

Energetics of the Water–Gas-Shift Reaction on the Active Sites of the Industrially Used Cu/ZnO/Al₂O₃ Catalyst

Felix Studt · Malte Behrens · Frank Abild-Pedersen

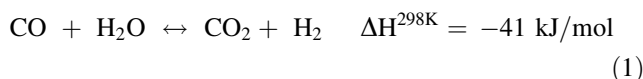
Received: 13 August 2014 / Accepted: 30 August 2014 / Published online: 14 September 2014
© Springer Science+Business Media New York 2014

Abstract The energy profile for the water–gas-shift reaction has been calculated on the active sites of the industrially used Cu/ZnO/Al₂O₃ catalyst using the BEEF-vdW functional. Our theoretical results suggest that both active site motifs, a copper (211) step as well as a zinc decorated step, are equally active for the water–gas-shift reaction. We find that the splitting of water into surface OH* and H* constitutes the rate-limiting step and that the reaction proceeds through the carboxyl mechanism. Our findings also suggest that mixed copper-zinc step sites are most likely to exhibit superior activity.

Keywords Density functional theory calculations · Reaction mechanism · Methanol synthesis · Copper · Van der Waals

1 Main Text

The water–gas-shift (WGS) reaction (Eq. 1) is industrially relevant for several large-scale processes such as H₂ production, ammonia synthesis, and methanol synthesis [1]. It is also a promising CO clean-up step for H₂ streams in decentralized units for fuel cell applications [2]. The reaction is slightly exothermic (−41 kJ/mol), lower temperatures are hence advantageous, pushing the equilibrium towards high H₂ and low CO contents. Industrially, the reaction often takes place in two steps, a high temperature and a low temperature step. The focus of this work is on the low-temperature WGS where copper-zinc catalysts are employed as they exhibit high WGS activity at moderate temperatures (200–270 °C) [3, 4]. The same class of catalysts is also used to convert synthesis gas, a mixture of CO, CO₂ and H₂, to methanol [5]. Here, CO₂ is converted to methanol and water. Water subsequently reacts with CO to form CO₂ and H₂ via the WGS. Importantly, the WGS reaction is significantly faster than CO₂ hydrogenation to methanol and hence equilibrated under industrial methanol synthesis conditions [6].



Owing to the industrial importance of the WGS reaction, a number of theoretical studies based on density functional theory have been performed on model catalysts [7–13]. Most commonly, the (111) facet of copper has been investigated [7–10]. Surface science experiments have shown, however, that the WGS reaction on copper is extremely structure sensitive, with the Cu(110) surface being more active than Cu(111) [14–16]. Also, experimental studies with Cu nanoparticles deposited on a SiO₂ support by atomic layer epitaxy showed that defect sites on

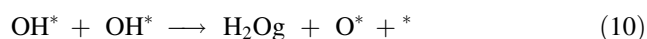
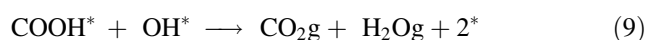
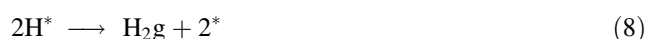
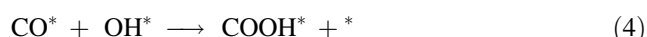
Electronic supplementary material The online version of this article (doi:10.1007/s10562-014-1363-9) contains supplementary material, which is available to authorized users.

F. Studt (✉) · F. Abild-Pedersen
SUNCAT Center for Interface Science and Catalysis, SLAC
National Accelerator Laboratory, Menlo Park, CA 94025, USA
e-mail: studt@slac.stanford.edu

