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Formic acid: a future bridge between the power and chemical industries†

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In the future hydrogen economy, formic acid is considered an efficient hydrogen storage molecule and a new C₁ building block for the chemical industry. Formic acid could be used as a sustainable carbon monoxide source. In the present work efficient catalysts for the decomposition of formic acid and its derivatives to carbon monoxide have been found. The proposed catalysts are widely available zeolites, making the process feasible for industrial scale applications. Thus, formic acid and its derivatives could be seen as liquid and storable versions of carbon monoxide, which could be directly used in the existing chemical value chain.

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Introduction

Sustainable energy supplies and the increase in their contribution to the overall power mix is one of the main challenges of this century. The use of wind and solar energy are of particular interest. However, besides the obvious advantages, the mentioned power sources are intrinsically dependent on fluctuating environmental conditions, resulting in periods of surplus and deficit energy.¹ In order to efficiently exploit renewable sources, surplus energy should be stored and then used when needed.

Many different solutions to this challenge can be foreseen, but for large applications, the first step is almost always the generation of hydrogen by water electrolysis.^{2,3} Hydrogen is one of the most efficient, cleanest and lightest fuels, which can be pressurized and stored in large quantities, under some constraints,^{2–4} near the production site. For large scale applications, chemical conversion of hydrogen into active intermediates can lead to liquid products, which would significantly ease the transportation and storage.^{2–4}

An example of such active intermediates is the CO₂/formic acid (FA) system. Loges *et al.*⁵ reported homogenous CO₂ hydrogenation, in the presence of an alkaline compound (amine), to form liquid formic acid–amine adducts (FAAA). The reaction is perfectly reversible and CO₂ hydrogenation is a

widely studied process, in which high catalyst activities and selectivities have been attained.^{6,7} Behr and Nowakowski⁸ described the synthesis of FAAA by the hydrogenation of carbon dioxide in a continuously operated miniplant, showing that it could be produced on relatively large scales.

Using a commercially available catalyst [RuCl₂(PPh₃)₃], FAAA can be decomposed to generate hydrogen at a high rate and at room temperature. However, FA and its derivatives (FAD) also represent a new C₁ raw material for the chemical industry. Methyl formate (MF) has already been successfully employed as a carbonylating agent for olefins,⁹ phenols¹⁰ and amines.¹¹ Alternatively, FA undergoes decomposition in the presence of a catalyst.^{12,13} If metal (especially noble metal) catalysts, or metal oxides like TiO₂,¹⁴ are used, the main products are H₂/CO₂. If acid catalysts are used, normally zeolites¹⁵ or immobilized mineral acids,¹⁶ the main products are CO/H₂O. Thus, FA could be used as a source of both H₂ and CO gases, entering the current chemical value chain based on syngas. For the same purpose dimethylformamide (DMF) can also be used.^{17,18}

FA and FAD mixtures can be seen as liquid and storable versions of carbon monoxide (CO), which can be directly used in the existing chemical value chain. If these are produced by CO₂ hydrogenation with H₂ generated by surplus renewable energy, it would create a bridge between the power and chemical industries. FA can thus be used to selectively and on demand generate not only H₂^{6,7,12,13,19,20} but also CO^{12–18} as presented in this work, where the industrial focus is novel and the key part of the article.

Experimental

Different catalysts were tested as summarized in Table 1. Only catalysts commercially available in large quantities were used.

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Table 1 Tested catalysts and their key specifications

Catalyst label name	Framework type	Producer	Product name	Module ^a	Crystallite size (μm)	Surface area (m ² g ⁻¹)
H-ZSM5-27	MFI	Südchemie-Clariant	Pentasil-27	27	2–5	403 ^b
H-ZSM5-55	MFI	Südchemie-Clariant	Pentasil-55	55	2–5	427 ^b
H-ZSM5-90	MFI	Südchemie-Clariant	Pentasil-90	90	2–5	408 ^b
H-ZSM5-28	MFI	Zeochem AG	V1148.4	28	1–3	380 ^c
H-Y-5	FAU	Zeolyst International	CBV 600	5.2	<1	660 ^c
γAl ₂ O ₃	N/A	Sasol	Puralox SCCa-5/200	N/A	1–3	200 ^c

^a Module measured as SiO₂ : Al₂O₃ (molar). ^b Measured data. ^c According to producer.

