Mechanisms of CO₂ reduction into CO and formic acid on Fe (100): a DFT study

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Abstract

Understanding the mechanism of CO₂ reduction on iron is crucial for the design of more efficient and cheaper iron electrocatalyst for CO₂ conversion. In the present study, we have employed spin-polarized density functional theory calculations within the generalized gradient approximation (DFT-GGA) to elucidate the mechanism of CO₂ reduction into carbon monoxide and formic acid on the Fe (100) facet. We also sort to understand the transformations of the other isomers of adsorbed CO₂ on iron as earlier mechanistic studies are centred on the transformations of the C_{2v} geometry alone and not the other possible conformations i.e., flip-C_{2v} and C_s modes. Two alternative reduction routes were considered i.e., the direct CO₂ dissociation against the hydrogen-assisted CO₂ transformation through formate and carboxylate into CO and formic acid. Our results show that CO₂ in the C_{2v} mode is the precursor to the formation of both products i.e., CO and formic acid. Both the formation and transformation of CO₂ in the C_s and flip-C_{2v} is challenging kinetically and thermodynamically compared to the C_{2v} mode. The formic acid formation is favoured over CO via the reverse water gas shift reaction mechanism on Fe (100). Both formic acid formation and CO formation will proceed via the carboxylate intermediate since formate is a stable intermediate whose transformation into formic acid is challenging both kinetically and thermodynamically.

Graphic abstract

Keywords RWGS · Mechanism · Hydrogenation · Carbon monoxide · Formic acid

Introduction

The catalytic CO₂ hydrogenation is crucial towards CO₂ mitigation. The two CO₂ reduction routes currently being explored are the direct hydrogenation into hydrocarbons

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and the initial CO₂ hydrogenation into CO (via the reverse water gas shift (rWGS) reaction) prior to hydrogenation into hydrocarbons [1–6]. CO₂ conversion to CO via the rWGS reaction (Eq. 1) is attractive as CO is the feedstock for the production of longer chain hydrocarbons (liquid fuels) via the Fischer–Tropsch process [7]. In a 1:1 CO₂ and H₂ reaction ratio, both CO and the formic acid are plausible products. Formic acid is widely employed in the leather and rubber industries and is a feedstock in the production of numerous chemicals, like sweeteners and fibre [6].

Since the rWGS reaction is a reversible process, catalysts that favour the rWGS reaction are known to be equally active for the water gas shift (WGS) reaction. For example, copper [8], apart from its high reactivity for low-temperature WGS reactions, shows a high selectivity towards CO production over CH₄ in mixtures of CO₂ and H₂ [9]. Although iron has been reported to be an inefficient catalyst for the WGS reaction [10], it is a very stable catalyst at elevated temperatures and hence is employed extensively in the high temperature WGS reaction [11]. Iron has also been reported to stabilize Cu for CO production [8]. The two competing mechanisms reported for the WGS mechanisms are the formate pathway (associative mechanism), and the redox pathway (decomposition mechanism) [12, 13]. DFT calculations on clean and pre-adsorbed Fe (110) [10] and Fe₃O₄ (111) [14] reported the redox mechanism as the most preferred path. Despite the extensive research on the WGS mechanism on iron-based catalysts, mostly oxides [11], little is known about the rWGS reaction mechanisms on single metal iron crystals towards identifying a more efficient iron surface for the rWGS reaction.

Other metals like Pt and Ru in solid oxide fuel cells, were found to be controlled by formate decomposition [15], and direct dissociation paths [16], respectively. Chen et al. [17] observed formate as a key intermediate on the Cu/Al₂O₃ catalyst system. A similar mechanism is reported on Cu/SiO₂ surface [18] while the redox mechanism is seen on pure Cu(110) [19] and Cu/ZnO [20], systems with the slowest step being the dissociation step [19]. DFT investigations of the rWGS reaction mechanism on nickel (211) indicated the redox path to be favoured both kinetically and thermodynamically [21]. Despite earlier DFT calculations [22–24] have reported the spontaneous formation of anionic CO₂^{δ−} species on all the low-Miller indices of iron surfaces, to the best of our knowledge, no systematic theoretical study has been conducted to understand the mechanism of the rWGS reaction on iron. In the present study, the catalytic CO₂ hydrogenation intermediates and reaction barriers leading to carbon monoxide and formic acid production on iron (100) have been studied.

