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Formic acid: a future bridge between power and chemical industry

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In the future hydrogen economy, formic acid is considered an efficient hydrogen storage molecule and a new C_1 building block for the chemical industry. Formic acid could be used as a sustainable carbon monoxide source. In the present work an efficient catalyst for decomposition of formic acid and its derivatives to carbon monoxide has been found. The proposed catalysts are widely available zeolites, making it feasible for industrial scale application. Thus, formic acid and its derivatives could be seen as a liquid and storable version of carbon monoxide, which could be directly used in the existing chemical value chain.

Introduction

Sustainable energy supplies and increase of their contribution in overall power mix is one of the main challenges of this century. Use of wind and solar energy are of particular interest. However, besides obvious advantages, the mentioned power sources are intrinsically depending from fluctuating environmental conditions, resulting in periods of surplus and deficit.[1] In order to efficiently exploit renewable sources, energy surplus should be stored and reused 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 constrains[2-4], near the production side. For large scale applications, a chemical conversion of hydrogen into active intermediates could lead to liquid products, which would significantly eases the transport and storage.[2-4]

An example of such active intermediates could be the CO_2 / formic acid (FA) system. Loges et al.[5] reported homogenous CO_2 hydrogenation, in the presence of an alkaline compound (amine), to liquid formic-acid-amine-adducts (FAAA). The reaction is perfectly reversible and the CO_2 hydrogenation is a widely studied process, in which high catalyst activities and selectivities have been attained.[6,7] Behr and Nowakowski[8] described synthesis of FAAA by hydrogenation of carbon dioxide in a continuously operated miniplant – showing that it could be produced in relatively large scales.

Using a relatively available catalyst $[RuCl_2(PPh_3)_3]$, FAAA could be decomposed to generate hydrogen at high rate and at room temperature. However, FA and its derivatives (FAD) also could represent a new C_1 raw material for the chemical industry. Methyl formiate (MF) had been already successfully employed as carbonylating agent for olefins[9], phenols[10] and amines[11]. Alternatively, FA undergoes decomposition in presence of a catalyst[12,13]. If metal (especially noble metal) catalysts, or metal oxides like TiO_2,[14] are used, the main products are H_2 / CO_2. In case acid catalysts are used, normally zeolites[15] or immobilized mineral acids,[16] the main products are CO/H_2O. Thus, FA could be used as source of both, H_2 and CO, gases, entering the current chemical value chain based on syngas. For the same purpose also dimethylformamide (DMF) can be used.[17,18]

FA and FAD mixtures could be seen as a liquid and storable version of carbon monoxide (CO), which could be directly used in the existing chemical value chain. If these are produced by CO_2 hydrogenation with H_2 generated by surplus of renewable energies, it would create a bridge between power and chemical industry. FA can thus be used to generate selectively and on demand not only H_2[6,7,12,13,19,20] but also CO[12-18] as presented in this work, where the industrial focusing is novel and the key part of the article.

Experimental part

Different catalyst had been tested as summarized in table 1. Only commercially available in large quantities were used. Clearly it cannot be excluded that custom made or exotic zeolites could lead to better results, but their chance to be

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Table 1 Used catalysts and their key specification.

Catalyst Label Name	Framework Type	Producer	Product Name	Module[a]	Crystallite Size (µm)	Surface Area (m^2/g)
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_2O_3	N/A	Sasol	Puralox SCCa-5/200	N/A	1-3	200[c]

[a] Module measured as SiO_2:Al_2O_3 (molar)
[b] Measured data
[c] According to producer

employed in large industrial processes would be limited.

Detailed characterization and experimental are provided as Electronic Supplementary Information (ESI).