Clearly this cannot exclude the fact that custom made or exotic zeolites could lead to better results, but their chance to be employed in large industrial processes would be limited.

Detailed characterization and experimental procedures are provided in the ESI.†

Results and discussion

To achieve decomposition of formic acid and its derivatives on an industrial scale, a gaseous heterogeneously catalysed process should be used. Preferably a widely available solid acid catalyst has to be employed. Zeolites appear to be the most suitable candidates.¹⁵ Their multiple applications²¹ mean they are easily available in large quantities. They also offer a variety of different acid centers,²² and so the properties can be relatively easily modified.^{23,24}

The challenge is represented by the use of an acid catalyst in the presence of a base (water or amines as the reaction product and part of the feed), which could lead to adsorption onto the acid centers and their blockage, resulting in catalyst deactivation. Fine tuning of the catalyst acidity, preventing strong adsorption and at the same time providing high activity, can be one of the strongest tools to develop a good catalyst. Also, depending on the nature of the acid sites (*i.e.* Brønsted and Lewis acid sites²²), different reaction mechanisms and products may be expected.²⁵ Understanding the active sites and mechanism is necessary to develop an optimal catalyst.

To tune the catalyst acidity and verify our working hypothesis, three zeolite ZSM5 samples with different module values were chosen as catalysts. The differences between their acidities were confirmed by temperature programmed ammonia desorption (TPAD) tests. Weakly bound ammonia desorption was observed at $T \sim 250$ °C (Fig. 1). This desorption temperature corresponds to the one reported for desorption from Lewis acid sites.²⁶ Desorption of ammonia from Brønsted acid centers was recorded at $T \sim 500$ °C. The integral area of the desorbed ammonia increases with decreasing module value, which confirms that the density of acid centers in H-ZSM5-27 is much higher than in H-ZSM5-90. The desorption temperature from Brønsted acid centers also increases with decreasing module value (Fig. 1 from 475 °C to 550 °C); therefore, stronger adsorption of products could be expected for H-ZSM5-27.

Fig. 1 TPAD measurements of H-ZSM5 catalysts with different module values.

The influence of the catalyst acidity on the substrate adsorption/desorption processes was confirmed by TGA-MS of the zeolites impregnated with 88% FA. It could be expected that FA present on the H-ZSM5-90 surface will be mostly physisorbed, while on the H-ZSM5-27 surface it will mostly be chemisorbed. Indeed, the recorded mass loss occurs at a lower temperature for the material with lower acidity (Fig. 2,

Fig. 2 TGA differential data of the H-ZSM5 catalysts with different module values impregnated with 88% FA in water.

H-ZSM5-90) and at a higher temperature for the more acidic one (Fig. 2, H-ZSM5-27). H-ZSM5-27 will strongly adsorb FA but also water, which could lead to its deactivation. On the other hand, the H-ZSM5-90 acidity may be too low to provide high conversion.

