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How to Translate the $[LCu_2(H)]^+$ - Catalysed Selective Decomposition of Formic Acid into H_2 and CO_2 from the Gas Phase into a Zeolite.

Marjan Krstić,[a] Qiuyan Jin,[b] George N. Khairallah,[b] Richard A. J. O'Hair*[b] and Vlasta Bonačić-Koutecký*[a,c]

Dedicated to Profs. John H. Bowie and Michael I. Bruce on the occasions of their 80th birthdays.

Abstract: Translating a homogenous catalyst into a heterogeneous catalyst requires a fundamental understanding of how the catalyst "fits" into the zeolite and how the reaction is influenced. Previous studies of bimetallic catalyst design identified a potent copper homobinuclear catalyst, $[(L)Cu_2(H)]^+$ for the selective decomposition of formic acid. Here, a close interplay between theory and experiment shows how to preserve this selective reactivity within zeolites. Gas-phase experiments and DFT calculations showed that switching from 1,1-bis(diphenylphosphino)-methane ligand to the 1,8-naphthyridine ligand produced an equally potent catalyst. DFT calculations show that this new catalysts neatly fits into a zeolite which does not perturb reactivity, thus providing a unique example on how "heterogenization" of a homogenous catalyst for the selective catalyzed extrusion of carbon dioxide from formic acid can be achieved, with important application in hydrogen storage and *in situ* generation of H_2.

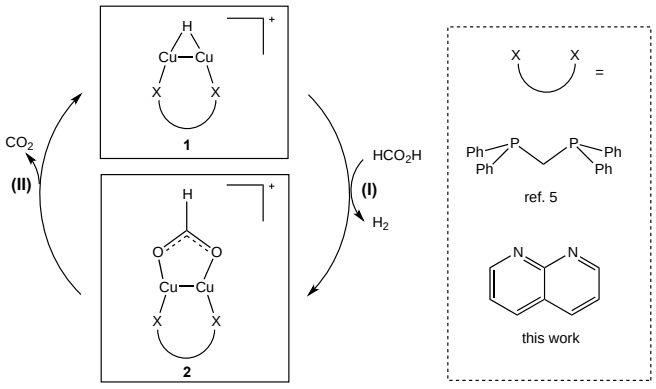
Introduction

Zeolites, with their unique porous structures and diverse sizes, have proven their worth as frameworks for the design of robust catalysts with specific applications.[1] A potent example of a selective transition metal zeolite based catalyst that exploits the combination of adsorption and catalytic properties is Cu-SSZ-13, which is used in the ammonia-assisted Selective Catalytic Reduction (NH_3-SCR) of NO_x as a key emission control method for lean-burn diesel engines.[2]

The marriage of computational and experimental methods offers opportunities to create tailor-made zeolite catalysts based on a molecular level understanding.[3] A particular attractive concept that takes advantage of the strengths of homogenous and heterogenous catalysis is the "heterogenization" of a homogenous catalyst.[4] Here we use a combination of theory and gas-phase experiments to establish the requirements to "heterogenize" our recently designed phosphine ligated coinage metal hydrides for the catalytic and selective gas-phase decomposition of formic acid into carbon dioxide and hydrogen (eq. 1),[5-7] a reaction crucial for the use of formic acid in hydrogen storage applications.[8]

$$HCO_2H \rightarrow H_2 + CO_2 \quad (1)$$

The gas-phase catalytic cycle involves two steps. Firstly, a ligated binuclear "M1M2(H)$^+$" scaffold (M1 and M2 are coinage metal cations) is dehydrogenated by reaction with formic acid, producing the formate $[(L)M1M2(O_2CH)]^+$ and H_2 (Scheme 1, Step I). Decarboxylation of $[(L)M1M2(O_2CH)]^+$ via collision induced dissociation (CID) regenerates the catalyst $[(L)M1M2(H)]^+$ (Scheme 1, Step II). The nature of the bisphosphine ligand,[5] metal [6] and stoichiometry [7] were all found to play key roles, with $[(dppm)Cu_2(H)]^+$ (dppm = 1,1-bis(diphenylphosphino)-methane) emerging as the most effective catalyst.[6]



Scheme 1. Selective decarboxylation of formic acid via a two-step catalytic cycle involving bimetallic catalysis. Step (I) is an ion-molecule reaction with formic acid; Step (II) involves liberation of CO_2 under CID conditions.