F. Studt · F. Abild-Pedersen
Department of Chemical Engineering, Stanford University,
Stanford, CA 94305, USA

M. Behrens
Faculty of Chemistry and CENIDE, University of Duisburg-
Essen, Universitätsstr. 7, 45141 Essen, Germany

the Cu surface play a major role for the WGS activity by helping water activation and CO binding [17, 18]. The structure sensitivity has also been confirmed theoretically using stepped (110) and (321) surfaces [12, 13]. Most of these density functional theory studies have been performed using the PW91 functional [19], effects of the exchange–correlation functional on the H₂O dissociation step using the PBE [20] and RevPBE [21] functional have also been considered [22]. We have shown recently that the BEEF-vdW [23] functional yields a more quantitative description of the conversion of CO₂ and hydrogen to methanol over copper and copper-zinc surfaces [24, 25]. This can be attributed to the inclusion of van der Waals (vdW) forces in the description of adsorbate–surface interactions for larger adsorbates with dangling bonds. The intermediates of the WGS reaction are similar to those involved in CO₂ hydrogenation and we therefore employ the BEEF-vdW functional in order to develop a quantitative picture of the WGS reaction. There is an old [26] and ongoing [2] debate about the mechanism of the low temperature WGS reaction, where mainly an associative mechanism via decomposition of a formate intermediate or a regenerative mechanism through complete (redox) or partial (carboxylate) dissociation of water have been discussed. For ceria supported Cu catalysts, there is recent ample experimental evidence that formate is a spectator species rather than an intermediate [27–30]. Herein, we consider a range of possible reactions involved in the WGS reaction network in the context of the redox and carboxylate mechanisms¹ that have also been described in earlier studies: [10].



where intermediates with an asterisk are adsorbed on the surface. An asterisk denotes a free site on the surface.

Recent experimental and theoretical work has identified the active site motif of the Cu/ZnO/Al₂O₃ catalyst that is used industrially to convert a mixture of CO₂, CO and H₂

to methanol [31]. Like the WGS reaction, methanol synthesis was found to be structure sensitive, here defects such as step sites are responsible for the high activity of the catalysts. It was further possible to identify the active sites for CO (a clean Cu(211) step) as well as CO₂ hydrogenation (a Zn-doped Cu(211) step), and the industrially used methanol catalyst is thought to contain mainly the latter [25, 32]. Herein we report a detailed theoretical analysis of the WGS reaction using these two active site motifs (see Fig. 1). Employing the BEEF-vdW functional in connection with these active site motifs should give us a quite realistic description of the WGS reaction for the industrially employed Cu/ZnO/Al₂O₃ catalyst.

All DFT calculations were performed using the Quantum-Espresso code [33] using the ASE interface [34]. The active site motifs are identical to those reported earlier [25] and gas-phase CO₂ and H₂ energies were corrected as described elsewhere [25, 35]. Details about the calculational setup can be found in the experimental section. Figure 2 shows the calculated free energy diagram of the WGS reaction on a stepped Cu(211) surface via the (a) redox and (b) carboxyl mechanism.

We will start by discussing the redox mechanism of the WGS reaction (Fig. 2a). Here the highest free energy barrier is the dissociation of OH* to O* and H*. This barrier is 2.16 eV above gas-phase CO and H₂O, thus being prohibitively high. O* can also be produced via reaction of two OH* to yield water and O*. The corresponding free energy barrier is significantly lower being only 1.51 eV in terms of free energy. Both splitting of water to OH* and H* and the oxidation of CO* to CO₂ have a lower free energy.

The bottleneck of the carboxyl mechanism (Fig. 2b) lies in the decomposition of COOH* to CO₂ and H*. This transition state is located at 2.26 eV. Decomposition with the help of surface OH* (similar to that described for O–H splitting in the redox mechanism) substantially reduces the barrier to 1.20 eV. The rate determining step for the carboxyl mechanism is thus splitting of water to yield OH* and H*. The free energy barrier is 1.39 eV in. The results for both, the redox and carboxyl mechanism are in qualitative agreement with earlier studies on the (111) surface of Cu [10]. Based on the free energy diagram one would expect that the carboxyl mechanism dominates the total rate of the WGS reaction as the pathway proceeds via a free energy pathway that is about 0.1 eV lower than that of the redox pathway. H₂O activation seems to constitute the rate-determining step. Both observations are in agreement with theoretical and kinetic studies on the Cu(111) surface [10].

Under the reaction conditions chosen here (see figure caption of Fig. 2), the H₂O splitting free energy barrier is 1.39 eV above the educts, H₂O (and CO). Given no other limitations this barrier would roughly correspond to a reaction rate of 10⁻¹ per site and second using harmonic

¹ The term “redox mechanism” was originally introduced as “surface redox mechanism” in order to distinguish it from the true “redox mechanism” taking place on high-temperature iron oxide catalysts.

