      |

*Table S17: Numerical continuous factors used in the RSM in hydrogen atmosphere*

| Factor             | Units  | Minimum | Maximum | Coded Low | Coded High | Mean | Std. Dev. |
|--------------------|--------|---------|---------|-----------|------------|------|-----------|
| Temperature (A)    | °C     | 250.00  | 550.00  | -1 ↔ 300.00 | +1 ↔ 500.00 | 400  | 87.0      |
| Reaction time (B)  | min    | 1.00    | 60.00   | -1 ↔ 10.00  | +1 ↔ 50.00  | 30.5 | 17.1      |
| Catalyst loading (C) | wt.%  | 2.25    | 9.75    | -1 ↔ 3.50  | +1 ↔ 8.50  | 6.00 | 2.18      |
Table S18: Responses and their obtained values in the RSM in nitrogen atmosphere

| Response          | Units | Observations | Minimum | Maximum | Mean | Std. Dev. | Ratio |
|-------------------|-------|--------------|---------|---------|------|-----------|-------|
| Conversion        | %     | 34.00        | 0.242   | 1       | 0.83 | 0.25      | 4.13  |
| Oxalate yield     | %     | 34.00        | 0.009   | 0.919   | 0.52 | 0.32      | 102.11|
| Carbonate yield   | %     | 34.00        | 0.014   | 0.550   | 0.17 | 0.18      | 38.08 |
| Carbon balance    | %     | 34.00        | 0.553   | 1       | 0.85 | 0.17      | 1.81  |

**Analysis: Conversion in hydrogen atmosphere**

The results we receive for the conversion of formate in hydrogen atmosphere are shown for the range of each factor in Figure S20 below. Note, that due to the nature of the central composite design the values for the two remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in Figure S20A, has the clearest trend of all factors and the conversion increases on average with increasing temperature. For the reaction time (Figure S20B) the conversion rate seems separated in two of lower and higher conversion regimes. This indicates the presence of interactions between two factors. Generally, the conversion appears to be increasing with long reaction times. The conversion appears independent of catalyst loading as the achieved conversions are equally spread.
through the design space. The potential presence of interacting factors justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.

Figure S20 Shows the raw data obtained for conversion for all three factors temperature (A), reaction time (B) and catalyst loading (C).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.96 meaning that 96% of the results can be explained with the variables offered in our experiments.
This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the conversion. The Predicted R² of 0.9122 is in reasonable agreement with the Adjusted R² of 0.9422 and adequate precision measures 22.54 indicating that this model can be used to navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in Figure S21A.

![Predicted vs. Actual](image)

**Figure S21**: Predicted versus actual values for conversion in the DoE with hydrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.

The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for formate conversion in hydrogen atmosphere are shown in Table S19. For the full quadratic model, it becomes apparent that catalyst loading has no significant influence on the conversion. Only interactions between temperature and reaction times are significant interacting terms. Quadratic terms of temperature and reaction time are significant. All of which exhibit p-values
higher than 0.01. Using this cut-off, we realize that A, B, AB, A², B² are significant model terms.

The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for formate conversion in hydrogen atmosphere are shown in Table S20. The overall model F-value of 60.75 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 90.46 is greatly improved compared to the full quadratic model implies the model is significant. The improved reduced model containing only the most significant factors has a lower R² value and only 94.17% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.9313) and Predicted R² (0.9026) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 22.54 to 24.79.

Compared to the full quadratic model, the actual vs. predicted values have slightly moved closer to the convergence line as shown in Figure S21B.

Table S19: Full results of full quadratic RSM for conversion in hydrogen atmosphere

