A DFT investigation of the mechanisms of CO$_2$ and CO methanation on Fe (111)

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Abstract
Insight into the detailed mechanism of the Sabatier reaction on iron is essential for the design of cheap, environmentally benign, efficient and selective catalytic surfaces for CO$_2$ reduction. Earlier attempts to unravel the mechanism of CO$_2$ reduction on pure metals including inexpensive metals focused on Ni and Cu; however, the detailed mechanism of CO$_2$ reduction on iron is not yet known. We have, thus, explored with spin-polarized density functional theory calculations the relative stabilities of intermediates and kinetic barriers associated with methanation of CO$_2$ via the CO and non-CO pathways on the Fe (111) surface. Through the non-CO (formate) pathway, a dihydride CO$_2$ species (H$_2$CO$_2$), which decomposes to aldehyde (CHO), is further hydrogenated into methoxy, methanol and then methane. Through the CO pathway, it is observed that the CO species formed from dihydroxycarbene is not favorably decomposed into carbide (both thermodynamically and kinetically challenging) but CO undergoes associative hydrogenation to form CH$_2$OH which decomposes into CH$_2$, leading to methane formation. Our results show that the transformation of CO$_2$ to methane proceeds via the CO pathway, since the barriers leading to alkoxy transformation into methane are high via the non-CO pathway. Methanol formation is more favored via the non-CO pathway. Iron (111) shows selectivity towards CO methanation over CO$_2$ methanation due to differences in the rate-determining steps, i.e., 91.6 kJ mol$^{-1}$ and 146.2 kJ mol$^{-1}$, respectively.

Keywords Spin-polarized DFT-GGA · CO$_2$ methanation · CO methanation · Methanol formation · Reaction mechanism

Introduction
Carbon dioxide (CO$_2$) is a cheap, non-toxic and abundant carbon-one (C1) source for chemical processes [1–7] and its transformations into fuel offer solutions to the problem of global warming as well as helping to meet the world’s increasing energy needs [8].

The catalytic hydrogenation of CO$_2$ into methane (natural gas) by the Sabatier reaction is an important process as natural gas has a range of applications such as electricity generation by gas and steam turbines, heating of buildings and cooking [9, 10].

CO$_2$ + 4 H$_2$ → CH$_4$ + 2 H$_2$O $\Delta H_{298K} = -252.9$ kJ mol$^{-1}$.

Despite the simplicity of the reaction, CO$_2$ methanation mechanism appears quite difficult to establish as several different opinions have been expressed on the nature of intermediate compounds involved and the rate-determining step [7]. Generally, two mechanisms have been proposed for CO$_2$ methanation, i.e., by the associative mechanism (non-CO pathway) or by the decomposition mechanism, where there is CO$_2$ direct dissociation into CO prior to methane formation, with the further reduction of CO through the CO methanation pathway [11–14]. Also for CO methanation, there is no consensus for the mechanism, whether by the alkoxy (CH$_3$O) intermediate or the CO decomposed carbide intermediate [7].

Late 3$d$ metals, i.e., Fe, Ni, Cu, Co and Zn are metals thought to be responsible for CO$_2$ reduction in nature [15–19]. These transition metals in iron sulfide clusters are thought to provide the needed electrons for the reduction
process in the pre-biotic processes leading to the onset of life at the deep sea vents [18, 19], whereby CO$_2$ was converted into diverse organic molecules under reducing conditions at ambient temperature and pressure. Although Fe, Co, Ni, Cu and Zn surfaces have been identified for CO$_2$ activation and reduction experimentally, the reaction mechanism to producing hydrocarbons like methane is still not well understood on these surfaces [20, 21] and the earlier hydrogenation mechanism studies have focused mainly on Cu [22] and Ni surfaces [11–13, 23–27].