While a range of "ship-in-a-bottle" catalysts that entrap a metal complex in the nanocavity of a zeolite have been prepared,[9,10] the transformation of a gas-phase catalyst into a zeolite framework has not previously been considered. Conceptually, this requires a joint approach using theory and gas-phase

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experiments to find the catalyst that best fits into the zeolite whilst still maintaining its reactivity.

Results and Discussion

The challenge of bisphosphine ligands.

The ZSM-5 zeolite was chosen because of its large pores and sole construction from "SiO" units. Initial modelling efforts highlighted that the $[(dppm)Cu_2(H)]^+$ was too bulky to fit into the ZSM-5 zeolite as shown in Figure 1 a), and so the phenyl groups were replaced by methyl groups to generate $[(dmpm)Cu_2(H)]^+$ (dmpm = 1,1-bis(dimethylphosphino)-methane), as shown in Figure 1 b) which did not significantly alter the gas-phase catalytic cycle. Furthermore, the structures and energies of key species associated with both steps of the catalytic cycle readily translate from the gas-phase into the ZSM-5 zeolite (compare Figures S1 and S2). Unfortunately, the dmpm ligand is pyrophoric, making its ready use impractical.

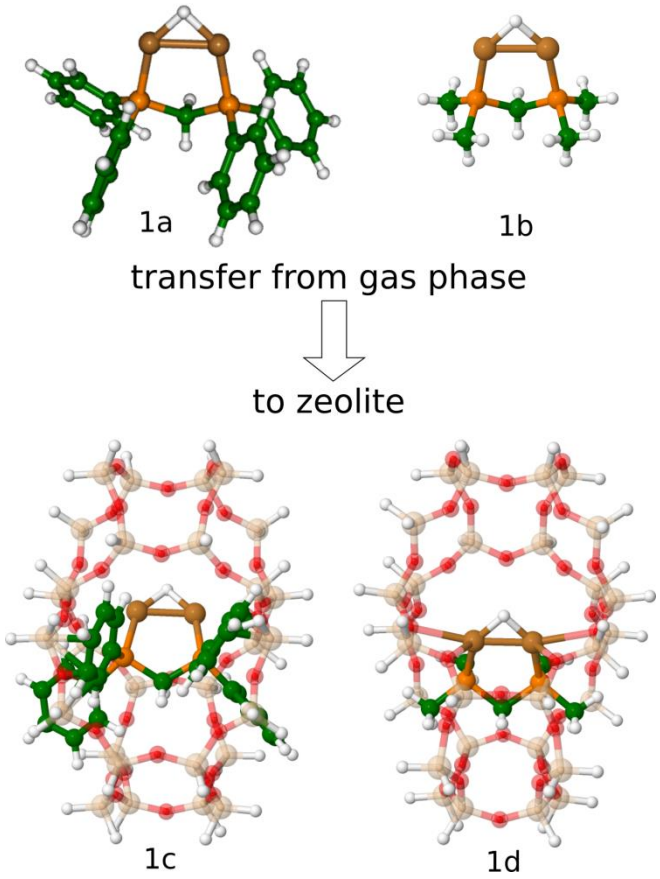


Figure 1. Lowest energy structures for 1a $Cu_2H(dppm)^+$ and 1b $Cu_2H(dmpm)^+$; 1c and 1d transfered into ZSM-5 zeolite. Color coding of atoms are: green – carbon, orange – phosporus, white – hydrogen, brown – copper, red – oxygen, pink – silicon.

Using gas-phase experiments to evaluate the use of 1,8-naphthyridine (napy) as a ligand.