The acidity of H-ZSM5-55 lies in between the two previously mentioned materials. Thus, its mass loss curve should indicate the presence of chemi- and physisorbed substrate. As demonstrated in Fig. 2, the recorded mass loss of H-ZSM5-55 consists of two steps: the first one is the release of physisorbed compounds (similar to that of H-ZSM5-90), and the second one, starting from ~ 115 °C, is the release of chemisorbed compounds (similar to that of H-ZSM5-27). The TGA measurements are in good agreement with the TPD experiments, and confirm that the catalyst acidity could significantly affect its performance. TGA mass loss can be attributed to desorbed water and formic acid (88% FA in H_2O was used), as well as FA derived products (CO and water). To verify and quantify this, the desorbed gases were analyzed by MS. A first release of physisorbed water can be clearly seen at around 100 °C (Fig. 3), accompanied by the desorption of physisorbed formic acid (m/z 46, peak maximum at 140 °C). At higher temperatures (180 °C), a release of CO associated with a second release of water can be observed. This can be attributed to the chemisorbed formic acid that at this temperature decomposes on the active sites and releases its products, namely CO and H_2O . The same trend was also observed for H-ZSM5-55, even though, due to the different acidity, the relative ratio between physisorbed and chemisorbed compounds was different (Fig. 3). Similar to the TGA measurements, at temperatures above 200 °C no processes were observed.

Based on these observations, the optimum catalyst for FA decomposition should have the right balance between acidity and hydrophobicity. A strongly acidic catalyst is expected to be very active, but would rapidly deactivate due to water adsorption. Catalytic performance tests were carried out to verify and find the most suitable module for formic acid decomposition. The conversion values (at 5 h time-on-stream (TOS) after reaching steady state) recorded for the H-ZSM5-55 catalyst differ

Table 2 Representative formic acid conversion values (at 5 h TOS) recorded over the H-ZSM5 catalysts with different module values, and $\gamma\text{Al}_2\text{O}_3$. Test temperature of 190 °C, 1.2 g of catalyst, and HCOOH (98%) flow of 1.6 mL h^{-1}

Catalyst	Conversion (%)	Reaction rate ($\text{mmol}_{\text{CO}} \text{ g}_{\text{Cat}}^{-1} \text{ h}^{-1}$)
H-ZSM5-55	81	28 ^a
H-ZSM5-27	52	18
H-ZSM5-90	47	16
$\gamma\text{Al}_2\text{O}_3$	2	0.7

^a Reaction rate could be underestimated as it was measured at 81% conversion.

significantly from the other tested materials (Table 2), whereas the conversion over H-ZSM5-27 and H-ZSM5-90 is comparable. This suggests that module $M = 55$ represents the ideal balance between the acidity and water adsorption strength for this substrate and temperature. In all the tests, the selectivity towards CO was higher than 99.6%. The missing 0.4% from the carbon mass balance could be attributed, in the worst case, to a H_2/CO_2 pair. Traces of H_2 were sporadically seen, especially for the non-optimized reaction conditions. In many cases the C balance was around 99.9%–100.1% with full selectivity towards CO.

For comparison purposes, $\gamma\text{Al}_2\text{O}_3$, which only has Lewis acid sites,^{27,28} was tested (Table 2). The FA conversion values did not exceed 2%, which clearly indicates that Lewis acid sites are inactive for formic acid decomposition, whereas strong Brønsted acid sites are necessary for the dehydration.

In industrial conditions, only technical grade (88% – azeotropic composition) formic acid will probably be employed. To verify the suitability of the selected catalyst, a long-term stability test was carried out using this technical grade mixture. Under optimized conditions, the H-ZSM5-55 activity and selectivity towards CO remains stable for longer than 220 h time-on-stream (see ESI† Fig. S2).

By hydrogenating CO_2 in the presence of amines, ammonium formates and formamides can be formed.^{5,8,13} The decomposition of formamides should also be catalyzed by strong acid

Fig. 3 MS spectra of H-ZSM5-27 and H-ZSM5-55 impregnated with 88% FA in water recorded during the TGA tests.

centers. Therefore, these catalysts were also tested for the decomposition of dimethylformamide (DMF) and diethylformamide (DEF). Bearing in mind that the thermodynamics of formamide decomposition are less favorable than for formic acid, and the products are amines, which will adsorb stronger than water, a higher reaction temperature is expected to be necessary.