Computational details

All calculations were carried out within the framework of spin-polarized density functional theory (DFT) as implemented in the Quantum ESPRESSO package [25]. The generalized gradient approximation (GGA), with the Perdew, Burke, Ernzerhof (PBE) exchange–correlation functional [26] were used to calculate the total free energies. The surface was described by a slab model, where periodic boundary conditions were applied to the central super-cell so that it is reproduced periodically throughout space. XcrysDen [27] software was employed for the visualization of structures and electron densities. The Fermi-surface effects were treated by the smearing technique of Fermi–Dirac, using a smearing parameter of 0.03 Ry. The energy threshold defining self-consistency of the electron density was set to 10^{−6} eV. Using convergence tests, the kinetic energy cut off of the plane wave basis set was set to 40 Ry and 320 Ry for the charge density cut off. Also, by convergence tests, the Monkhorst–pack K-points grid of (11 × 11 × 11) and (3 × 3 × 1) was sufficient to describe the bulk and the *p* (3 × 3) super-cell, respectively. The Climbing Image Nudged Elastic Band (CI-NEB) method was used to determine the energy barriers and the transition state structures on the surface. Vibrational frequencies of the transition state structures were characterized by a single imaginary frequency.

Results and discussion

The low-Miller index (100) surface was cleaved from the optimized bulk using the METADISE code [28], which does not only consider periodicity in the plane direction but also provides the different atomic layer stacking resulting in a zero dipole moment perpendicular to the surface plane, as is required for reliable and realistic surface calculations. The slab was constructed with 6 atomic layers in thickness and a vacuum of 12 Å was introduced to the system along the *z*-axis to avoid interactions between periodic slabs. All gaseous adsorbates were optimized in a cubic box of size 20 Å. In all calculations, adsorbates and the topmost 3 layers of the substrate were allowed to relax while the bottom 3 layers were fixed at the bulk position. Neighbouring adsorbates in laterally repeating units of the slabs were more than 5 Å apart, to prevent interaction between repeated units. A *p*(3 × 3) slab (Fig. 1) was employed to mimic the Fe (100) surface.

Fig. 1 Top and side view of a $p(3 \times 3)$ super-cell of Fe (100)

Fig. 2 Optimized structures of CO₂ adsorption in (a) C_{2v} mode (b) flip-C_{2v} mode and (c) C_s mode at the hollow site of a $p(3 \times 3)$ Fe (100) surface

CO₂ adsorption

The preferred CO₂ adsorption site on the clean Fe (100) surface has been reported to be the hollow site [24]. At the hollow site, we considered CO₂ binding through the carbon and the two oxygen atoms in the 3 possible configurations (see Fig. 2) i.e. C_{2v} mode, flip-C_{2v} mode (observed on the Fe (111) facet) [29] and the C_s mode. In the C_{2v} mode, CO₂ binds through the carbon and two oxygen atoms in a v shape (see Fig. 2a). In the flip-C_{2v} mode, CO₂ binds through the carbon and two oxygen atoms with a flipped v shape to the surface (see Fig. 2b). In the C_s adsorption mode, CO₂ binds through a single oxygen and carbon atom as shown in Fig. 2c. Upon geometry optimization, the flip-C_{2v} mode was seen to be unstable with an adsorption energy of 0.91 eV and not favourable formed on the Fe (100) surface. This is due to the difference in surface topology between Fe (100) and Fe (111), since the flip-C_{2v} mode has been reported on Fe (111). The surface packing of the (100) surface is more packed than the stepped (111) surface, and the open nature of the (111) surface therefore stabilizes CO₂ even in the flip-C_{2v} mode. CO₂ binds most strongly in the C_{2v} mode with an adsorption energy of -1.34 eV. Apart from the 'v' shape structure, we have also obtained the C_s mode with a less stable adsorption energy of -1.26 eV. In both of these configurations, we observe elongation in the C–O bonds from 1.19 Å in the gaseous state and change in the $\alpha(\text{OCO})$ angles, suggesting an activated CO₂ species. In the C_{2v} mode, the two C–O bonds were calculated to be 1.35 Å, whereas, for the C_s mode, these were calculated at 1.30 Å and 1.36 Å. In the unstable flip-v mode, CO₂ is bound and still activated to 1.35 Å as seen in the C_{2v} mode (see Table 1). This is consistent with the work of Nassir in 1993, who only observed the C_s and C_{2v} activated CO₂ modes on the hollow site of Fe (100) at 110 K [30]. This is due to the high instability of the CO₂