We next decided to replace the bisphosphine ligand with the 1,8-naphthyridine (napy) ligand. This ligand was chosen since it: has a compact rigid and planar structure; has been used to form binuclear copper carboxylate complexes;[9] and $[(napy)Cu_2(O_2CAr)]^+$ complexes have been shown to readily decarboxylate under CID conditions.[12] Gratifyingly, a series of multistage mass spectrometry (MS^n) experiments showed that replacement of dppm with napy did not alter the selective decarboxylation of formic acid. Thus $[(napy)Cu_2(D)]^+$, formed via CID on $[(napy)Cu_2(O_2CCD_2CD_2C_6D_5)]^+$ (Figure S3a) reacted with formic acid to produce $[(napy)Cu_2(O_2CH)]^+$ (Figure S3b), which upon CID generates $[(napy)Cu_2(H)]^+$. Mass selection of this hydride followed by reaction with formic acid also generates $[(napy)Cu_2(O_2CH)]^+$ (Figure 2(a)) and CID reforms $[(napy)Cu_2(H)]^+$ (Figure 2(b)), thereby closing the catalytic cycle. In terms of evaluating the catalytic cycle, kinetic measurements (Figures S4 and S5) reveal that both $[(napy)Cu_2(H)]^+$ and $[(napy)Cu_2(D)]^+$ react with formic acid at the collision rate (Table S1), while the dominant product of CID of $[(napy)Cu_2(O_2CH)]^+$ is the $[(napy)Cu_2(H)]^+$, with only a minor amount of $[(napy)Cu]^+$ being formed via copper formate loss (Scheme S1). The selective chemistry observed in both steps of the catalytic cycle coupled with the multistage mass spectrometry capabilities of the ion trap allowed us to transverse the catalytic cycle four times with little loss of ion signal (Figure S3). Thus the newly developed $[(napy)Cu_2(H)]^+$ is essentially as effective a catalyst as the previously reported $[(dppm)Cu_2(H)]^+$.

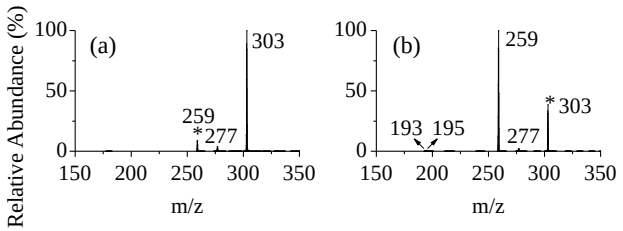


Figure 2. LTQ mass spectra obtained for the MS^n CID (or IMR) experiments of: (a) IMR of $[(napy)^{63}Cu^{65}Cu(H)]^+$ (*m/z* 259) with formic acid; (b) CID of $[(napy)^{63}Cu^{65}Cu(O_2CH)]^+$ (*m/z* 303). An activation time 30 ms was used for the CID experiments and 300 ms for the IMR experiments. The concentration of formic acid ($[HO_2CH]$ ion trap = 5 x 10^9 molecules.cm^{-3}) was kept low so as to minimize ion-molecule reactions during the CID time. A * represents the mass-selected precursor ion.

Using DFT calculations to examine the mechanism and energetics of the reactions of $[(napy)Cu_2(H)]^+$ and $[(napy)Cu_2(O_2CH)]^+$.

A key finding is that the DFT calculated profile shown in Figure 3 remains almost unchanged in comparison with the one obtained for $[(dppm)Cu_2H]^+$, serving as a proof-of-principle that the cooperative effect between the "$Cu_2(H)^+$" scaffold and the ligand (Scheme 1) is responsible for the selective bimetallic reactivity. The calculated energetics are consistent with the experiments. In order for it to occur under the near thermal conditions of the ion-trap, Step 1 of the catalytic cycle must be an exothermic process with barriers that lie below the separated reactants. Figure 3 shows that this is the case, with the formation of an initial complex between $[(napy)Cu_2(H)]^+$ and formic acid, which

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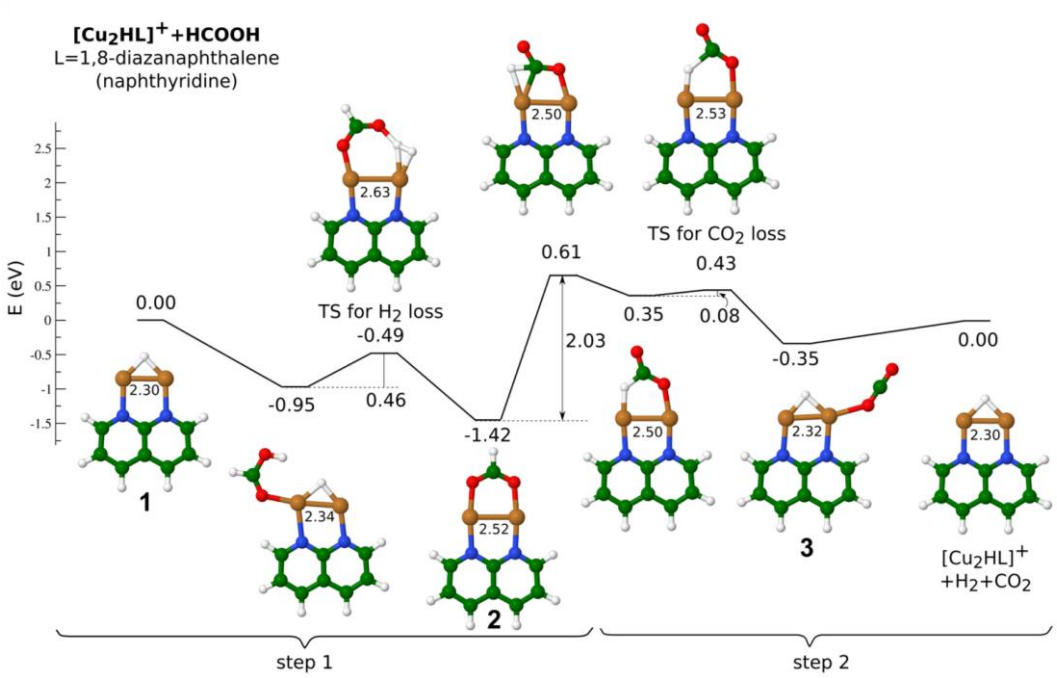