As previously done, TGA-MS analysis on the catalyst impregnated with the substrates was carried out to optimize the catalyst and reaction conditions. The desorption profile resembles the one obtained with FA but the maximum release of CO is shifted in the range 220–320 °C (Fig. 4). With increasing module value, the amount of physisorbed compounds decreases. Another mass loss at temperatures above 500 °C was observed (Fig. 4, left), where dimethylamine and NH₃ were released. At this temperature, the strongly adsorbed DMA decomposes *via* Hoffmann elimination.^{29,30} Clearly this is something unwanted, as the amine component should be recycled. From this, it is clear that the working temperature of this catalyst is higher than the one used for formic acid, due to thermodynamic considerations, but lower than the decomposition temperature of the associated amine. Moreover, strong amine adsorption on the Brønsted acid centers suggests that they could be blocked if the reaction is conducted at temperatures below 500 °C. To have a stable catalyst, different acid centers will be required to catalyze the decomposition of the formamides. In zeolites, different acid centers can be generated by modifying the preconditioning temperature.

At elevated temperatures, Brønsted acid sites are transformed into Lewis acid sites.³¹ The use of temperatures higher than 500 °C could also result in migration of Al into extra-framework positions (Al_{Ex}), inducing significant complexity into the character of possible active sites in the catalyst. The amount and nature of Al_{Ex} depend strongly on the applied pre-treatment conditions, zeolite structure, and Al-content.^{32–34} Therefore, the existence of various Lewis acid sites and Al forms in the examined zeolites and their participation in the decomposition reaction after exposure to high temperature during preconditioning is expectable.

Table 3 Representative diethylformamide conversion values recorded over H-ZSM5-27 preconditioned at different temperatures. Test temperature of 280 °C, 0.6 g of catalyst, DEF flow of 0.5 mL h^{−1}

Catalyst precondition temperature (°C)	Conversion (%)	Reaction rate (mmol _{CO} g _{Cat} ^{−1} h ^{−1})
300	22	1.6
600	30	2.2

To further investigate this aspect, reactions over ZSM5 preconditioned at different temperatures (300 °C and 600 °C) have been compared. As shown for the example of diethylformamide decomposition over H-ZSM5-27 (Table 3), the conversion value is higher for the catalyst preconditioned at a higher temperature, which has more Lewis acid centers and extra-framework aluminum species.^{32,33} Under the applied reaction conditions, the catalyst exhibits noticeable activity (even after 335 h in the long-term stability test – see ESI† Fig. S4), and its selectivity towards CO (≥99.6%) and the corresponding amine is maintained (no amine decomposition products were detected).

From this it can be concluded that Lewis acid centers do not seem to be irreversibly blocked by the amine during the reaction. The conversion difference could be caused by the conversion of Brønsted acid sites into Lewis acid centers during preconditioning at a higher temperature.

To shed some more light onto the role of different active sites, the catalysts were characterized by operando spectroscopy (DRIFT). As shown for the example of H-ZSM5-27 preconditioned at 600 °C, three distinctive absorption bands can be recognized in the OH-vibration region of the fresh catalyst (Fig. 5a). The band at 3740 cm^{−1} (I) can be assigned to isolated silanol groups.^{35–37} This band does not change when the catalyst is taken from nitrogen gas to reaction conditions, as the silanol groups are not participating in the reaction due to their low acidity. A second band, typical for zeolite ZSM5, can be seen at 3600 cm^{−1} (II). This band corresponds to isolated bridging acidic hydroxyl groups generated by aluminum in the

Fig. 4 (Left) TGA differential data of the H-ZSM5 catalysts with different module values impregnated with dimethylformamide (DMF). (Right) MS spectra of H-ZSM5-55 impregnated with dimethylformamide, recorded during the TGA tests. DMA = dimethylamine.

Fig. 5 DRIFT spectra of the H-ZSM5-27 catalyst at 280 °C: (a) fresh catalyst under N₂ flow; (b) catalyst under diethylformamide vapor flow; (c) catalyst after contact with the substrate, flushed with N₂; (d) catalyst after heating for 30 min at 500 °C.