Table 1 Optimized geometries of activated and hydrogenated carbon dioxide molecule, η is the coordination number i.e., the number of surface Fe atoms linked to CO₂

Structure	E_{ads}/eV	Fe–C/Å	C–O/Å	C–H/Å	C–OH/Å	O–H/Å	η
a	–1.34	2.1	1.35	–	–	–	5
b	0.91	1.89	1.35	–	–	–	4
c	–1.26	1.95	1.30, 1.36	–	–	–	4
1a	–2.11	–	2.4	1.1	–	–	4
1b	–0.85	2.1	1.35	–	1.48	0.99	5
1c	–1.41	2.1	1.35	1.10	1.51	0.99	4
2a	–2.11	2.03	1.35	1.10	–	–	4
2b	–1.97	1.77	1.19	–	2.99	–	3
2c	–1.41	2.1	1.35	1.10	1.15	0.99	4
3a	–1.31	1.94	1.32, 1.52	–	–	–	5
3b	–1.97	1.77	1.19	–	2.99	–	3
3b ii	–1.08	1.95	1.32	–	1.37	0.99	4
3c	–2.63	1.77	1.19	–	–	0.99	5

Fig. 3 Guess structures for the hydrogenation of CO_2 through oxygen and carbon centres

in the flip- C_{2v} mode on Fe (100), making this adsorbed species transient and not favourably formed and observed.

Upon the adsorption of CO_2 , we considered CO_2 hydrogenation by gaseous hydrogen through different hydrogenated conformations to identified the stable compounds formed as indicated in Fig. 3. CO_2 can either be hydrogenated through the carbon of CO_2 i.e., 1a, 2a and 3a, or through the oxygen atom i.e., 1b, 2b and 3b, or through both carbon and oxygen i.e., 1c, 2c and 3c.

As seen in Fig. 4, after optimisation, hydrogen adsorption to CO_2 through the carbon centre to form formate, Figs. 1a and 2a, is more favoured (-2.11 eV) over through the oxygen centre to form carboxylate (-0.85 eV and -1.08 eV), Figs. 1b and 3b ii. However, the interatomic distances show that hydrogen binds more strongly to oxygen ($\text{O}-\text{H}=0.99$ Å) than to carbon ($\text{C}-\text{H}=1.10$ Å) centre showing that the oxygen is a more electronegative centre for hydrogenation. Hydrogenation of CO_2 also leads to CO_2 decomposition and hydroxyl formation on the surface of iron as seen in Figs. 2b and 3b. In all hydrogenation cases, the adsorption energies

are seen to be exothermic. Formic acid formation energy was calculated to be -1.41 eV (in Figs. 1c and 2c) while the ($\text{CO} + \text{H}_2\text{O}$) formation energy is -2.63 eV. All adsorption energies and interatomic distances of the hydrogenated CO_2 species are tabulated in Table 1. These adsorption conformations are further explored via the hydrogen assisted and non-hydrogen-assisted transformation into molecular formic acid formation and decomposed CO formation on the Fe (100) surface.