| Source           | Sum of Squares | df | Mean Square | F-value | p-value |
|------------------|----------------|----|-------------|---------|---------|
| Model            | 2.02           | 9  | 0.2240      | 60.75   | < 0.0001|
| A-Temperature    | 0.8092         | 1  | 0.8092      | 219.49  | < 0.0001|
| Term            | Coefficient | df | Coefficient | df | Significance |
|-----------------|-------------|----|-------------|----|--------------|
| B - Reaction time | 0.5072      | 1  | 0.5072      | 1  | < 0.0001     |
| C - Catalyst loading | 0.0032   | 1  | 0.0032      | 1  | 0.3579       |
| AB              | 0.2502      | 1  | 0.2502      | 1  | < 0.0001     |
| AC              | 0.0095      | 1  | 0.0095      | 1  | 0.1215       |
| BC              | 0.0028      | 1  | 0.0028      | 1  | 0.3912       |
| A²              | 0.2992      | 1  | 0.2992      | 1  | < 0.0001     |
| B²              | 0.1151      | 1  | 0.1151      | 1  | < 0.0001     |
| C²              | 0.0186      | 1  | 0.0186      | 1  | 0.0341       |
| Residual        | 0.0885      | 24 | 0.0037      |    |              |
| Lack of Fit     | 0.0811      | 5  | 0.0162      | 19 | < 0.0001     |
| Pure Error      | 0.0074      | 19 | 0.0004      |    |              |
| Cor Total       | 2.10        | 33 |             |    |              |
Table S20: Full results of reduced quadratic RSM for conversion in hydrogen atmosphere

| Source        | Sum of Squares | df  | Mean Square | F-value | p-value   |
|---------------|----------------|-----|-------------|---------|-----------|
| Model         | 1.98           | 5   | 0.3963      | 90.46   | < 0.0001  |
| A-Temperature | 0.8092         | 1   | 0.8092      | 184.73  | < 0.0001  |
| B-Reaction time | 0.5072      | 1   | 0.5072      | 115.77  | < 0.0001  |
| AB            | 0.2502         | 1   | 0.2502      | 57.11   | < 0.0001  |
| A²            | 0.3305         | 1   | 0.3305      | 75.44   | < 0.0001  |
| B²            | 0.1330         | 1   | 0.1330      | 30.35   | < 0.0001  |
| Residual      | 0.1227         | 28  | 0.0044      |         |           |
| Lack of Fit   | 0.1153         | 9   | 0.0128      | 32.98   | < 0.0001  |
| Pure Error    | 0.0074         | 19  | 0.0004      |         |           |
| Cor Total     | 2.10           | 33  |             |         |           |

The coefficient estimate listed in Table S21 is a measure of how each of the terms effect the oxalate yield and the combined effect of each factor including their linear and quadratic terms are shown in Figure S22. In the case of formate conversion in hydrogen atmosphere the linear term of temperature has the biggest effect on formate conversion. Other than in nitrogen, the reaction time has an almost equal influence in this case. The overall effect of the linear terms is dampened by its quadratic term and interaction the interaction terms. From a chemical point of view, the increase
of conversion with the increase of the factor values make sense as higher temperatures, longer reaction times and better removal of side-products by purging drive the reaction. Temperature is the main driver for the reaction to occur, and we observe a saturation of influence of temperature at higher values due to the high overall conversion which can only reach a maximum of 1. A longer time at given temperature increases the likeliness of the conversion. This effect is pronounced at lower reaction temperatures and the model reflects as can be seen in Figure S23. The lack of benefit from higher catalyst loadings is unexpected as the presence of more catalytic species should have an impact on conversion especially at lower reaction times and lower temperatures.

Table S21: Estimated model coefficients for significant factors describing the model for formate conversion in hydrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor         | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|----------------|----------------------|----|----------------|------------|-------------|-----|
| Intercept      | 0.9964               | 1  | 0.0209         | 0.9537     | 1.04        |
| A-Temperature  | 0.1799               | 1  | 0.0132         | 0.1528     | 0.2070      | 1.0000 |
| B-Reaction time| 0.1424               | 1  | 0.0132         | 0.1153     | 0.1695      | 1.0000 |
| AB             | -0.1250              | 1  | 0.0165         | -0.1589    | -0.0911     | 1.0000 |
| A²             | -0.1372              | 1  | 0.0158         | -0.1696    | -0.1049     | 1.02  |
Figure S22: Influence of (A) Temperature, (B) Reaction time and (C) Catalyst loading on the conversion of formate at median values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and purging are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.
Analysis: Oxalate yield in hydrogen atmosphere