Results and discussion

To achieve decomposition of formic acid and its derivatives in industrial scale, a gaseous heterogeneously catalysed process, should be used. Preferably a widely available solid acid catalyst has to be employed. Zeolites appear as the most suitable candidates.[15] Multiple applications[21] makes them easily available in large quantities. They are also offering a variety of different acid centers[22], which properties can be relatively easily modified.[23,24]

The challenge is represented by the use of an acid catalyst in presence of base (water or amines as 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 in the same time providing high activity, can be one of the strongest tool to develop a proper catalyst. Also depending from the nature of acid sites (i.e. Brønsted and Lewis acid sites[22]), different reaction mechanisms and products may be expected.[25] Understanding of active sites and mechanism will be 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. Differences between their acidity were confirmed by temperature programmed ammonia desorption (TPAD) tests. Weakly bind ammonia desorption was observed at T~250°C (Fig. 1). This desorption temperature correspond to the one reported for desorption from Lewis acid sites.[26] Desorption of ammonia from Brønsted acid centers was recorded at T~500°C. The integral area of desorbed ammonia is increasing with decreasing module value, which confirms that the density of acid centers in H-ZSM5-27 is much higher than in H-ZSM5-90. Desorption temperature from Brønsted acid centers is also increasing with decreasing module value (Fig. 1 from 475°C to 550°C); therefore, stronger adsorption of products could be expected for H-ZSM5-27.

Influence of the catalysts acidity on the substrate adsorption/desorption processes was confirmed by TGA-MS of zeolites impregnated with 88% FA. It could be expected that FA present on H-ZSM5-90 surface will be mostly physisorbed while on H-ZSM5-27 chemisorbed. Indeed, the recorded mass loss occurs at lower temperature for material with lower acidity (Fig. 2 H-ZSM5-90) and at higher 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, H-ZSM5-90 acidity may be too low to provide high conversion. H-ZSM5-55 acidity lay in between the two previously mentioned materials. Thus, its mass loss curve should indicate

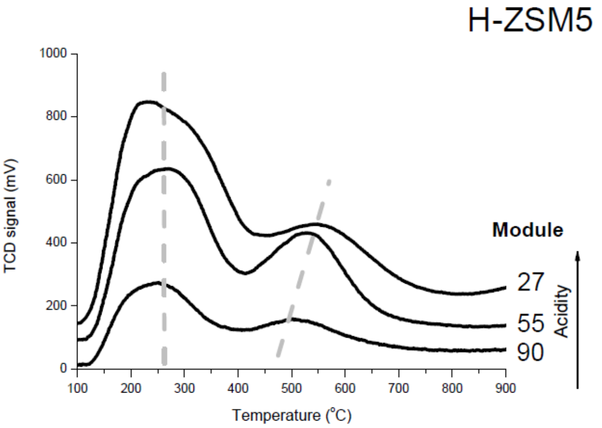

Fig. 1 TPAD measurement of H-ZSM5 catalyst with different module values.

presence of chemi- and physisorbed substrate. As demonstrated on Fig. 2 H-ZSM5-55, the recorded mass loss consists of two steps: first one, a release of physisorbed compounds (similar to that of H-ZSM5-90); and second one, starting from ~115°C, a release of chemisorbed compounds (similar to that of H-ZSM5-27). The TGA measurements stay in good agreement with the TPAD 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), but also to FA derived products (CO and water). To verify and quantify this, the desorbed gases were analyzed by MS. First release of physisorbed water is clearly to see at around 100°C (Fig. 3), accompanied by desorption of phisisorbed 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 was observed. This can be attributed to the chemisorbed formic acid that at this temperature decomposes on the active sites and release its product, namely CO and H_2O. The same trend was observed also for H-ZSM5-55, even if due to the different acidity, the relative ratio between physisorbed and chemisorbed compounds is different (Fig. 3). Similar like in the case of TGA measurements, at the 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 could be expected to be very active, but could rapidly deactivate due to water adsorption. Catalytic performance tests were done to verify that and find the most suitable module for formic acid decomposition. The conversion values (at 5h time on stream TOS – after reaching steady state) recorded for H-ZSM5-55 catalyst differs significantly from other tested materials (Table 2), whereas, the conversion over H-ZSM5-27 and -90 is comparable. This suggests that module M=55 represent 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 worst case, to H_2/CO_2 pair. Traces of H_2 were sporadically seen, especially for not optimized reaction conditions. In many cases the C balance closed around 99.9%-100.1% with full selectivity towards CO.