CO_2 reduction mechanism

To elucidate the mechanism of CO_2 reduction into CO and HCOOH , two proposed reaction schemes were explored. Scheme 1 shows the pathways leading to CO formation. Hydrogenation of CO_2 in the C_{2v} adsorption mode could lead to carboxylate formation whose hydroxyl could be picked by hydrogen via TSa2 to form product. CO_2 in the C_s geometry could lead to CO_2 decomposition into CO and hydroxyl, hence the barrier for CO_2 dissociation was

Fig. 4 Optimized structures of hydrogenated carbon dioxide molecule

Scheme 1 Reaction scheme showing possible pathways leading to CO production; red arrows correspond to CO_2 transformation from the C_{2v} adsorption mode and black arrows correspond to CO_2 transformations from the C_s adsorption mode

considered through the hydrogen-assisted CO_2 dissociation via TSc2 and hydrogen unassisted CO_2 decomposition into CO via TSc3. Scheme 2 shows the pathways leading to formic acid production, CO_2 can be reduced through the carboxylate or formate intermediates into formic acid. Transition state structures along these pathways were then sorted for and the reaction profiles for these transformations shown in Figs. 5 and 6.

CO_2 reduction into CO

As shown in the reaction profile diagram in Fig. 5, the transition states leading to CO formation were determined. The barrier to direct CO_2 dissociation was sort from the least stable CO_2 activated molecule, in the C_s mode (c) which is a most likely reactive species to dissociation. The barrier to

Fig. 5 Energy profile diagram for the conversion of CO_2 into CO

CO_2 activation is seen to be 2 eV and the rate determining step is seen to be the barrier for the decomposition step of 6.40 eV, which makes this pathway very unlikely for CO formation. Hydrogenation of the C_s molecule to carboxylate is more favoured kinetically through a barrier of 1.54 eV. Upon the formation of carboxylate, OH hydrogenation to water requires an energy of 1.40 eV. Hence, the rate limiting step is seen to be 1.54 eV which will enable carboxylate formation. The dissociative hydrogenation of CO_2 in the C_s mode is most feasible transformation of CO_2 in the C_s mode, requiring an energy of 0.17 eV. Surface hydroxyl is then hydrogenated via a barrier of 1.49 eV, this makes the CO_2 activation step the most challenging step for the C_s pathways. A barrier of 0.17 eV through TSA1 is required to activate CO_2 in the C_{2v} preferred mode. CO_2 in the C_{2v} mode requires a lower barrier of 0.30 eV to form carboxylate which transforms through a barrier of 1.40 eV to form CO. Considering the varies pathways for CO_2 transformation through the reverse water gas shift mechanism to

Scheme 2 Reaction scheme showing possible pathways leading to formic acid production; red arrows correspond to CO_2 transformation from the C_{2v} adsorption mode and blue arrows correspond to CO_2 transformations from the flip- C_{2v} adsorption mode

Fig. 6 Energy profile diagram for the conversion of CO₂ into formic acid

CO and water, CO₂ is adsorbed and activated in the C_{2v} mode, a thermodynamically favoured step ($\Delta E = -1.34$ eV) with a barrier of 0.17 eV. Activated CO₂ is hydrogenated through an unfavoured thermodynamic step through a barrier of 0.30 eV. Carboxylate OH is then hydrogenated into an unstable product ($\Delta E = -0.68$ eV), through the rate limiting step of 1.40 eV. Product formation however from the decomposed CO and hydroxyl intermediate (2b) is both thermodynamically and kinetically more challenging than the associative path.

CO₂ reduction into formic acid

Formate formation can proceed via the hydrogenation of the flip-C_{2v} mode or the hydrogenation and concerted flip of CO₂ from the C_{2v} mode into formate. Via the flip-C_{2v} CO₂ activated molecule, adsorption is seen to be both thermodynamically and kinetically challenging, requiring an energy barrier of 6.40 eV and reaction energy of 0.9 eV to occur. Due to the instability and high activation barrier the flip-C_{2v} is not a likely species to be formed on the Fe (100) surface. This activated CO₂ species if formed will transform in a barrierless step to formate. Preferred activated CO₂ mode can be hydrogenated into carboxylate or formate. As seen in Fig. 6, the transformation to carboxylate is an endothermic step while conversion to formate is exothermic step. Transformation to formate is also kinetically more favoured, through a barrier of 0.09 eV and is sequentially hydrogenated through the oxygen via a barrier of 0.96 eV to form formic acid. The rate limiting step through the formate intermediate is seen to be formic acid formation step via a barrier of 0.96 eV. Carboxylate although not favoured thermodynamically, requires an