The results we receive for the conversion of formate in hydrogen atmosphere are shown for the range of each factor in Figure S24 below. Note, that due to the nature of the central composite design the values for the two remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in Figure S24A, has the clearest trend of all factors and the oxalate yield shows a parabolic behaviour with a clear maximum around 400 °C. At higher temperatures the achieved yields decrease drastically. For the reaction time (Figure S24B) the conversion rate seems separated in two of lower and higher conversion regimes. This indicates the presence of interactions between two factors. Overall, the
oxalate yield appears to be increasing with long reaction times up until 30 minutes. Catalyst loading appears to have no effect on oxalate yields as the results are equally spread through the design space. The potential presence of interacting factors justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.91 meaning that 91% of the results can be explained with the variables offered in our experiments. This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the oxalate yield. The Predicted $R^2$ of 0.8198 is in reasonable agreement with the Adjusted $R^2$ of 0.8783 and adequate precision measures 15.62 indicating that this model can be used to navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in Figure S25A.
Figure S24 Shows the raw data obtained for oxalate yields for all three factors temperature (A), reaction time (B) and catalyst loading (C).

Figure S25: Predicted versus actual values for oxalate yields in the DoE with hydrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.
The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for oxalate yield in hydrogen atmosphere are shown in Table S22. For the full quadratic model, it becomes apparent that catalyst loading has no significant influence on the oxalate yield. Only interactions between temperature and reaction times are significant interacting terms. Quadratic terms of temperature and reaction time are significant. All of which exhibit p-values higher than 0.01. Using this cut-off, we realize that A, B, AB, A², B² are significant model terms.

The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for oxalate yield in hydrogen atmosphere are shown in Table S23. The overall model F-value of 27.47 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 55.24 is greatly improved compared to the full quadratic model implies the model is significant. The improved reduced model containing only the most significant factors has a lower R² value and only 90.80% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.8915) and Predicted R² (0.8509) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 15.62 to 21.25.
Compared to the full quadratic model, the actual vs. predicted values have slightly moved closer to the convergence line as shown in Figure S25B.
Table S22: Full results of full quadratic RSM for oxalate yields in hydrogen atmosphere

| Source             | Sum of Squares | df | Mean Square | F-value | p-value |
|--------------------|----------------|----|-------------|---------|---------|
| Model              | 3.10           | 9  | 0.3442      | 27.47   | < 0.0001|
| A-Temperature      | 0.5453         | 1  | 0.5453      | 43.52   | < 0.0001|
| B-Reaction time    | 0.0933         | 1  | 0.0933      | 7.45    | 0.0117  |
| C-Catalyst loading | 0.0058         | 1  | 0.0058      | 0.4645  | 0.5020  |
| AB                 | 0.5698         | 1  | 0.5698      | 45.48   | < 0.0001|
| AC                 | 0.0021         | 1  | 0.0021      | 0.1687  | 0.6849  |
| BC                 | 0.0010         | 1  | 0.0010      | 0.0823  | 0.7767  |
| A²                 | 1.79           | 1  | 1.79        | 142.76  | < 0.0001|
| B²                 | 0.1950         | 1  | 0.1950      | 15.56   | 0.0006  |
| C²                 | 0.0031         | 1  | 0.0031      | 0.2481  | 0.6230  |
| Residual           | 0.3007         | 24 | 0.0125      |         |         |
| Lack of Fit        | 0.2359         | 5  | 0.0472      | 13.82   | < 0.0001|
| Pure Error         | 0.0648         | 19 | 0.0034      |         |         |
| Cor Total          | 3.40           | 33 |             |         |         |
Table S23: Full results of reduced quadratic RSM for oxalate yields in hydrogen atmosphere

| Source       | Sum of Squares | df | Mean Square | F-value | p-value |
|--------------|----------------|----|-------------|---------|---------|
| Model        | 3.09           | 5  | 0.6171      | 55.24   | < 0.0001|
| A-Temperature| 0.5453         | 1  | 0.5453      | 48.81   | < 0.0001|
| B-Reaction time| 0.0933      | 1  | 0.0933      | 8.35    | 0.0074  |
| AB           | 0.5698         | 1  | 0.5698      | 51.01   | < 0.0001|
| A²           | 1.81           | 1  | 1.81        | 161.91  | < 0.0001|
| B²           | 0.1920         | 1  | 0.1920      | 17.19   | 0.0003  |
| Residual     | 0.3128         | 28 | 0.0112      |         |         |
| Lack of Fit  | 0.2480         | 9  | 0.0276      | 8.07    | < 0.0001|
| Pure Error   | 0.0648         | 19 | 0.0034      |         |         |
| Cor Total    | 3.40           | 33 |             |         |         |