For comparison purposes also γAl_2O_3, which has only Lewis acid sites[27,28], has been tested (Table 2). FA conversion values did not exceed 2%, which clearly indicates that Lewis acid sites are inactive in the formic acid decomposition, whereas strong Brønsted acid sites are necessary for the dehydration.

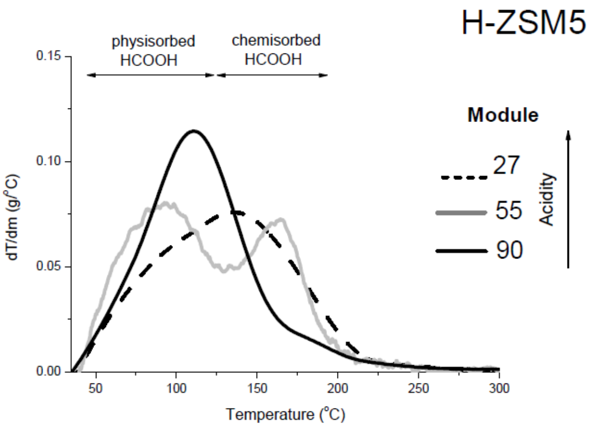

Fig. 2 TGA measurement differential data of H-ZSM5 catalyst with different module values, impregnated with 88% FA in water.

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

By hydrogenating CO_2 in presence of amines, ammonium formiates and formamides could be formed.[5,8,13] Formamides decomposition also should be catalyzed by strong acid centers. Therefore, these catalysts were also tested for the decomposition of dimethylformamide (DMF) and diethylformamide (DEF). Having in mind that the thermodynamic of formamide decomposition is less favorable than for formic acid, and the products are amines, which will adsorb stronger than water, a higher reaction temperature could be expected.

As done previously, TGA-MS analytics on catalyst impregnated with the substrates were done to optimize the catalyst and reaction conditions. The desorption profile resemble the one obtained with FA but maximum release of CO is shifted in the range 220-320°C (Fig. 4). With increasing module the amount of physisorbed compounds is decreasing. Another mass loss at temperatures above 500°C, was observed (Fig. 4-left) where dimethylamine and NH_3 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 should be 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 reaction is conducted at temperatures below 500°C. To have a stable catalyst, different acid centers will be required to catalyze the formamides decomposition. In zeolites, different acid centers can be generated by modifying the preconditioning temperature.

At elevated temperatures Brønsted acid sites are transformed to Lewis acid sites.[31] Use of temperatures higher than 500°C could also result in migration of Al into extra-framework positions (Al_{Ex}), inducting significant complexity into character of possible active sites in the catalyst. The amount and nature of Al_{Ex} depends strongly from the applied pretreatment conditions, zeolite structure, and its Al-content.[32-34] Therefore, existence of various Lewis acid sites and Al forms

Table 2. Representative formic acid conversion values (at 5h TOS) recorded over H-ZSM5 catalyst with different module values, and γAl_2O_3. Tests temperature 190°C, 1.2 g catalyst, HCOOH (98%) flow 1.6 mL/h.