Fig. 6 Conversion of different substrates (formic acid 98% (HCOOH); dimethylformamide (DMF); diethylformamide (DEF)) versus time-on-stream over $\gamma\text{Al}_2\text{O}_3$. Test temperatures: 190 °C for HCOOH, 280 °C for formamides; 0.6 g of catalyst, substrate flow of 0.5 mL h⁻¹.

framework positions (Al_F).^{35,37} In the zeolites pretreated at lower temperatures there are no additional peaks in the OH-vibration region besides the two aforementioned ones.^{35–38}

The band located at 3655 cm⁻¹ (II) occurs only when the zeolite had been exposed to elevated temperatures^{32,33,38} high enough for aluminum migration from the framework to the extra-framework positions. This band can be assigned to –OH groups tied to Al_{Ex} species, which are still partially connected to the zeolite framework *via* two bonds.^{33,37}

The intensity of these last two bands is significantly reduced when the catalyst has been exposed to dimethylformamide vapors at the test reaction temperature (280 °C) (Fig. 5b). The collected spectrum indicates that both acid center types (Al_F and Al_{Ex}) are occupied by the substrate or by the corresponding amine. After flushing the catalyst with N₂, the recorded spectrum changes again (Fig. 5c). The absorption band representing Al_{Ex} recovers to the same intensity as for the fresh catalyst, whereas the peak at 3600 cm⁻¹ does not. Thus, amines adsorbed on strong Brønsted acid sites remain adsorbed at the reaction temperature. Only after heating the sample at 500 °C can the adsorbed compounds leave the catalyst surface (Fig. 5d). This fits with the observation from TGA-MS and these species probably could leave only after complete decomposition. Therefore, under the reaction conditions, a majority of the Brønsted acid sites generated by Al_F are occupied by the amine, which is the main source of the initial activity loss and deactivation. As the catalyst activity stabilizes after a few hours and the higher temperature pretreated sample is slightly more active than the lower temperature pretreated sample, it seems that the acid sites associated with Lewis acid sites or/and extra-framework aluminum species should be capable of decomposing formamides. Unfortunately, DRIFT measurements do not provide any direct information about Lewis acid sites. Considering the activity of the catalyst preconditioned at 300 °C (a temperature that would not generate any significant amount of Al_{Ex} species), Lewis acid centers should also have an active role in the DEF decomposition.

To further confirm our hypothesis that Lewis acid sites are responsible for formamide decomposition, target experiments over $\gamma\text{Al}_2\text{O}_3$, using DMF and DEF as substrates, were performed (Fig. 6). As expected, unlike in the formic acid case, a significant amount of formamide was decomposed. However, fast deactivation was observed and up to 70% dimethylamine and diethylamine decomposed (Hofmann elimination products were detected, *e.g.* methylamine, ethylamine, ethen). One can speculate that after formamide decomposition over $\gamma\text{Al}_2\text{O}_3$, the corresponding amine also undergoes decomposition, causing the observed deactivation. Another plausible mechanism could lead through the amine group decomposition as the first step as traces of methylformamide and ethylformamide were detected in the reaction liquid products, and subsequent N–COH bond cleavage with CO release as the second step. It should be clarified that no amine decomposition products were detected when the reaction was conducted over the zeolites.

This difference could be caused by different strengths and space densities (*i.e.* multisite processes) of the active sites. Even if this hypothesis remains speculative as the exact decomposition mechanism requires further investigation, it is clear that higher pretreatment temperatures (600 °C), which generate more Lewis acid and extra-framework sites, is preferred in this case.

To confirm the long term stability of these systems, the reaction profiles for different catalysts were measured. All the tested H-ZSM5 catalysts are active for dimethylformamide and diethylformamide decomposition (Fig. 7 and 8). Selectivity towards CO was never lower than 99.6%. As expected, formamide conversion depends strongly on the catalyst module. Contrary to the formic acid experiments, the mentioned dependence is monotonic, which clearly indicates that the conversion increases with the amount of aluminum in the material and, as its corollary, the amount of suitable active sites.