Fig. 1 Active site motifs of the Cu- and Zn-site. Cu atoms are depicted in *orange*, Zn atoms are depicted in *grey*

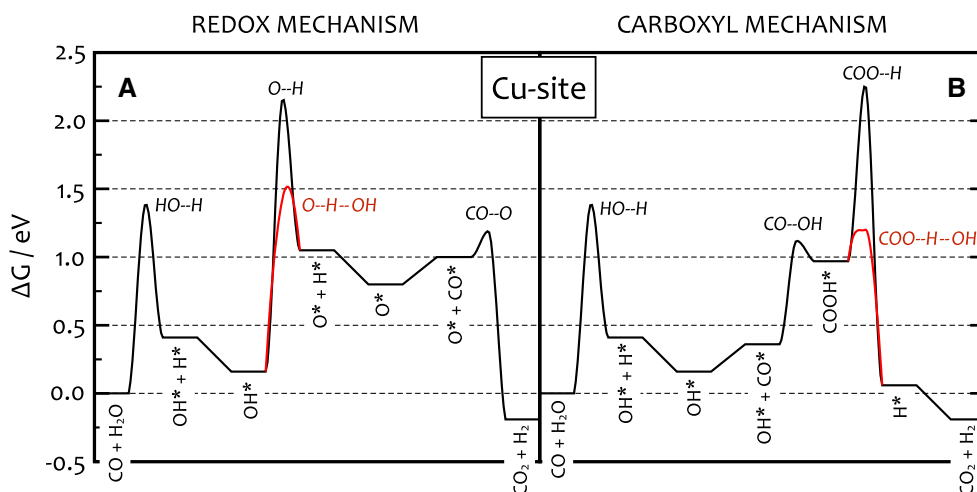
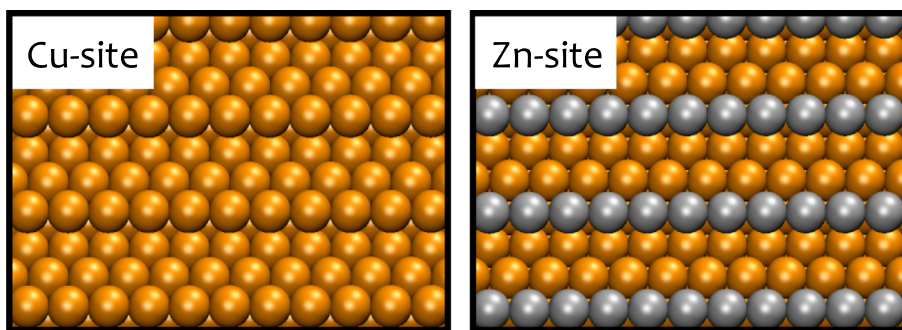


Fig. 2 Gibbs-free energy diagram of the water–gas-shift reaction via the redox (a) and carboxyl (b) mechanism on the Cu(211) surface (denoted here as the Cu-site). Reactions including hydrogen abstraction via adsorbed OH are depicted in red. All energies are relative to

CO + H₂O in the gas phase and the clean surfaces. Gibbs free energies were calculated at a temperature of 500 K, and standard pressure of all molecules