Figure 3. DFT-calculated energy profile for the two reaction steps in the catalytic cycle for $[(napy)Cu_2(H)]^+$ in the gas-phase. All structures were fully optimized using DFT method with the hybrid B3LYP functional[23] and def2-TZVP atomic basis set which has been used for all atoms.

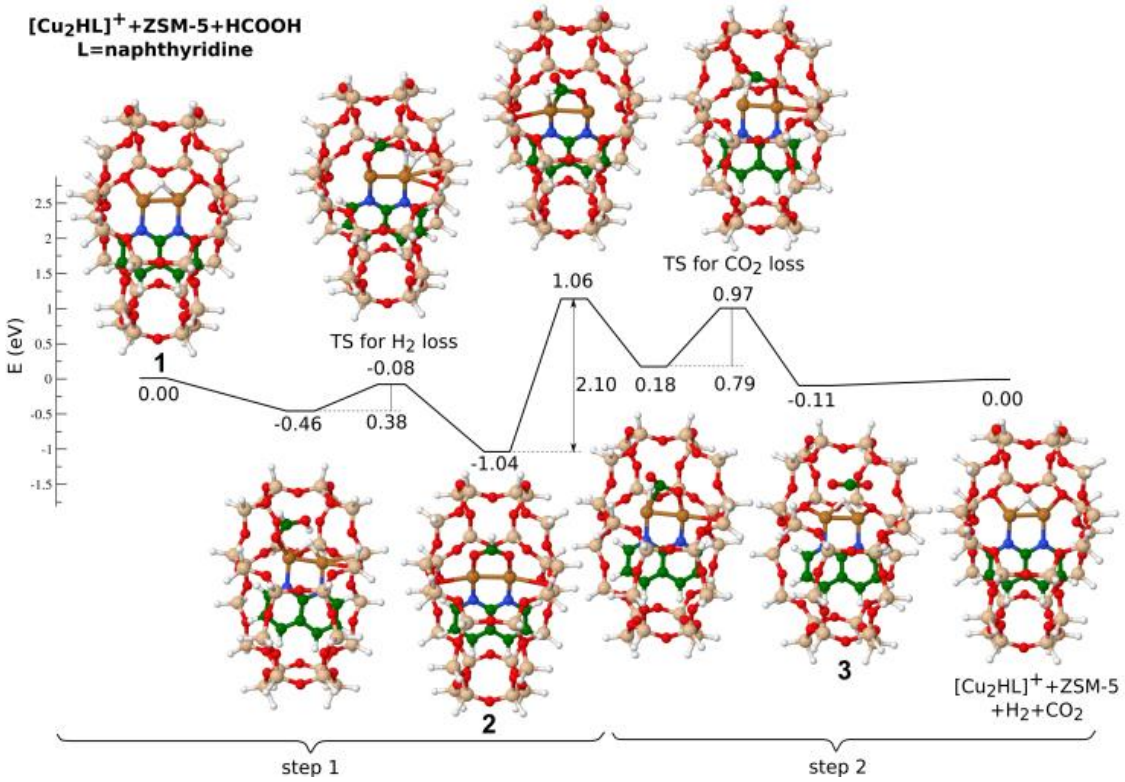


Figure 4. DFT-calculated energy profile for the two reaction steps in the catalytic cycle for the "ship in a bottle" $[(napy)Cu_2(H)]^+$/ZSM-5 zeolite system. All structures were fully optimized using DFT method with the RI-PBE functional and def2-TZVP atomic basis set which has been used for all atoms.