energy of 0.3 eV to be formed and is subsequently hydrogenated into formic acid via a barrier of 0.16 eV, where carbon is protonated to form formic acid. The rate limiting barriers show that CO₂ transformation to formic acid will proceed via the carboxylate intermediate. Activated C_{2v} CO₂ is formed through a barrier of 0.17 eV in an exothermic step ($\Delta E = -1.34$ eV). CO₂ is then protonated into carboxylate ($\Delta E = -1.08$ eV) through a barrier of 0.3 eV and further protonated to formic acid ($\Delta E = -1.41$ eV). Both CO and formic acid reactions will proceed favourably via the carboxylate intermediate and not the formate or decomposed CO₂ pathway. Comparing the rate limiting steps, the rWGS reaction (1.40 eV) is less favoured on Fe (100) compared to formic acid formation (0.3 eV). Carboxylate transformation into formic acid is favoured kinetically and thermodynamically over its transformation into CO.

Comparing our results with other DFT simulations on transition metals, we observe in this work that the hydrogen-assisted dissociation of CO₂ via carboxylate is favoured over the direct dissociation of CO₂ into CO. This is contrary to what is observed on the Ni (211) surface where the direct dissociation is seen to be preferred kinetically over hydrogen-assisted CO₂ transformation [21]. Our result is however consistent with the work of Vesseli and co., on Ni (110), where carboxylate led to CO formation and formate is too stable to be transformed [31, 32]. Our previous studies on Fe (111), also shows that CO is preferentially formed from carboxylate and flipped-C_{2v} CO₂ is stable and converted via a barrier of 0 eV into formate [29]. These results show that surface topology and composition affect the formation of surface species and the impact on the preferred reaction mechanisms for formic acid formation.

Summary and conclusions

A detailed spin-polarized DFT-GGA calculation has been utilized to elucidate the mechanisms of CO₂ conversion into CO via the rWGS reaction and the conversion to formic acid as an alternative reaction on Fe (100) surface. Rate-limiting barriers of 0.3 eV and 1.40 eV were computed for the production of formic acid and CO, respectively, indicating that the formic acid production reaction will proceed faster than the formation of CO. CO₂ associative transformation of CO₂ via carboxylate on Fe (100) is favoured over its dissociative transformation via carbonyl into CO. Our results reveal that although CO₂ binds on the Fe (100) surface in C_{2v} and C_s mode at the hollow site, CO₂ adsorption in the flipped-C_{2v} mode is seen to be thermodynamically and kinetically challenging. CO₂ in the C_{2v} mode is seen to be the most preferred CO₂ adsorption mode and the precursor leading to the formation of desired products i.e., CO and formic acid. Formic acid is selectively produced via the carboxylate pathway over the formate pathway. The high stability of the formate intermediate ($\Delta E = -2.11$ eV) and the energetics to transform it into formic acid ($E_a = 0.96$ eV) shows that formate formation could be a dead-end along that pathway. Fe surfaces with lower surface work functions may be promising for the rWGS as they favour easier charge transfer and stronger CO₂ binding in the 'v' mode which is the precursor to carboxylate and product formation.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s40243-021-00194-w>.