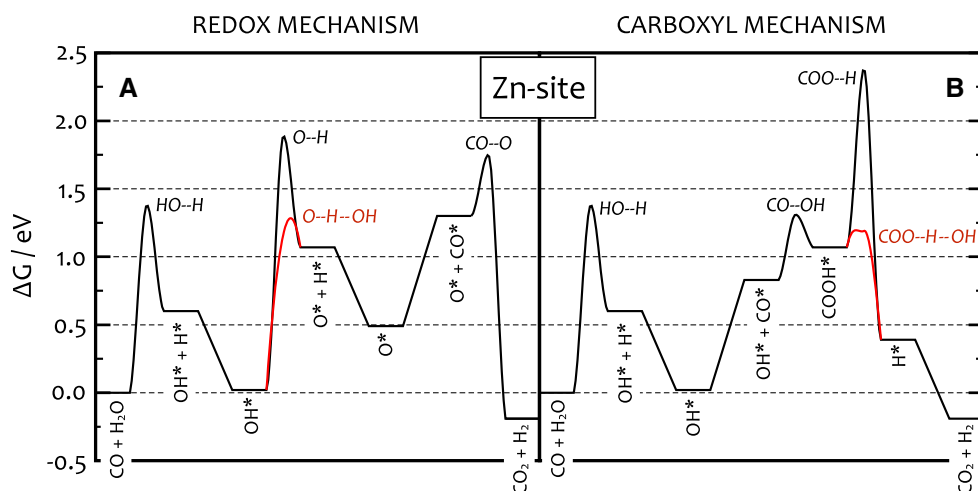
transition state theory. This highest free energy barrier is about 0.1 eV below those found for the hydrogenation of CO₂ to methanol when employing the BEEF-vdW functional [24, 25], and in fair agreement with experimentally reported turnover rates of 10⁻² s⁻¹ [10, 36]. These rates are reported per total copper surface area, whereas steps usually only comprise 5 % of the total surface. Importantly, the difference of 0.1 eV between WGS and methanol synthesis would indicate that the WGS reaction is about 1 order of magnitude faster than methanol synthesis and hence equilibrated as observed experimentally [6, 14].

Figure 3 shows the free energy diagram of the WGS reaction over a Zn-doped Cu(211) step (denoted Zn-site, see also Fig. 1). We employ a fully Zn-doped copper step in our model here. We note that such sites only cover a fraction of active sites in a Cu/ZnO catalyst [25], as the extend of Zn surface alloying depends on the reduction potential of the reaction gas mixture [32]. Depicted are both the redox and carboxyl mechanism in analogy to what was discussed above for the Cu-site (see Fig. 2). Despite the different active site motif, the main conclusions that

can be drawn for the energetics of the WGS reaction do not change significantly compared to the Cu-site. The carboxyl mechanism is the dominating pathway, surface OH helps reducing the barrier of the COO-H transition state significantly, and dissociation of water constitutes the rate-determining step. In fact, dissociation of H₂O on the Zn-site has essentially the same barrier as dissociation on the Cu-site (1.38 vs. 1.39 eV). One would therefore expect that the rate of the WGS reaction is very similar on the Cu- and the Zn-site and certainly within the error of DFT. Indeed, there are experimental results that show that Zn-addition to Cu nanoparticles supported on different irreducible oxides clearly promotes CO₂ conversion reactions like methanol synthesis and the reverse WGS reaction, but has a much lower effect on the forward WGS reaction or methanol steam reforming [37, 38], where the rate limiting step is related to water activation.

One can also speculate about the activity of mixed Cu–Zn-sites as these are likely present on the Cu/ZnO catalyst. The amount of Cu–Zn-sites depends on the preparation of the catalyst as well as the applied reaction conditions.

Fig. 3 Gibbs-free energy diagram of the water–gas-shift reaction via the redox (a) and carboxyl (b) mechanism on then a Zn covered copper step (see Fig. 1). Reactions including hydrogen abstraction via adsorbed OH are depicted in red. All energies are relative to $\text{CO} + \text{H}_2\text{O}$ in the gas phase and the clean surfaces. Gibbs free energies were calculated at a temperature of 500 K



Interestingly, atomic hydrogen and intermediates bound through carbon bind stronger on the Cu-site, whereas intermediates bound through oxygen bind stronger on the Zn-site [25]. This can be seen for example for the case of water splitting (see Figures, 2 and 3). Here, OH^* binds 0.14 eV stronger whereas H^* binds 0.33 eV weaker on the Zn-site. Both effects compensate each other so that the combined $\text{OH}^* + \text{H}^*$ binding energy and the corresponding H_2O dissociation barrier are almost the same for the two surfaces. Mixed Cu–Zn-sites should in principle have lower transition states as water splitting would result in H^* binding to Cu and OH^* binding to Zn, so that both species are stabilized to a maximum degree. The Cu/ZnO catalyst can therefore be thought of being comprised of Cu- and Zn-sites having similar activity as well as extremely active mixed Cu–Zn-sites. Performance catalysts will expose a high number of these mixed Cu–Zn-sites to maximize their beneficial interplay.