The coefficient estimate listed in Table S24 is a measure of how each of the terms effect the oxalate yield and the combined effect of each factor including their linear and quadratic terms are shown in Figure S26. In the case of oxalate yields in hydrogen atmosphere the quadratic and linear term of temperature has the biggest effect on oxalate yield. Due to the high intercept value the interpretation of the coefficients becomes more difficult. A strong interaction between temperature and reaction time is apparent and higher temperatures appear to have a strong negative effect on
oxalate yields, which can be seen by the magnitude of the coefficient for the quadratic term and in the factor influence in Figure S26A. Reaction times appear to have a lesser effect on the oxalate yield but also for this factor a maximum is present within the chosen design space as visible in Figure S26B. Catalyst loading has no effect on the oxalate yield. From a chemical point of view, the presence of a maximum of oxalate yield make sense. In the regime leading up to the maximum, the conversion of formate to oxalate is reigning. After the maximum, higher temperatures, longer reaction times lead to the decomposition of the formed oxalate to carbonate. In Figure S27 we can see that other that compared to using a nitrogen atmosphere, high oxalate yields can be achieved at lower reaction temperatures and shorter reaction times. The lack of benefit from higher catalyst loadings is unexpected as the presence of more catalytic species should have an impact on conversion especially at lower reaction times and lower temperatures.

Table S24: Estimated model coefficients for significant factors describing the model for obtained oxalate yields in hydrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where $VIF = 1$ stands for fully orthogonal factors.

| Factor   | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|----------|----------------------|----|----------------|------------|-------------|-----|
| Intercept| 0.8300               | 1  | 0.0333         | 0.7618     | 0.8982      |     |
Figure S26: Influence of (A) Temperature, (B) Reaction time and (C) Catalyst loading on the oxalate yield at median values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and purging are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.

Figure S27: Contour-plot for oxalate yields development due the interaction of temperature and reaction time in hydrogen atmosphere with reduced quadratic design.
Analysis: Carbonate yield in hydrogen atmosphere
The results we receive for carbonate yields in hydrogen atmosphere are shown for the range of
each factor in Figure S28 below. Note, that due to the nature of the central composite design the
values for the two remaining parameters were not kept constant. However, this still allows to
identify trends of the influence of each of the factors. Temperature, as visible in Figure S28A, has
the clearest trend of all factors and the carbonate yields increase with increasing reaction
temperatures in a seemingly exponential manner. This is in line with the decreasing oxalate yields
observed for higher reaction temperatures. The reaction time (Figure S28B) longer reaction times also on average increase carbonate yields but the data appears to be separated in two parts which indicates the presence of an interaction between factors. Catalyst loading appears to have no effect on carbonate yields as the results are equally spread through the design space. The potential presence of interacting factors justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.
Figure S28 Shows the raw data obtained for carbonate yields for all three factors temperature (A), reaction time (B) and catalyst loading (C).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.96 meaning that 96% of the results can be explained with the variables offered in our experiments. This indicates that it is unlikely that other factors, not considered or controlled in our experiments influence the oxalate yield. The Predicted $R^2$ of 0.9101 is in reasonable agreement with the Adjusted $R^2$ of 0.9404 and adequate precision measures 22.46 indicating that this model can be used to navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in Figure S29A.

Figure S29: Predicted versus actual values for carbonate yields in the DoE with hydrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.
The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for carbonate yields in hydrogen atmosphere are shown in Table S25. For the full quadratic model, it becomes apparent that catalyst loading has no significant influence on the carbonate yield. Only interactions between temperature and reaction times are significant interacting terms. Quadratic term of temperature is significant. All of which exhibit p-values higher than 0.01. Using this cut-off, we realize that A, B, AB and A² are significant model terms. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for carbonate yields in hydrogen atmosphere are shown in Table S26. The overall model F-value of 58.88 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 11.48 is greatly improved compared to the full quadratic model implies the model is significant. The improved reduced model containing only the most significant factors has a lower R² value and only 93.9% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between R², Adjusted R² (0.9305) and Predicted R² (0.9074) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 22.45 to 30.12.
Compared to the full quadratic model, the actual vs. predicted values have are similarly distributed around the convergence line as shown in Figure S29B.