Catalyst	Conversion (%)	Reaction rate ($mmol_{CO}*g_{Cat}^{-1}*h^{-1}$)
H-ZSM5-55	81	28[a]
H-ZSM5-27	52	18
H-ZSM5-90	47	16
γAl_2O_3	2	0.7

[a] reaction rate could be underestimated as measured at 81% conversion

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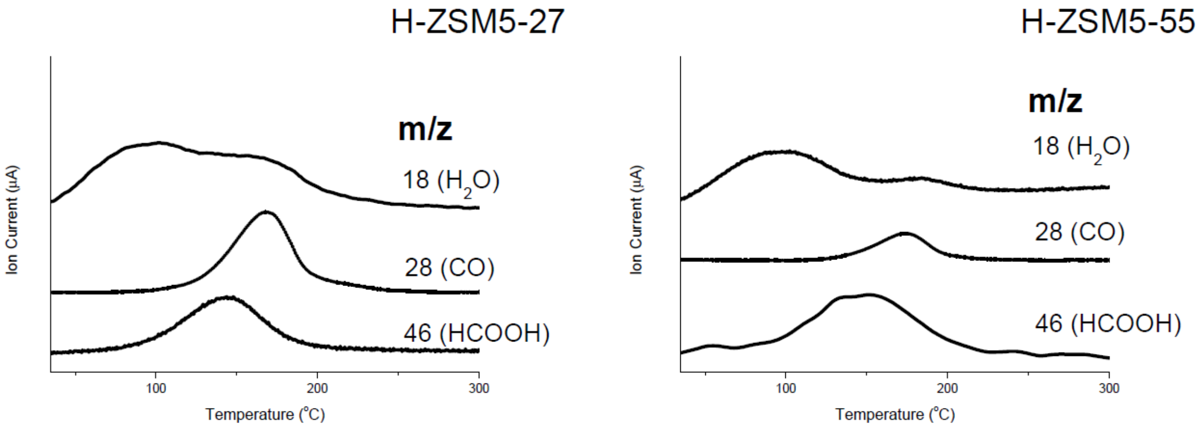

Fig. 3 MS spectra of H-ZSM5-27 and -55, impregnated with 88% FA in water recorded during TGA tests.

in the examined zeolites and their participation in the decomposition, after exposure to high temperature during precondition, is expectable.

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

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

To shed some more light onto the role of different active sites catalysts were characterized by operando spectroscopy (DRIFT). As shown on the example of H-ZSM5-27 preconditioned at 600°C, three distinctive absorption bands can be recognized in the OH-vibration region of fresh catalyst (Fig. 5a). The band at $3740cm^{-1}$(**I**) can be assigned to isolated silanol groups.[35-37] This band does not change from nitrogen gas to reaction condition, as due to their low acidity, silanol groups are not participating in the reaction. A second band, typical for zeolite ZSM5, can be seen at $3600cm^{-1}$(**III**). It corresponds to isolated bridging acidic hydroxyls generated by aluminum in framework positions (Al_f).[35,37] In the zeolites pretreated at lower temperatures there are no additional peaks in the OH-vibration region beside the two aforementioned ones.[35-38]
The band located at $3655cm^{-1}$(**II**) occurs only when the zeolite had been exposed to elevated temperatures[32,33,38] high enough for aluminum migration from framework to extra-framewok positions. It could 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 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 N_2 the recorded spectrum changes again (Fig. 5c). The absorption band representing Al_{Ex} recovers the same intensity as the fresh catalyst, whereas the peak at $3600cm^{-1}$ does not. Thus, amines adsorbed on strong Brønsted acid sites, remain adsorbed at the reaction temperature. Only after heating the sample at 500°C the adsorbed compounds could leave the catalyst surface (Fig. 5d). This fits with the observation of TGA-MS and these species probably could leave only after complete decomposition. Therefore, at the reaction conditions a majority of the Brønsted acid sites generated by Al_F is occupied by the amine, which is the main source of initial activity loss and deactivation. As the catalyst activity stabilize after few hours and higher temperature pretreated sample are slightly more active than lower temperature sample, it seems that acid sites associated to 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

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

Catalyst Precondition Tempreature (°C)	Conversion (%)	Reaction rate ($mmol_{CO}*g_{Cat}^{-1}*h^{-1}$)
300	22	1.6
600	30	2.2