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References

- Jiang, Z., Xiao, T., Kuznetsov, V.L., Edwards, P.P.: Turning carbon dioxide into fuel. *Philos. Trans. A. Math. Phys. Eng. Sci.* **368**, 3343–3364 (2010). <https://doi.org/10.1098/rsta.2010.0119>
- Whipple, D.T., Kenis, P.J.A.: Prospects of CO₂ utilization via direct heterogeneous electrochemical reduction. *J. Phys. Chem. Lett.* **1**, 3451–3458 (2010). <https://doi.org/10.1021/jz101267>
- Centi, G., Perathoner, S.: Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal. Today* **148**, 191–205 (2009). <https://doi.org/10.1016/j.cattod.2009.07.075>
- Razali, N.A.M., Lee, K.T., Bhatia, S., Mohamed, A.R.: Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: a review. *Renew. Sustain. Energy Rev.* **16**, 4951–4964 (2012). <https://doi.org/10.1016/j.rser.2012.04.012>
- Ma, J., Sun, N., Zhang, X., Zhao, N., Xiao, F., Wei, W., Sun, Y.: A short review of catalysis for CO₂ conversion. *Catal. Today* **148**, 221–231 (2009). <https://doi.org/10.1016/j.cattod.2009.08.015>
- Wang, W., Wang, S., Ma, X., Gong, J.: Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* **40**, 3703–3727 (2011). <https://doi.org/10.1039/c1cs15008a>
- Schulz, H.: Short history and present trends of Fischer–Tropsch synthesis. *186*, 3–12 (1999)
- Chen, C.S., Cheng, W.H., Lin, S.S.: Enhanced activity and stability of a Cu/SiO₂ catalyst for the reverse water gas shift reaction by an iron promoter. *Chem. Commun.* (2001). <https://doi.org/10.1039/b104279n>
- Lortie, M., Isaifan, R., Liu, Y., Mommers, S.: Synthesis of CuNi/C and CuNi/Al₂O₃ catalysts for the reverse water gas shift reaction. *Int. J. Chem. Eng.* **2**, 2 (2015). <https://doi.org/10.1155/2015/750689>
- Liu, S., Li, Y.W., Wang, J., Jiao, H.: Reactions of CO, H₂O, CO₂, and H₂ on the clean and precovered Fe(110) surfaces—a DFT investigation. *J. Phys. Chem. C* **119**, 28377–28388 (2015). <https://doi.org/10.1021/acs.jpcc.5b07497>
- Zhu, M., Wachs, I.E.: Iron-based catalysts for the high-temperature water-gas shift (HT-WGS) reaction: a review. *ACS Catal.* **6**, 722–732 (2016). <https://doi.org/10.1021/acscatal.5b02594>
- Khan, A., Smirniotis, P.G.: Relationship between temperature-programmed reduction profile and activity of modified ferrite-based catalysts for WGS reaction. *J. Mol. Catal. A Chem.* **280**, 43–51 (2008). <https://doi.org/10.1016/j.molcata.2007.10.022>
- Zhu, M., Wachs, I.E.: Resolving the reaction mechanism for H₂ formation from high-temperature water-gas shift by chromium-iron oxide catalysts. *ACS Catal.* **6**, 2827–2830 (2016). <https://doi.org/10.1021/acscatal.6b00659>
- Huang, L., Han, B., Zhang, Q., Fan, M., Cheng, H.: Mechanistic study on water gas shift reaction on the Fe₃O₄ (111) reconstructed surface. *J. Phys. Chem. C* **119**, 28934–28945 (2015). <https://doi.org/10.1021/acs.jpcc.5b09192>
- Pekridis, G., Kalimeri, K., Kaklidis, N., Vakouftsi, E., Iliopoulou, E.F., Athanasiou, C., Marnellos, G.E.: Study of the reverse water gas shift (RWGS) reaction over Pt in a solid oxide fuel cell (SOFC) operating under open and closed-circuit conditions. *Catal. Today* (2007). <https://doi.org/10.1016/j.cattod.2007.05.026>
- Avanesian, T., Gusmão, G.S., Christopher, P.: Mechanism of CO₂ reduction by H₂ on Ru(0001) and general selectivity descriptors for late-transition metal catalysts. *J. Catal.* (2016). <https://doi.org/10.1016/j.jcat.2016.03.016>
- Chen, C.-S., Cheng, W.-H., Lin, S.-S.: Mechanism of CO formation in reverse water–gas shift reaction over Cu/Al₂O₃ catalyst. *Catal. Lett.* **68**, 45–48 (2000). <https://doi.org/10.1002/adma.201402322>