On clean Ni surfaces, most of these results supported the decomposition mechanism. Bartholomew and Weatherbee [11] earlier on in 1982 had studied CO$_2$ hydrogenation on Ni and reported CO$_2$ dissociation to CO. Peebles and Goodman [12] later experimentally studied CO$_2$ methanation on the Ni (100) surface and reported CO and C intermediates leading to CH$_4$ formation. Marwood et al. [13] submitted that the formate species is a spectator and CO is the key intermediate to methane formation. On the other hand, other studies supported the formate pathway. For example, Fujita et al. [24] observed that the kinetics of CO$_2$ and CO were different during the methanation process. The amount of carbide (C) on Ni was lower for CO$_2$ methanation than that in the CO methanation reaction, and hence inferred that CO$_2$ and CO methanation occurred via different pathways. Schild et al. [28] reported the formate intermediate and pathway on nickel. Formate and other compounds like carbonates, formaldehyde, methylate and methanol were observed on copper and palladium in the hydrogenation of CO$_2$ and CO, where formate was the primary compound reduced to methane on both surfaces [29].

With the spin-polarized density functional theory with a generalized gradient approximation (DFT-GGA) exchange–correlation functional, the complete hydrogenation reaction pathways of CO$_2$ reduction to methane have been explored on Cu (211) [22] and Ni (110) [27] surfaces. It was found on Cu (211) that methane formation was preferred through the CO pathway via the carboxylate intermediate. However, the studies on Ni (110) revealed that the methane formation via hydroxycarbene intermediate requires a lower energy barrier than via carbon monoxide and formate intermediates. The mechanism of CO$_2$ methanation has been underexplored on iron; we have investigated both the kinetics and thermodynamics of CO$_2$ and CO methanation on Fe (111) surface.

**Computational details**

All geometry optimizations and total energy calculations were carried out using the spin-polarized density functional theory generalized gradient approximation (DFT-GGA) method. The plane-wave basis sets and ultra-soft pseudopotentials were employed within the Quantum ESPRESSO Package [30], which performs full self-consistent DFT calculations to solve the Kohn–Sham equations [31]. The Perdew, Burke, Ernzerhof (PBE) [32] GGA exchange–correlation functional was employed. The Fermi-surface effects were treated by the smearing technique of Fermi–Dirac, using a smearing parameter of 0.003 Ry. An energy convergence threshold defining self-consistency of the electron density was set to $10^{-6}$ eV and a beta defining mixing factor for self-consistency of 0.2 was used. The Grimme-D2 Van der Waals correction was employed in all calculations. The graphics of the atomic structures and the iso-surfaces of the differential electron density plots in this manuscript have been prepared with the XCrysDen software [33].

The surface was created from the optimized bulk using the METADISE code [34]. Surfaces were described with the slab model, where periodic boundary conditions are applied to the central super-cell, so that it is reproduced periodically throughout space [35]. A vacuum region of 12 Å perpendicular to each surface was tested to be sufficient to avoid interactions between periodic slabs. An energy cut-off of 40 Ry (544 eV) and charge density cut-off of 320 Ry (4354 eV) were employed for the expansion of the plane-wave basis set. This is sufficient to converge the total energy of the iron systems and the Brillion zone was sampled using $(9 \times 9 \times 9)$ and $(3 \times 5 \times 1)$ Monkhorst–Pack [36] k-points mesh for the bulk and $p(3 \times 2)$ surface, respectively. Each slab is made up of the 36 atoms whereby there are 6 layers and 6 atoms in each layer. In all calculations, the top 3 layers and adsorbate are allowed to relax and bottom 3 layers fixed to mimic the bulk material as employed in earlier computations [37, 38]. The Climbing Image Nudged Elastic Band (CI-NEB) method was used to determine all transition-state structures along the reaction coordinate. The importance of zero-point energy correction has been checked for smaller models and found to follow the same trend.

**Results and discussion**

**Reaction energies for CO$_2$ hydrogenation**

To explore the intermediates involved in the hydrogen-assisted CO$_2$ and CO methanation on the Fe (111) surface, several starting geometries were optimized by the stepwise hydrogen addition to CO$_2$ and CO, which were optimized to obtain stable conformations (see Figure S1 of the supporting information file). The inter-atomic distances of the structures in Figure S1 are reported in Table S1 of the supporting information file. Upon obtaining all the optimized ground-state structures, the transition-state structures were sought for along two possible pathways, i.e., the non-CO
pathway through the formate intermediate and the CO pathway through the carboxylate intermediate. Series of elementary steps were considered within each of the two reaction pathways and a systematic representation is illustrated in Figs. 1, 2 and Table 1.