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then proceeds via a single transition state that lies 0.49 eV below separated reactants to produce H_2 and the thermodynamically favoured O,O-bridged formate complex, $[(napy)Cu_2(O_2CH)]^+$. In contrast, Step 2 is endothermic as it requires energization of $[(napy)Cu_2(O_2CH)]^+$ through multiple collisions with the helium bath gas during the CID process. The DFT calculations reveal that both copper centers play a role in the decarboxylation process, which involves two steps (Figure 3). The first step involves breaking one of the Cu-O bonds to isomerize the O,O- bridged formate to its O-bound form, and is the rate determining step. The next step involves decarboxylation, to give the O bound $[(napy)Cu_2(H)(OCO)]^+$ complex, which then loses CO_2.

Translating the gas-phase $[(napy)Cu_2(H)]^+$ catalysts into a zeolite.

Having established that $[(napy)Cu_2(H)]^+$ is an effective catalyst, we next used DFT calculations to examine whether this more compact catalyst could be incorporated into a zeolite while still maintaining its catalytic properties. The DFT calculated energy profile (Figure 4) highlights that translation of decomposition of formic acid into H_2 and CO_2 from the gas phase into a zeolite is indeed possible. The loss of H_2 in the first step remains energetically favourable with respect to its gas phase counterpart and the second step for removal of CO_2 is not significantly disfavoured energetically with respect to the gas phase (see Table S2 for a direct comparison of the energetics of all species). While there are obvious changes in the Mulliken charges on placing the gas-phase $[(napy)Cu_2(H)]^+$ catalyst into the zeolite (Figure S6), these are clearly less important than maintaining the overall structure of the catalysts. Thus a comparison of the structural features of all species associated with the reaction coordinate in the gas-phase and in the zeolite (Table S3) reveals that the zeolite pores allow conservation of the ligated "$Cu_2(H)^+$" scaffold, which is the key actor required for the selective decomposition of formic acid into H_2 and CO_2.

Ruling out reactivity of formic acid at zeolite sites.

There are two potential decomposition pathways for formic acid: (1) into H_2 and CO_2; (2) formation of H_2O and CO.[13] How might the zeolite facilitate either of these pathways? It is unlikely that the zeolite will play a direct role in the decomposition of formic acid into H_2 and CO_2 since a previous study has shown that this requires reengineering the zeolite to include more basic germanium sites.[14] In order to verify that decomposition of formic acid into H_2O and CO is not zeolite-induced, we have investigated interaction of formic acid with the O and Si atoms of the zeolite. Three different complexes between formic acid and $[(napy)Cu_2(H)]^+$ embedded in a zeolite have been surveyed along their structural optimization pathways. Structures and associated energies are shown in Figures S7-S9, which illustrate that formic acid binds exclusively at the "$Cu_2(H)^+$" scaffold. Thus the zeolite is unlikely to directly contribute to the decomposition pathways for formic acid, and instead acts as a nanocontainer for the $[(napy)Cu_2(H)]^+$ catalyst.

Balancing the cation charge: counter-anion versus fixed charge ligand.

An important final consideration is that the gas-phase experiments require a net charge of +1 on the copper complexes associated with the catalytic cycle necessary for their detection using mass spectrometry. In contrast, the overall charge for the "ship-in-a-bottle" catalysts needs to be 0. This can be achieved using a counter anion. Although we have not investigated the ideal counter anion, some comments on the suitability of different classes of anions are offered. Small anions are undesirable since they can both potentially move in and out of the zeolite and also bind to the metal centre to disrupt the catalytic cycle. A potential solution is to apply Krossing's concept of "gas phase cations in the condensed phase" in which a bulky, weakly-coordinating anion (WCA) is used.[15,16]

An alternative approach is to use a fixed charge anionic ligand, which when bound to the "$Cu_2(H)^+$" scaffold produces a metal complex with a net charge of 0. Ideally, the modification of the napy ligand by the installation of a functional group that contains a negative charge should neither influence the "fit" of the complex in the zeolite nor change its mode of reactions. With regards to the latter point, based on the design of other fixed charge ligands, the 1,8-naphthyridine-3-sulfonate ligand is likely to be a suitable candidate to generate the complex $[(3\text{-}O_3S\text{-}napy)Cu_2(H)]$.[17] Indeed, the results of the DFT calculations confirm that for the neutral system the energy profile for the Step 1 of the catalytic reaction is almost identical with the one obtained for cationic $[(napy)Cu_2(H)]^+$ system (cf. Table S2). The reason for this is that influence of negative ligand on the charge of the one of Cu atoms is relatively small in spite the fact that the system is neutral as illustrated by Mulliken charges in Figure S6. This means that the charges on the key catalytic subunit remain almost unchanged, which leads to similar energy profiles for cationic and neutral systems.