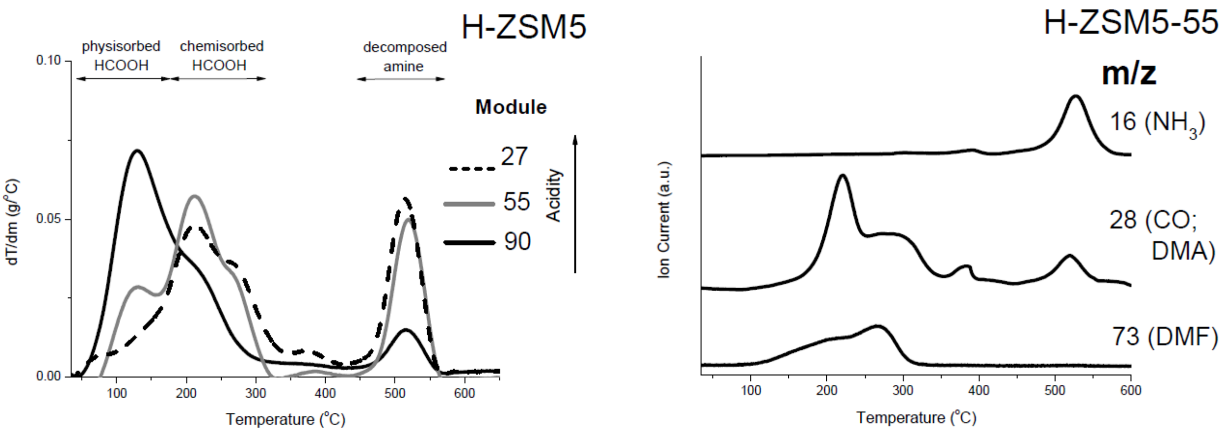

Fig. 4 *(LEFT)* TGA measurement TGA measurement differential data of H-ZSM5 catalyst with different module values, impregnated with dimethylformamide - DMF. *(RIGHT)* MS spectra of H-ZSM5-55, impregnated with dimethylformamide recorded during TGA tests. DMA – dimethylamine.

(a temperature that would not generate any significant amount of Al_{Ex} species), Lewis acid centers should have also an active role in the DEF decomposition.

To further confirm our hypothesis that Lewis acid sites are responsible for formamide decomposition, a target experiments over γAl_2O_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 γAl_2O_3, the corresponding amine also undergoes decomposition, causing the observed deactivation. Another plausible mechanism could lead through 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 second step. It should be clarified that no amine decomposition products were detected when the reaction was conducted over the zeolites.

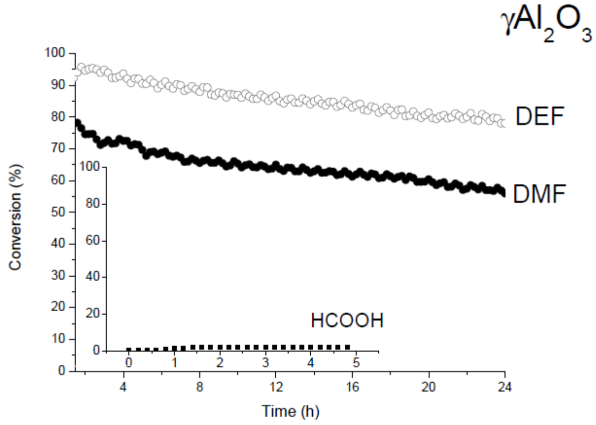

Fig. 6 Conversion of different substrates (formic acid 98%-HCOOH; dimethylformamide-DMF; diethylformamide-DEF) versus time on stream over γAl_2O_3. Test temperature: 190ºC for HCOOH; 280ºC for formamides, 0.6g catalyst, substrate flow 0.5 mL/h.