The relative energies ($\Delta E$) for the ground-state structures and the transition-state structures were calculated relative to the isolated slab, $\text{CO}_2(\text{g})$ and $x\frac{1}{2}\text{H}_2(\text{g})$, using the formula shown below:

$$\Delta E = E_{\text{(final)}} - E_{\text{(initial)}},$$

where $E_{\text{(final)}}$ is the energy of the ground-state or transition-state structure and $E_{\text{(initial)}}$ is the energy of the gas-phase starting materials.

CO$_2$ adsorption on Fe (111) is seen to require an energy barrier of $-4.6$ kJ mol$^{-1}$ [38]. In this study, hydrogenation of the Fe (111) surface is also seen to be barrier less and dissociative; hence, atomic hydrogen co-adsorption is explored in each elementary step via the Langmuir–Hinshelwood-type reaction. As shown in Fig. 3, along the non-CO path, formate formed from CO$_2$ hydrogenation (reaction barrier $=0.1$ kJ mol$^{-1}$) could be hydrogenated into CHO and OH (via TS1a), formic acid (via TS1b) or dihydride-CO$_2$ species (via TS1c). It is seen that formate goes through the highest barrier to form decomposed species (CHO+OH) (barrier $=271.1$ kJ mol$^{-1}$). Formate transformation into formic acid is more favorable (barrier $=120.6$ kJ mol$^{-1}$); however, a much lower kinetic barrier is seen for the production of the dihydride-CO$_2$ species, i.e., H$_2$CO$_2$ (65.9 kJ mol$^{-1}$). H$_2$CO$_2$ is transformed into aldehyde (CHO) upon further hydrogenation (barrier $=98.4$ kJ mol$^{-1}$). Although the formation of the aldehyde is thermodynamically and kinetically challenging, the further hydrogenation of the aldehyde through TS1e requires a moderate barrier of 20.6 kJ mol$^{-1}$ to produce a stable methoxy species of energy $-98.4$ kJ mol$^{-1}$. Methanation of methoxy is very challenging requiring an energy barrier of 186.5 kJ mol$^{-1}$ and thus making it a very slow process which might not be realized. However, methanol formation requires a lower barrier of 115.6 kJ mol$^{-1}$. Kinetically, the methanation of CO$_2$ via the non-CO pathway will selectively proceed via the following intermediates; formate, dihydride-CO$_2$, aldehyde and methoxy. Methanol formation is more favored kinetically through this pathway, with the rate-limiting step for formic acid, methanol, methane formation to be 127.6 kJ mol$^{-1}$, 115.6 kJ mol$^{-1}$ and 186.5 kJ mol$^{-1}$, respectively.

Along the CO pathways, CO$_2$ hydrogenation into carboxylate requires an energy barrier of 96 kJ mol$^{-1}$ (see
Carboxylate hydrogenation leads to dihydroxycarbene formation with a barrier of 146.2 kJ mol\(^{-1}\). Dihydroxycarbene, being an unstable intermediate, once formed prefers to decompose into CO (TS2b = 28.9 kJ mol\(^{-1}\)) than to rearrange into formic acid (TS2c = 156.2 kJ mol\(^{-1}\)). The further decomposition of CO into carbide is seen to be both kinetically and thermodynamically challenging through TS2e, (with an energy barrier of 137.2 kJ mol\(^{-1}\)) implying the carbide formation is unlikely to occur. CO would rather produce HCO requiring an energy barrier of 91.6 kJ mol\(^{-1}\). Further hydrogenation of HCO could lead to the formation of three possible intermediates, a decomposed CH\(^+\) hydroxyl intermediate (with the highest barrier i.e. 191.8 kJ mol\(^{-1}\)), an alcohol group (barrier of 114.3 kJ mol\(^{-1}\)) or the alkoxy group (which has the least energy barrier i.e. 55.9 kJ mol\(^{-1}\)). Therefore, the carbon center of HCO is further hydrogenated to form H\(_2\)CO. H\(_2\)CO could further be hydrogenated into H\(_2\)CO (TS2j = 4.5 kJ mol\(^{-1}\)) or CH\(_2\)OH (TS2k = 28.8 kJ mol\(^{-1}\)). CH\(_2\)OH is preferred and decomposes into CH\(_2\) through a barrier of 65.4 kJ mol\(^{-1}\) (TS2l). CH\(_2\) is then protonated into CH\(_3\) and methane. Kinetically via the CO pathway, CO\(_2\) selectively converts into methane through the carboxylate, dihydroxycarbene, CO, alkoxy and alkyl intermediates. The slowest step for formic acid, CO, methanol and methane formation via the CO pathway involves the energy barriers, 156.2 kJ mol\(^{-1}\), 146.2 kJ mol\(^{-1}\), 146.2 kJ mol\(^{-1}\), 146.2 kJ mol\(^{-1}\), respectively.