Table S25: Full results of full quadratic RSM for carbonate yields in hydrogen atmosphere

| Source       | Sum of Squares | df | Mean Square | F-value  | p-value |
|--------------|----------------|----|-------------|----------|---------|
| Model        | 1.00           | 9  | 0.1115      | 58.88    | < 0.0001|
| A-Temperature| 0.7482         | 1  | 0.7482      | 395.21   | < 0.0001|
| B-Reaction time | 0.0604     | 1  | 0.0604      | 31.91    | < 0.0001|
| C-Catalyst loading | 0.0071  | 1  | 0.0071      | 3.73     | 0.0653  |
| AB           | 0.0419         | 1  | 0.0419      | 22.15    | < 0.0001|
| AC           | 0.0001         | 1  | 0.0001      | 0.0525   | 0.8208  |
| BC           | 0.0001         | 1  | 0.0001      | 0.0623   | 0.8051  |
| A²           | 0.1433         | 1  | 0.1433      | 75.67    | < 0.0001|
| B²           | 0.0022         | 1  | 0.0022      | 1.18     | 0.2875  |
| C²           | 0.0103         | 1  | 0.0103      | 5.43     | 0.0285  |
| Residual     | 0.0454         | 24 | 0.0019      |          |         |
| Lack of Fit  | 0.0391         | 5  | 0.0078      | 23.55    | < 0.0001|
| Pure Error   | 0.0063         | 19 | 0.0003      |          |         |
| Cor Total    | 1.05           | 33 |             |          |         |
Table S26: Full results of reduced quadratic RSM for carbonate yields in hydrogen atmosphere

| Source       | Sum of Squares | df | Mean Square | F-value | p-value |
|--------------|----------------|----|-------------|---------|---------|
| Model        | 0.9847         | 4  | 0.2462      | 111.48  | < 0.0001|
| A-Temperature| 0.7482         | 1  | 0.7482      | 338.82  | < 0.0001|
| B-Reaction time | 0.0604     | 1  | 0.0604      | 27.36   | < 0.0001|
| AB           | 0.0419         | 1  | 0.0419      | 18.99   | 0.0002  |
| A²           | 0.1341         | 1  | 0.1341      | 60.74   | < 0.0001|
| Residual     | 0.0640         | 29 | 0.0022      |         |         |
| Lack of Fit  | 0.0577         | 10 | 0.0058      | 17.37   | < 0.0001|
| Pure Error   | 0.0063         | 19 | 0.0003      |         |         |
| Cor Total    | 1.05           | 33 |             |         |         |

The coefficient estimate listed in Table S27 is a measure of how each of the terms effect the oxalate yield and the combined effect of each factor including their linear and quadratic terms are shown in Figure S30. The production of carbonate in hydrogen atmosphere is mainly determined by increasing temperature. Both the linear and quadratic term positively contribute to the achieved carbonate yield and the exponential behaviour becomes visible in Figure S30A. Increasing reaction times and their interaction with temperature also contribute to higher carbonate yields. As all terms
are positive, we obviously do not see a local maximum of carbonate formation within our design space as seen in Figure S31. The catalyst loading has no effect on the carbonate yield. From a chemical point of view, the increase of carbonate yield with temperature and time makes sense as the formed oxalate decomposes. Our model and the choice of parameter space was not designed to describe carbonate yield but rather to optimize oxalate yield. The model term for carbonate yield helps to explain the decrease of oxalate formation, yet if the goal was to study the carbonate formation and subsequent decomposition, the design space would need to be expanded. We would then expect a maximum for carbonate yield due to the decomposition of carbonate at even higher temperatures and reaction times. The lack of benefit towards carbonate formation from higher amounts of hydroxide (catalyst) suggests that it is not involved in a bimolecular reaction with oxalate or formate towards carbonate as suggested by Gorski.2

Table S27: Estimated model coefficients for significant factors describing the model for obtained carbonate yields in hydrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor     | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|------------|----------------------|----|---------------|------------|-------------|-----|
| Intercept  | 0.1072               | 1  | 0.0115        | 0.0838     | 0.1307      |     |
Table:

| Factor          | Coefficient 1 | Coefficient 2 | Coefficient 3 | Coefficient 4 | Coefficient 5 |
|-----------------|---------------|---------------|---------------|---------------|---------------|
| A-Temperature   | 0.1730        | 1             | 0.0094        | 0.1538        | 0.1922        | 1.0000        |
| B-Reaction time | 0.0492        | 1             | 0.0094        | 0.0299        | 0.0684        | 1.0000        |
| AB              | 0.0512        | 1             | 0.0117        | 0.0272        | 0.0752        | 1.0000        |
| A²              | 0.0866        | 1             | 0.0111        | 0.0639        | 0.1094        | 1.0000        |

Figure S30: Influence of (A) Temperature, (B) Reaction time and (C) Catalyst loading on the carbonate yield at median values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and purging are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.