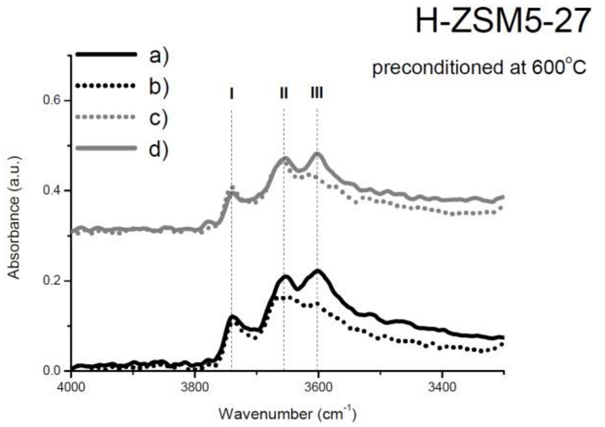

Fig. 5 DRIFT spectra of H-ZSM5-27 catalyst at 280ºC: a) fresh catalyst under N_2 flow; b) catalyst under diethylformamide vapors flow; c) catalyst after contact with the substrate, flushed with N_2; d) catalyst after heating for 30 min at 500ºC.

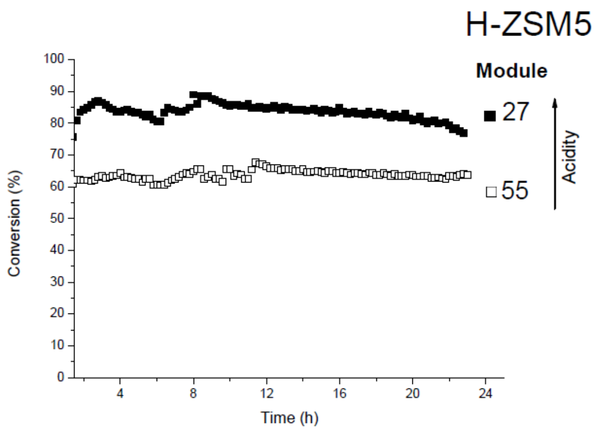

Fig. 7 Dimethylformamide conversion versus time on stream over H-ZSM5 catalyst with different module values. Test temperature 280ºC, 0.6g catalyst, DMF flow 0.5mL/h.

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

Module	Surface Area (m^2/g)	Mean Pore Diameter (Å)
27	403	3.3
55	427	3.4
90	408	3.8

Molecule Size (Å)	Substrate name
3.6 x 4.2	Dimethylformamide
3.8 x 5.4	Diethylformamide

This difference could be caused by different strength and space density (*i.e.* multisite process) 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 and extra-framework sites, should be preferred in this case.

To confirm the long time stability of these systems the reaction profile for different catalysts was measured. All tested H-ZSM5 are active in 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 amount of aluminum in the material and, as its corollary, amount of suitable active sites.

As we would expect from Fig. 6, DEF conversion should be higher than DMF (due to thermodynamic condiserations), however we observed a much higher activity in DMF decomposition (up to 90%) compared to DEF (around 30%). This is probably due to internal mass diffusion limitations, as the larger DEF (see table 4) is probably less prone to penetrate deeply the narrow channels of ZSM-5 compared to DMF.

Indeed higher conversion was observed on microcrystalline ZSM5 (denoted ZSM5-28 1-3µm) compared to ZSM5-27 (3-5µm) - 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 diffusion limitation of these large formamide molecules could have, H-form of zeolite Y was tested (Fig. 10). The faujasite structure of zeolite Y provides better acid sites accessibility than relatively narrow pores of ZSM5. Moreover, compared to ZSM5, the applied zeolite Y could be synthesized with 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 position occurs to a higher extent than in the case of MFI structure, and is also well described in the literature.[30,39] Thus, 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 ≥ 99.6%. γAl_2O_3, as already seen in Fig. 6, deactivates very rapidly and only in the first few hours TOS is comparable to H-Y.