Support effects are well known to play an important role in Cu-catalyzed WGS. It was found that oxides help to dissociate H_2O and that in particular oxygen vacancies in the supports are active in this respect and lower the activation energy of WGS [39]. In addition to Cu/ZnO, many recent reports focused on Cu/CeO₂, for which an even higher promotion effect was detected [40]. Surface science studies revealed that Cu surfaces with a decoration of ceria nanoparticles do not only promote the reaction by facilitating H_2O dissociation, but that in addition a substantial surface reconstruction of Cu was triggered by the presence of ceria [41]. This leads to the formation of many microterraces, which according to the structure-sensitivity of the reaction represents an additional independent oxide promotion effect. We note that our model of the active site(s) accounts for both effects, the reactivity of surface defect sites and the presence of reduced support species, by the stepped nature of the (211) model surface and by the

(partial) decoration of the step with reduced Zn atoms, respectively. Thus, our results are largely consistent with the experimental evidence that defects and metal-support interaction plays a major role in activating H_2O .

In summary we employed the BEEF-vdW functional to show how the WGS reaction is catalyzed over the Cu- and Zn-site of the industrial Cu/ZnO/Al₂O₃ catalyst. The reaction is found to proceed via the carboxyl pathway with H_2O dissociation being the rate-determining step, similar to what has been observed for Cu(111) surfaces. This is also in agreement with recent experimental evidence supporting the carboxyl mechanism [42]. Based on calculated barriers for H_2O dissociation on would expect turnover frequencies in the range of 10^{-1} per site and second in agreement with experimental data. We note here, however, that in order to make quantitative predictions about the reaction mechanism, possible rate-determining steps, and the reaction rates one would need to employ microkinetic or kinetic Monte Carlo simulations of the WGS reaction.

2 Methods

All calculations have been performed with the Quantum Espresso code [33] using a plane-wave basis set in the generalized gradient approximation. The plane-wave cutoff used in all calculations was 500 eV and the density cutoff was 5000 eV. The calculations were performed using the BEEF-vdW exchange–correlation functional, a functional that explicitly takes long-range dispersion forces into account [23]. The stepped Cu surface and the Zn substituted Cu surface (see Fig. 1) used to calculate the water–gas-shift energetics have been modeled using a 12 layered (3×1) unit cell resulting in a slab with 4 layers in the (111) direction having monoatomic steps between (111) facets with a (100) geometry. More than 12 Å of vacuum

have been included to separate periodic images and the Brillouin zone has been sampled using a $(4 \times 4 \times 1)$ Monkhorst–Pack grid [43]. In all calculations the adsorbates and the atoms in the two topmost (111) layers were allowed to relax until forces became smaller than 0.05 eV/Å. The vibrational frequencies used to determine the zero-point energy and entropic contributions to the free energy have all been calculated within the harmonic approximation. Tables S1 and S2 list the total energies, zero-point energies, entropies and heat capacities of intermediates and transition states. For all transition state structures on the stepped Cu surface we found a single imaginary frequency thus identifying the geometry as a first-order saddle-point on the potential energy surface.

3 Supporting Information

Supporting information contains total energies of intermediates and transition states. This material is available free of charge via the Internet at <http://pubs.acs.org>

Acknowledgments We gratefully acknowledge the support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences to the SUNCAT Center for Interface Science and Catalysis. The authors would like to thank Jens K. Nørskov for fruitful discussions.