Conclusion

In conclusion, DFT calculations highlight that the cooperative effects of the "$Cu_2(H)^+$" scafold and the ligand neccessary for the selective decomposition of formic acid remain unchanged on translating from the gas-phase into the ZSM-5 zeolite. This first example of the "heterogenization" of a gas-phase catalyst shows that the gas-phase mechanism is maintained within the zeolite due to the role of $[LCu_2H]^+$ as the key actor, with the zeolite taking on the role of an inert nanocontainer to encapsulate the catalyst. The issue of balancing the requisite net charge for MS based studies when translating the gas phase catalyst into a zeolite can be dealt with by using a suitable fixed charge ligand. Unlike the "heterogenization" of a solution phase homogenous catalysis, where the precise identity of the catalyst can be difficult to pin down,[18] the concept of using basic theoretical and experimental investigations to take a stoichiometrically well-defined gas-phase catalyst and translate it into a zeolite opens up new possibilities for the design of catalysts.

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Experimental Section

Mass spectrometry experiments: Gas-phase experiments on $[(napy)Cu_2(H)]^+$, formed as discussed in the Supporting Information, were carried out using a Finnigan linear quadrupole (LTQ) mass spectrometer modified to allow the study of IMR.[19] The unimolecular fragmentation/dissociation of mass-selected $[(napy)Cu_2(O_2CH)]^+$ occurred via CID using a normalized collision energy of 20 and an activation time of 30 ms. The CID isolation width was 1 *m/z*. IMRs were carried by delivering a measured concentration of formic acid into the helium bath gas, and rates were measured by varying the reaction time.

Theoretical methods

The Zeolite catalyst model has been built from the crystal structure of the ZSM-5 zeolite. The elementary unit representing a typical repeating pore consisting of 28 silicon and 77 oxygen atoms was selected. Terminal oxygen atoms were substituted by 42 hydrogen atoms to replace the broken Si-O bonds. These H atoms were held fixed during geometry optimizations used for the search of local minima and transition states, which include relaxation of the remaining Si and O atoms of the zeolite pore framework within the DFT method. The ligated copper hydride $[(napy)Cu_2(H)]^+$ was inserted in optimized ZSM-5 model pore. The extensive search for lowest energy structures and transition states of this complex system were performed using the PBE functional[20] with resolution of identity (RI) method [21] in combination with def2-TZVP atomic basis set [22], which have been used for all atoms. Reaction profiles were constructed from a series of calculated local minima and transition states along the reaction path.

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Keywords: Bimetallic catalysis • Formic Acid • Selective Decarboxylation • Zeolites • DFT calculations

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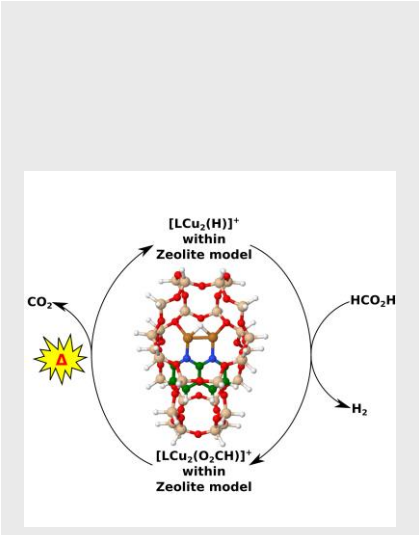
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Layout 1:

COMMUNICATION

Catalysis

"Heterogenization" of a homogenous catalyst: To fit the stoichiometrically well-defined gas-phase catalyst $[LCu_2(H)]^+$, designed for the selective decomposition of formic acid into H_2 and CO_2, into a zeolite requires switching the bulky 1,1-bis(diphenylphosphino)-methane ligand with the 1,8-naphthyridine ligand. The gas-phase mechanism is maintained within the zeolite.



Marjan Krstić, Qiuyan Jin, George N. Khairallah, Richard A. J. O'Hair and Vlasta Bonačić-Koutecký**

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How to Translate the $[LCu_2(H)]^+$ Catalysed Selective Decomposition of Formic Acid into H_2 and CO_2 from the Gas-phase into a Zeolite.

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