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 and extra-framework aluminum are active, which suggest a different reaction mechanism. Accessibility and diffusion limitations could play also an important role, especially for large formamides molecules. Based on these

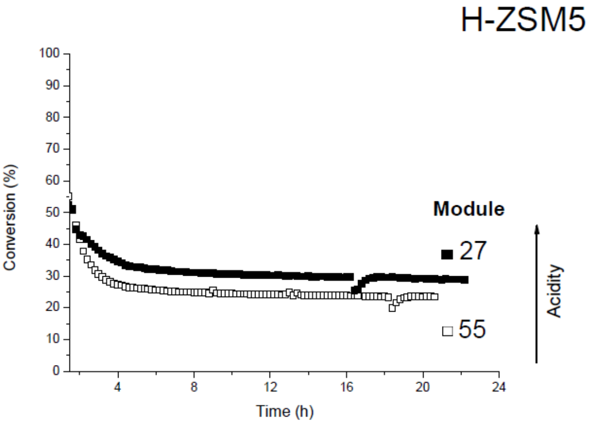

Fig. 8 Diethylformamide conversion versus time on stream over H-ZSM5 catalyst with different module values. Test temperature 280ºC, 0.6g catalyst, DEF flow 0.5mL/h.

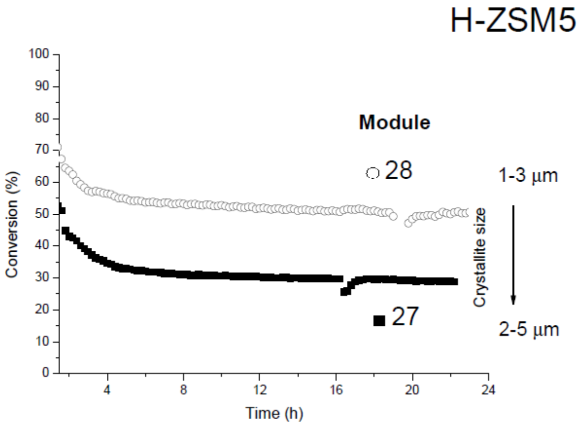

Fig. 9 Diethylformamide conversion versus time on stream over H-ZSM5-27 and H-ZSM5-28 catalyst with different crystallite sizes. Test temperature 280ºC, 0.6g catalyst, DEF flow 0.5mL/h.

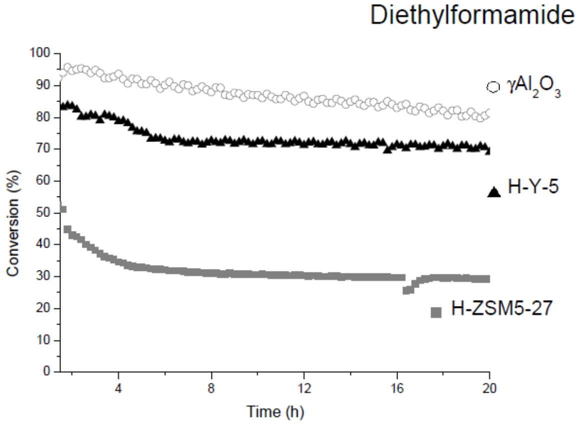

Fig. 10 Comparison of diethylformamide (DEF) conversion versus time on stream over various catalysts. Test temperature: 280ºC; 0.6g catalyst, substrate flow 0.5mL/h.

consideration optimized catalysts (in terms of acidity, crystallite size, pore structure) had 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 CO_2 hydrogenation, had been found to be feasible and could represent a novel, storable and sustainable[40] source of CO for the chemical industry in a society not depending solely on fossil resources.

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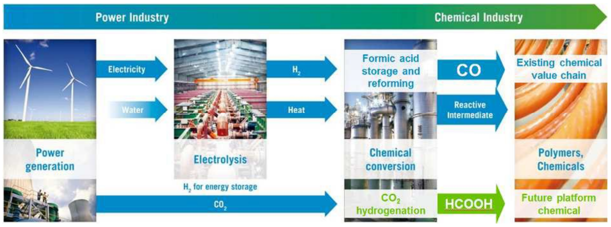

Formic acid could bridge the power and chemical industry sustainably integrating into the existing chemical value chain.