Figure S31: Contour-plot for carbonate yields development due the interaction of temperature and reaction time in hydrogen atmosphere with reduced quadratic design

Analysis: Carbon balance in hydrogen atmosphere
The carbon balances we observe in hydrogen atmosphere are shown for the range of each factor in Figure S32 below. Note, that due to the nature of the central composite design the values for the two remaining parameters were not kept constant. However, this still allows to identify trends of the influence of each of the factors. Temperature, as visible in Figure S32A, has the clearest trend of all factors and the carbon balance shows decreases with increasing temperatures. The carbon balance appears to be equally spread through the design space for reaction time and catalyst loading. For reaction time a separation in two regimes seems to be present, yet no clear effect of interaction is visible overall. The potential presence of interacting factors justifies the use of a quadratic model to identify the interaction and deconvolute the linear, two-factor interactions and quadratic terms. After the deconvolution the magnitude of each terms influence can be estimated.
Figure S32 Shows the raw data obtained for carbon balance for all three factors temperature (A), reaction time (B) and catalyst loading (C).

The data was not processed prior to model formation. We initially use the full quadratic model, as initially intended by choice of a central composite design. Overall, we reach a high $R^2$ value of 0.87 meaning that 87% of the results can be explained with the variables offered in our experiments. This indicates that it is unlikely that other main factors, not considered or controlled in our experiments influence the oxalate yield. The Predicted $R^2$ of 0.7463 is in reasonable agreement with the Adjusted $R^2$ of 0.8198 and adequate precision measures 12.80 indicating that this model
can be used to navigate the design space. An equal and continuous distribution of the data through the space and close correlation between predicted and actual values is achieved as shown in Figure S33A.

Figure S33: Predicted versus actual values for carbon balance in the DoE with hydrogen atmosphere. The colouring represents the conversion where blue is no conversion and red is full conversion. On the left side (A) for the full and on the right side (B) for the reduced model.

The results of the full quadratic model including sum of squares, df and Mean Square for the RSM for carbon balance in hydrogen atmosphere are shown in Table S28. For the full quadratic model, it becomes apparent that catalyst loading, and reaction time have no significant influence on the carbon balance. Hence also no two-factor interaction terms are significant. The quadratic term of temperature is significant. All of which exhibit p-values higher than 0.01. Using this cut-off, we realize that A and A² are significant model terms and used in the reduced model. The results of the improved quadratic model including sum of squares, df and Mean Square for the RSM for
carbon balance in hydrogen atmosphere are shown in Table S29. The overall model F-value of 17.69 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. With the improved model the overall model F-value of 68.62 is greatly improved compared to the full quadratic model implies the model is significant. The improved reduced model containing only the most significant factors has a lower $R^2$ value and only 81.57% of the results can be explained with the variables offered in our experiments. Yet, the closer resemblance between $R^2$, Adjusted $R^2$ (0.8038) and Predicted $R^2$ (0.7681) indicates a higher quality prediction which is also apparent from the adequate Precision which increased from 12.81 to 22.85.

Compared to the full quadratic model, the actual vs. predicted values have slightly moved closer to the convergence line as shown in Figure S33B.