Comparing the rate-limiting step leading to the formation of the desired products, i.e. CO, formic acid, methanol and methane along both the CO and non-CO pathways, the preferred pathway leading to the formation of these products can be determined. Of the two pathways explored (CO and non-CO pathways), the one providing the least rate-limiting step indicates selectivity and is the preferred pathway. Formic acid is preferentially produced via the non-CO pathway through the following intermediates: CO\(_2\), COHOH and formate intermediates, with the rate-determining step being the hydrogenation of formate into formic acid (127.6 kJ mol\(^{-1}\)). Methanol production from CO\(_2\) is favored via the non-CO pathway as well as through the following intermediates: CO\(_2\), formate, dihydroide-CO\(_2\), CH\(_2\)O and methoxy intermediates, with rate-determining step being the hydrogenation of methoxy to methanol (115.6 kJ mol\(^{-1}\)). Methanol will be selectively

**Table 1** Elementary steps, illustrations as seen in reaction schemes (Figs. 1, 2) for the transformation of CO\(_2\) via the non-CO and CO pathways

| Reactants | Transition States | Products |
|-----------|-------------------|----------|
| HCOO\(^+\) + H\(^+\) | TS1a | HCO\(^+\) + OH\(^-\) |
| HCOOH\(^+\) + H\(^+\) | TS1b | HCOOH\(^+\) |
| H\(_2\)CO\(_2\)\(^+\) + H\(^+\) | TS1c | H\(_2\)CO\(_2\)\(^+\) |
| H\(_2\)CO\(^+\) + H\(^+\) + OH\(^-\) | TS1d | H\(_2\)CO\(^+\) + OH\(^-\) |
| H\(_2\)CO\(^+\) + H\(^+\) + OH\(^-\) | TS1e | H\(_2\)CO\(^+\) + OH\(^-\) |
| H\(_2\)CO\(^+\) + H\(^+\) + OH\(^-\) | TS1f | H\(_2\)CO\(_2\)\(^+\) |
| H\(_2\)CO\(_2\)\(^+\) + H\(^+\) + H\(_2\)O | TS1g | CH\(_2\)OH\(^+\) + H\(_2\)O |
| H\(_2\)CO\(_2\)\(^+\) + H\(^+\) + H\(_2\)O | TS1h | CH\(_4\) + O\(^+\) + H\(_2\)O |
| CH\(_4\) + O\(^+\) + H\(_2\)O | TS1i | CH\(_4\) + OH\(^-\) + H\(_2\)O |
| CH\(_2\)OH\(^+\) + H\(^+\) + H\(_2\)O | TS1j | CH\(_2\)OH\(^+\) + H\(_2\)O |
| COOH\(^+\) + H\(^+\) | TS2a | HCOOH\(^+\) |
| HOCO\(^+\) | TS2b | CO\(^+\) + H\(_2\)O |
| CO\(^+\) + H\(^+\) + H\(_2\)O | TS2c | HCO\(^+\) + H\(_2\)O |
| CO\(^+\) + H\(^+\) + H\(_2\)O | TS2d | CO\(^+\) + H\(_2\)O |
| CO\(^+\) + H\(^+\) + H\(_2\)O | TS2e | C\(^+\) + O\(^+\) + H\(_2\)O |
| HCO\(^+\) + H\(^+\) + H\(_2\)O | TS2f | HCOOH\(^+\) |
| HCO\(^+\) + H\(^+\) + H\(_2\)O | TS2g | HCOOH\(^+\) |
| HCO\(^+\) + H\(^+\) + H\(_2\)O | TS2h | CH\(_2\)OH\(^+\) |
| C\(^+\) + O\(^+\) + H\(^+\) + H\(_2\)O | TS2i | CH\(_2\)OH\(^+\) |
| H\(_2\)CO\(_2\)\(^+\) + H\(^+\) + H\(_2\)O | TS2j | CH\(_3\)OH\(^+\) |
| H\(_2\)CO\(_2\)\(^+\) + H\(^+\) + H\(_2\)O | TS2k | CH\(_3\)OH\(^+\) |
| CH\(_2\)OH\(^+\) + H\(^+\) + H\(_2\)O | TS2l | CH\(_3\)OH\(^+\) |
| CH\(_3\)\(^+\) + H\(^+\) + H\(_2\)O | TS2m | CH\(_4\) + 2 H\(_2\)O |