As we would expect from Fig. 6, DEF conversion should be higher than DMF conversion (due to thermodynamic

Fig. 7 Dimethylformamide conversion versus time-on-stream over the H-ZSM5 catalysts with different module values. Test temperature of 280 °C, 0.6 g of catalyst, DMF flow of 0.5 mL h⁻¹.

Fig. 9 Diethylformamide conversion versus time-on-stream over H-ZSM5-27 and H-ZSM5-28 catalysts with different crystallite sizes. Test temperature of 280 °C, 0.6 g of catalyst, DEF flow of 0.5 mL h⁻¹.

Fig. 8 Diethylformamide conversion versus time-on-stream over the H-ZSM5 catalysts with different module values. Test temperature of 280 °C, 0.6 g of catalyst, DEF flow of 0.5 mL h⁻¹.

Fig. 10 Comparison of diethylformamide (DEF) conversion versus time-on-stream over various catalysts. Test temperature of 280 °C; 0.6 g of catalyst, substrate flow of 0.5 mL h⁻¹.

considerations), however we observed a much higher activity for DMF decomposition (up to 90%) compared to DEF decomposition (around 30%). This is probably due to internal mass diffusion limitations, as the larger DEF molecule (see Table 4) is probably less prone to penetrate deeply in the narrow channels of ZSM-5 compared to DMF.

Indeed higher conversion was observed on microcrystalline ZSM5 (denoted ZSM5-28, 1–3 μm) compared to ZSM5-27 (3–5 μm) (Fig. 9). This difference cannot be attributed to the minimal change in module, and must be associated with the crystallite size.

Considering the important role that the diffusion limitations of these large formamide molecules could have, the H-form of zeolite Y was tested (Fig. 10). The faujasite structure of zeolite Y provides better acid site accessibility than the relatively narrow pores of ZSM5. Moreover, compared to ZSM5, the applied zeolite Y could be synthesized with a higher Al-content (module value of 5.2), which should additionally boost the formamide conversion. In the zeolite Y, migration of framework aluminum to extra-framework positions occurs to a higher extent than in the case of the MFI structure, and is also well

Table 4 Surface area and mean pore diameter values of the H-ZSM5 catalysts with different module values, and molecular size of dimethylformamide and diethylformamide (determined by molecular simulations)

Module	Surface area (m ² g ⁻¹)	Mean pore diameter (Å)	Molecule size (Å)	Substrate name
27	403	3.3	3.6 × 4.2	Dimethylformamide
55	427	3.4	3.8 × 5.4	Diethylformamide
90	408	3.8		

described in the literature.^{30,39} Thus, a higher concentration of suitable acid sites in the catalyst could be achieved by an adequate pretreatment.

As expected, higher diethylformamide conversion is achieved over zeolite H-Y (Fig. 10) than over H-ZSM5-27, maintaining the selectivity towards CO and the amine $\geq 99.6\%$. $\gamma\text{Al}_2\text{O}_3$, as already seen in Fig. 6, deactivates very rapidly and is only comparable to H-Y in the first few hours (TOS).

Conclusions

Formic acid and its derivatives (dimethylformamide and diethylformamide) were decomposed over H-forms of various zeolites. It was found that for formic acid, Brønsted acid sites are responsible for dehydration, while for formamides, mainly Lewis acid and extra-framework aluminum are active, which suggests a different reaction mechanism. Accessibility and diffusion limitations could also play important roles, especially for large formamide molecules. Based on these considerations, optimized catalysts (in terms of acidity, crystallite size and pore structure) have been suggested and tested for several hundred hour time-on-stream to validate their industrial applicability. The high selectivity towards CO and catalyst stability is achieved by properly tuning the strength of the catalyst acid centers.

Decomposition of formic acid or its derivatives, resulting from CO₂ hydrogenation, has been found to be feasible and could represent a novel, storable and sustainable⁴⁰ source of CO for the chemical industry in a society not dependent solely on fossil resources.

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