*Table S28: Full results of full quadratic RSM for carbon balance in hydrogen atmosphere*

| Source         | Sum of Squares | df  | Mean Square | F-value | p-value   |
|----------------|----------------|-----|-------------|---------|-----------|
| Model          | 0.7907         | 9   | 0.0879      | 17.69   | < 0.0001  |
| A-Temperature  | 0.5944         | 1   | 0.5944      | 119.65  | < 0.0001  |
| B-Reaction time| 0.0219         | 1   | 0.0219      | 4.41    | 0.0465    |
| C-Catalyst loading | 0.0079 | 1   | 0.0079      | 1.58    | 0.2205    |
| AB             | 0.0028         | 1   | 0.0028      | 0.5556  | 0.4633    |
|        | Value 1  | Value 2  | Value 3  | Value 4  |
|--------|---------|---------|---------|---------|
| AC     | 0.0035  | 1       | 0.0035  | 0.6980  | 0.4117  |
| BC     | 0.0002  | 1       | 0.0002  | 0.0322  | 0.8592  |
| A²     | 0.1583  | 1       | 0.1583  | 31.88   | < 0.0001 |
| B²     | 0.0033  | 1       | 0.0033  | 0.6652  | 0.4228  |
| C²     | 0.0105  | 1       | 0.0105  | 2.12    | 0.1585  |
| Residual | 0.1192 | 24      | 0.0050  |         |         |
| Lack of Fit | 0.0632 | 5       | 0.0126  | 4.28    | 0.0089  |
| Pure Error | 0.0561 | 19      | 0.0030  |         |         |
| Cor Total | 0.9099 | 33      |         |         |         |
Table S29: Full results of reduced quadratic RSM for conversion in hydrogen atmosphere

| Source       | Sum of Squares | df  | Mean Square | F-value | p-value |
|--------------|----------------|-----|-------------|---------|---------|
| Model        | 0.7422         | 2   | 0.3711      | 68.62   | < 0.0001|
| A-Temperature| 0.5944         | 1   | 0.5944      | 109.89  | < 0.0001|
| A²           | 0.1479         | 1   | 0.1479      | 27.34   | < 0.0001|
| Residual     | 0.1677         | 31  | 0.0054      |         |         |
| Lack of Fit  | 0.1116         | 12  | 0.0093      | 3.15    | 0.0125  |
| Pure Error   | 0.0561         | 19  | 0.0030      |         |         |
| Cor Total    | 0.9099         | 33  |             |         |         |

The coefficient estimate listed in Table S30 is a measure of how each of the terms effect the carbon balance of each factor including their linear and quadratic terms are shown in Figure S34.

In hydrogen atmosphere the reaction temperature is the only significant factor decreasing the overall carbon balance with increasing values. The presence of the quadratic term pronounces the decrease towards higher temperatures as seen in Figure S34A. From a chemical view, this effect of temperature makes sense as high temperatures stimulate the decomposition of the carbonous contents to elemental carbon or gaseous carbonous compounds. Yet, we would also expect that longer reaction times contribute to the decomposition as they increase the chance for the decomposition to occur, especially given the seemingly slower reaction rates of the decomposition.
observed in the nitrogen atmosphere. The fact that the decomposition and alteration of carbon balance only occurs in a relatively small part of the design-space explains the relatively poor model quality. In our case the goal was to study the influences on oxalate yield and not a precise description of the degradation of the formed oxalate. If this degradation was to be studied extensively, the design-space should be expanded towards higher temperatures and reaction times.

Yet, as this expansion would decrease the prediction strengths of the model for oxalate yields, we did not incorporate higher reaction times and temperatures. For our purpose the insight in decomposition is sufficient.

Table S30: Estimated model coefficients for significant factors describing the model for carbon balance in hydrogen atmosphere. The intercept is the overall average of all runs and coefficients are adjustments around that average based on the settings chosen for each factor. The coefficient estimate explains the change in response per unit change in the factor value at constant values for the remaining factors. The variance inflation factor (VIF) is a measure of factor orthogonality where VIF = 1 stands for fully orthogonal factors.

| Factor      | Coefficient Estimate | df | Standard Error | 95% CI Low | 95% CI High | VIF |
|-------------|----------------------|----|---------------|-----------|-------------|-----|
| Intercept   | 0.9202               | 1  | 0.0180        | 0.8836    | 0.9568      |     |
| A- Temperature | -0.1542             | 1  | 0.0147        | -0.1842   | -0.1242     | 1.0000 |
| A²          | -0.0910              | 1  | 0.0174        | -0.1265   | -0.0555     | 1.0000 |
Figure S34: Influence of (A) Temperature, (B) Reaction time and (C) Catalyst loading on the carbon balance at median values for the remaining factors in the reduced quadratic model. Note that catalyst loading, and reaction time are no longer considered a contributing factor and thus a straight line. The dotted bands show the limits of the 95% confidence interval.