

Mechanistic Studies on the Hydrogenation of Carbon Dioxide over Copper Alkoxide in Metal-Organic Frameworks

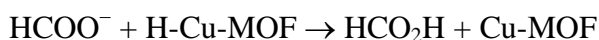
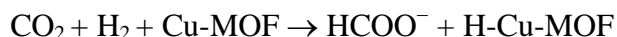
Thana Maihom^{a,b}, Michael Probst^b and Jumras Limtrakul^a

^a*Department of Chemistry and Center for Advanced Studies in Nanotechnology and its Applications in Chemical, Food and Agricultural Industries, Kasetsart University, Bangkok 10900, Thailand*

^b*Institute of Ion Physics and Applied Physics, University of Innsbruck, 6020 Innsbruck, Austria*

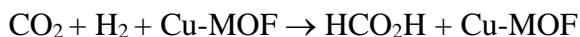
The reaction mechanisms of the hydrogenation of carbon dioxide (CO₂) to formic acid over Cu-alkoxide functionalized metal organic framework (MOF) have been investigated by means of calculations with the M06-L [1] density functional. This method has already been found to be suitable to describe adsorption and reaction in porous materials such as zeolites and MOF systems [2-3]. Two different pathways, stepwise and concerted, are considered in this study.

In the stepwise mechanism, the reaction is assumed to proceed in two steps, in the first step CO₂ is hydrogenated to a formate intermediate. In step 2, the formate is further hydrogenated into formic acid:



The activation energies for the two steps are 24.1 and 20.9 kcal/mol, respectively.

In the concerted mechanism, the hydrogenation of CO₂ to formic acid occurs in a single step:



Due to the large activation barrier of 67.8 kcal/mol associated with this pathway therefore the stepwise mechanism seems to be favored. The catalytic effect of Cu-MOF-5 is highlighted by comparing with the bare system in which the reaction takes place in one step with a barrier of 73.8 kcal/mol.

[1] Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, 41, 157.

[2] Wannakao, S.; Warakulwit, C.; Kongpatpanich, K.; Probst, M.; Limtrakul, J. *ACS Catalysis*, **2012**, 2, 986.

[3] Maihom, T.; Choomwattana, S.; Khongpracha, P.; Probst, M.; Limtrakul, J. *ChemPhysChem* **2012**, 13, 245.