References

- Hinrichsen KO, Kochloeff K, Muhler M (2008) In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley, Weinheim
- Ratnasamy C, Wagner JP (2009) *Catal Rev Sci Eng* 51:325
- Ovesen CV, Stoltze P, Nørskov JK, Campbell CT (1992) *J Catal* 134:445
- Ovesen CV, Clausen BS, Hammershøi BS, Steffensen G, Askgaard T, Chorkendorff I, Nørskov JK, Rasmussen PB, Stoltze P, Taylor P (1996) *J Catal* 158:170
- Hansen JB, Nielsen PEH (2008) In: Ertl G, Knözinger H, Schüth F, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley, Weinheim
- Lee S (2007) In: Lee S, Speight JG, Loyalka SK (eds) Handbook of alternative fuel technologies. CRC Press, Boca Raton
- Tang QL, Chen ZX, He X (2009) *Surf Sci* 603:2138
- Lin CH, Chen CL, Wang JH (2011) *J Phys Chem C* 115:18582
- Huang SC, Lin CH, Wang JH (2010) *J Phys Chem C* 114:9826
- Gokhale AA, Dumesic JA, Mavrikakis M (2008) *J Am Chem Soc* 130:1402
- Liu P, Rodriguez JA (2007) *J Chem Phys* 126:164705
- Fajín JLC, Cordeiro MNDS, Illas F, Gomes JRB (2009) *J Catal* 268:131
- Wang GC, Nakamura J (2010) *J Phys Chem Lett* 1:3053
- Yoshihara J, Campbell CT (1996) *J Catal* 161:776
- Campbell CT, Daube KA (1987) *J Catal* 104:109
- Nakamura J, Campbell JM, Campbell CT (1990) *J Chem Soc, Faraday Trans* 86:2725
- Chen CS, Lin JH, Lai TW, Liu BH (2009) *J Catal* 263:155
- Chen CS, Lai TW, Chen CC (2010) *J Catal* 273:18
- Perdew JP, Wang Y (1992) *Phys Rev B* 45:13244
- Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77:3865
- Zhang Y, Yang W (1998) *Phys Rev Lett* 80:890
- Fajín JLC, Illas F, Gomes JRB (2009) *J Chem Phys* 130:224702
- Wellendorff J, Lundgaard KT, Møgelhøj A, Petzold V, Landis DD, Nørskov JK, Bligaard T, Jacobsen KW (2012) *Phys Rev B* 85:235149
- Studt F, Abild-Pedersen F, Varley JB, Nørskov JK (2013) *Catal Lett* 143:71
- Studt F, Behrens M, Kunkes EL, Thomas N, Zander S, Tarasov A, Schumann J, Varley JB, Abild-Pedersen F, Nørskov JK, Schlögl R (2014) submitted
- Rhodes C, Hutchings GJ, Ward AM (1995) *Catal Today* 23:43
- Cámara AL, Chansai S, Hardacre C, Martínez-Arias A (2014) *Int J Hydr Ener* 39:4095
- Barrio L, Estrella M, Zhou G, Wen W, Hanson JC, Hungria AB, Hornés A, Fernández-García M, Martínez-Arias A, Rodriguez JA (2010) *J Phys Chem C* 114:3580
- Wang X, Rodriguez JA, Hanson JC, Gamarra D, Martínez-Arias A, Fernández-García M (2006) *J Phys Chem B* 110:428
- Yang Y, Mims CA, Disselkamp RS, Kwak JH, Peden CHF, Campbell CT (2010) *J Phys Chem C* 114:17205
- Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, Zander S, Girgsdies F, Kurr P, Kniep BL, Tovar M, Fischer RW, Nørskov JK, Schlögl R (2012) *Science* 336:893
- Kuld S, Conradsen C, Moses PG, Chorkendorff I, Sehested J (2014) *Angew Chem Int Ed* 53:5941
- Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M et al (2009) *J Phys: Condens Matter* 21:395502
- Bahn SR, Jacobsen KW (2002) *Comput Sci Eng* 4:56
- Peterson AA, Abild-Pedersen F, Studt F, Rossmel J, Nørskov JK (2010) *Energy Environ Sci* 3:1311
- Koryabkina NA, Phatak AA, Ruettinger WF, Farrauto RJ, Ribeiro FH (2003) *J Catal* 217:233
- Saito M, Wu J, Tomoda K, Takahara I, Murata K (2002) *Catal Lett* 83:1
- Fujitani T, Nakamura I, Uchijima T, Nakamura J (1997) *Surf Sci* 383:285
- Rodriguez JA, Liu P, Wang X, Wen W, Hanson J, Hrbek J, Pérez M, Evans J (2009) *Catal Today* 143:45
- Rodriguez JA, Liu P, Hrbek J, Evans J, Pérez M (2007) *Angew Chem Int Ed* 46:1329
- Senanayake SD, Stacchiola D, Rodriguez JA (2013) *Acc Chem Res* 46:1702
- Yang Y, Mims CA, Mei DH, Peden CHF, Campbell CT (2013) *J Catal* 298:10
- Monkhorst HJ, Pack JD (1976) *Phys Rev B* 13:5188