18. Chen, C., Cheng, W., Lin, S.: Study of reverse water gas shift reaction by TPD, TPR and CO₂ hydrogenation over potassium-promoted Cu/SiO₂ catalyst. 238, 55–67 (2003)
19. Ernst, K.H., Campbell, C.T., Moretti, G.: Kinetics of the reverse water-gas shift reaction over Cu(110). *J. Catal.* (1992). [https://doi.org/10.1016/0021-9517\(92\)90210-9](https://doi.org/10.1016/0021-9517(92)90210-9)
20. Fujita, S., Terunuma, H., Nakamura, M., Takezawa, N.: Mechanisms of methanation of carbon monoxide and carbon dioxide over nickel. *Ind. Eng. Chem. Res.* **30**, 1146–1151 (1991). <https://doi.org/10.1021/ie00054a012>
21. Cao, D.-B., Li, Y.-W., Wang, J., Jiao, H.: CO₂ dissociation on Ni(211). *Surf. Sci.* **603**, 2991–2998 (2009). <https://doi.org/10.1016/j.susc.2009.08.008>
22. Liu, C., Cundari, T., Wilson, A.: CO₂ reduction on transition metal (Fe Co, Ni, and Cu) surfaces: in comparison with homogeneous catalysis. *J. Phys. Chem. C.* **116**(9), 5681–5688 (2012)
23. Li, H.-J., Ho, J.-J.: Density functional calculations on the hydrogenation of carbon dioxide on Fe(111) and W(111) surfaces. *J. Phys. Chem. C.* **114**, 1194–1200 (2010). <https://doi.org/10.1021/jp909428r>
24. Kwawu, C.R., Tia, R., Adei, E., Dzade, N.Y., Catlow, C.R.A., De Leeuw, N.H.: CO₂ activation and dissociation on the low miller index surfaces of pure and Ni-coated iron metal: a DFT study. *Phys. Chem. Chem. Phys.* **19**, 19478–19486 (2017). <https://doi.org/10.1039/c7cp03466k>
25. Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I., Dal Corso, A., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M., Martin-Samos, L., Marzari, N., Mauri, F., Mazzarello, R., Paolini, S., Pasquarello, A., Paulatto, L., Sbraccia, C., Scandolo, S., Sclauzero, G., Seitsonen, A.P., Smogunov, A., Umari, P., Wentzcovitch, R.M.: QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter.* **21**, 395502 (2009). <https://doi.org/10.1088/0953-8984/21/39/395502>
26. Perdew, J.P., Burke, K., Ernzerhof, M.: Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996). <https://doi.org/10.1103/PhysRevLett.77.3865>
27. Kokalj, A.: XCrySDen-a new program for displaying crystal-line structures and electron densities. *J. Mol. Graph. Model.* **17**, 176–179 (1999). [https://doi.org/10.1016/S1093-3263\(99\)00028-5](https://doi.org/10.1016/S1093-3263(99)00028-5)
28. Watson, G.W., Kelsey, E.T., de Leeuw, N.H., Harris, D.J., Parker, S.C.: Atomistic simulation of dislocations, surfaces and interfaces in MgO (1996)
29. Kwawu, C.R., Aniagyei, A., Tia, R., Adei, E.: A DFT investigation of the mechanisms of CO₂ and CO methanation on Fe (111). *Mater. Renew. Sustain. Energy.* (2020). <https://doi.org/10.1007/s40243-020-0164-x>
30. Nassir, M.H.: Sequential carbon oxygen bond cleavage in chemisorption of CO₂ on Fe(100). *J. Vac. Sci. Technol.* **11**, 2104 (1993). <https://doi.org/10.1116/1.578376>
31. Vesselli, E., Rizzi, M., De Rogatis, L., Ding, X., Baraldi, A., Comelli, G., Savio, L., Vattuone, L., Rocca, M., Fornasiero, P., Baldereschi, A., Peressi, M.: Hydrogen-assisted transformation of CO₂ on nickel: the role of formate and carbon monoxide. *J. Phys. Chem. Lett.* **1**, 402–406 (2010). <https://doi.org/10.1021/jz900221c>
32. Vesselli, E., De Rogatis, L., Ding, X., Baraldi, A., Savio, L., Vattuone, L., Rocca, M., Fornasiero, P., Peressi, M., Baldereschi, A., Rosei, R., Comelli, G.: Carbon dioxide hydrogenation on Ni(110). *J. Am. Chem. Soc.* **130**, 11417–11422 (2008). <https://doi.org/10.1021/ja802554g>

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