\(^*\)Adsorbed species

Fig. 4). Carboxylate hydrogenation leads to dihydroxycarbene formation with a barrier of 146.2 kJ mol\(^{-1}\). Dihydroxycarbene, being an unstable intermediate, once formed prefers to decompose into CO (TS2b = 28.9 kJ mol\(^{-1}\)) than to rearrange into formic acid (TS2c = 156.2 kJ mol\(^{-1}\)). The further decomposition of CO into carbide is seen to be both

**Fig. 3** Energy profile diagram along the non-CO pathway

![Energy profile diagram](image-url)
produced from CO (over CO₂) via the following intermediates: carboxylate, dihydroxycarbene, CO, HCO, CH₂O and methoxy intermediates. The slowest step is the hydrogenation of CO into HCO (91.6 kJ mol⁻¹).

Methane and CO formation will occur via the carbonyl pathway; methane formation will proceed through the following intermediates: carboxylate, dihydroxycarbene, CO, HCO, H₂CO, H₂COH, CH₂ and CH₃. The slowest step for both the methanation and CO formation process involves carboxylate hydrogenation into dihydroxycarbene (146.2 kJ mol⁻¹). CO methanation is more favorable on Fe (111) over CO₂ methanation, occurring via the intermediates HCO, H₂CO, H₂COH, CH₂ and CH₃. CO methanation proceeds with the slowest step involving CO hydrogenation into HCO (91.6 kJ mol⁻¹), as seen earlier for methanol production from CO. CO hydrogenation controls both the rate of methanol and methane formation from CO₂; hence, these reactions are very competitive for CO reduction on Fe (111) and lowering the barrier for CO protonation is desirable to speed up both processes. Formate hydrogenation, methoxy hydrogenation and carboxylate hydrogen-assisted transformation into CO control the rate of CO₂ transformation to formic acid, methanol and methane, respectively. Thus, modified Fe (111) surfaces enhancing these reaction steps have the potential to improve the CO₂ conversion processes.

Fig. 4  Energy profile diagram along the CO pathway

Conclusion
Our spin polarized-D2-GGA-DFT calculations reveal that CO₂ methanation will occur via the CO pathway and not the non-CO pathway. Fe (111) selectively favors CO methanation over CO₂ methanation, since although the reaction pathways are similar, the highest energy barrier for CO₂ methanation is encountered during the hydrogen-assisted CO₂ transformation into CO via the carboxylate and dihydroxycarbene intermediates. Both the formation of formic acid and methanol will proceed via the non-CO pathway, while CO and methane will be formed via the CO pathway from CO₂. CO₂ methanation on Fe (111) will involve the initial sequential hydrogenation of CO₂ into carboxylate, dihydroxycarbene, CO, HCO, H₂CO, and CH₂OH. CH₂OH is then decomposed into CH₂ and protonated into CH₃ and methane. Altering the rate-determining steps on modified Fe (111) surface is promising for CO₂ transformation and valorization.
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