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CO dissociation on Ru and Co surfaces: The initial step in the Fischer–Tropsch synthesis

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ABSTRACT

Synthesis of fuel from syngas via the Fischer–Tropsch (F–T) process is considered to be one of the important reactions in the field of heterogeneous catalysis. Here, we present a short review on the mechanism of the CO dissociation which is regarded as the initial step in the F–T process. The analysis is based on the earlier and recent propositions on the carbide and hydrogen assisted mechanisms for the CO dissociation on Ru and Co surfaces.

1. Introduction

The history of the Fischer–Tropsch (F–T) synthesis to produce liquid fuel from syn-gas ($CO + H_2$) dates back to the early period of the 20th century [1–5]. Earlier, the application of F–T synthesis was only limited to the regions such as Germany and South-Africa which had coal reserves but lacked oil fields to produce conventional fuel [3]. In recent years, the increase in the demand for crude oil and access to the large natural gas reserves have made F–T synthesis as one of the promising alternatives to produce 'clean' fuel via intermediate syn-gas conversion. This led to a challenging task for the researchers from the industry and academia to explore the complex reaction processes which take place in the syn-gas conversion via the F–T process. A general consensus derived from experimental and theoretical studies about the elementary steps involved in the F–T synthesis can be categorized into (a) initiation, which involves the CO dissociation and CH_x formation, (b) propagation via the CH_x–CH_x coupling reactions and finally (c) the termination and desorption of the hydrocarbons. This process involves contrary reactions of bond breaking and forming on the metal surfaces [4]. Hence, an efficient balance between these reactions is necessary for a high selectivity towards the formation of long chain hydrocarbons. Considering this fundamental aspect, transition metals such as Ru and Co have proved to be highly selective for the F–T synthesis [4]. New developments in the experimental techniques have made possible to probe the F–T reactions on the Ru and Co nanoparticles [6–8]. This gave a detailed knowledge of the particle size dependence on product selectivity. The other important characteristic which can influence the molecular reactions in the F–T synthesis is the topology of the catalyst [9–11]. This led to the investigation of the reactivity of the specific active sites present on stepped and corrugated surfaces and nanoparticles which are absent on the flat surfaces [7,9,12–16]. Consequently, the molecular reaction pathways on the stepped and corrugated surfaces can be different compared to the flat surfaces which can be termed as structure sensitive reactions [9,10]. The competitive reaction pathways added to the complexity of the surface structure has made the study of F–T a challenging task.

CO dissociation is a crucial step to generate the CH_x intermediates necessary for propagation of the chain in the F–T synthesis [4]. Many propositions regarding the mechanism for a low barrier CO dissociation on Ru and Co surfaces have been suggested [11]. A fundamental question regarding the initial step of the F–T synthesis has been raised under syn-gas conditions ($CO + H_2$) as shown in Scheme 1 i.e. whether adsorbed CO directly dissociates into C and O ad-species which is referred to as the (a) carbide mechanism or is assisted by coadsorbed hydrogen to form either (b) HCO or (c) COH intermediates? Fischer and Tropsch proposed a carbide mechanism based on their earlier results [1]. Craxford and Riedel confirmed this mechanism on Co catalyst [17]. Later, this proposition was debated by many researchers who suggested that the initial step in the F–T synthesis is the hydrogenation of CO and not the carbide mechanism [18–23]. Here, we give a short review on the possible initial steps in the F–T synthesis on different Ru and

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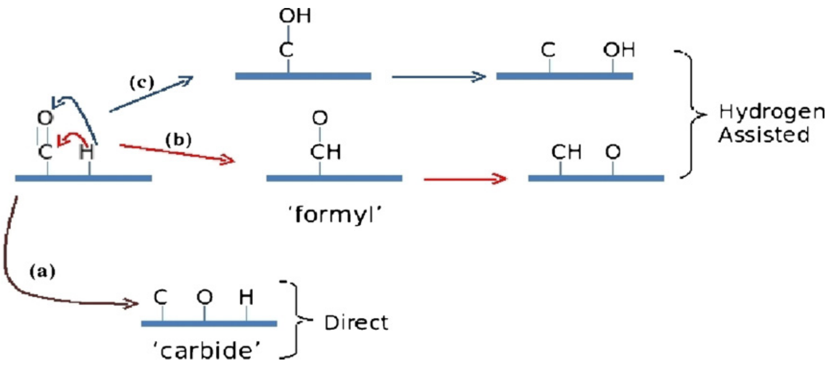

Scheme 1. Represents the possible pathways for the CO dissociation. (a), (b) and (c) correspond to the carbide, HCO and COH routes, respectively.

Co surfaces. We intend to present a critical analysis from the recent studies on direct and hydrogen assisted CO dissociation pathways.

2. CO dissociation on ruthenium surfaces

In the past, several experimental studies have shown that CO molecularly adsorbs on the flat Ru(0 0 0 1) surface [24]. However, CO dissociation is rather a difficult process and require high pressure and temperature. Fuggle et al. showed that under low pressure it is not possible to thermally dissociate CO [25]. Hence, they used electron bombardment to activate the CO bond on the flat surface. Mitchell et al. in an experimental work demonstrated that CO activation on Ru(0 0 0 1) surface via formyl intermediate has a lower barrier than the direct CO dissociation [19]. In this experiment they used Eley–Ridel mechanism where the gas phase H approaches adsorbed CO molecule to form formyl intermediate. This state was observed at 100 K, however upon annealing to 180–220 K, the formyl intermediate decomposes to CO and H. Contrary to this, Morgan et al. showed that under Langmuir–Hinshelwood conditions, where the CO and H are coadsorbed on the Ru surface, the formyl intermediate is highly endothermic and is undetectable from the HREELS [26]. This clearly implies that the formyl intermediate is highly unstable above 180 K and can only be stabilized at low temperatures.

Ciobica and van Santen in a theoretical study using periodic density functional theory (DFT) approach showed that the hydrogen assisted CO dissociation on flat Ru(0 0 0 1) surface has lower barrier than the direct CO dissociation [27]. They showed that the CO dissociation barrier on flat Ru(0 0 0 1) surface is 227 kJ/mol (Black line in Fig. 1). This barrier is about 51 kJ/mol higher than the desorption energy of CO which is also the apparent activation energy. One of the crucial factors for a high barrier for CO activation on the flat surface is the sharing of the metal atoms by the C and O atoms in the transition state (TS) as shown in Fig. 2(a). An alternative route via the formyl (HCO) intermediate was also proposed. They showed that the formation of HCO intermediate requires activation energy of 146 kJ/mol or 106 kJ/mol depending on different coadsorbed states of CO and H. The CO bond cleavage energy from the HCO intermediate was only 30 kJ/mol [27]. This implies that the CO dissociation via the formyl intermediate on dense Ru(0 0 0 1) surface has lower barrier than the direct CO dissociation. One should note that the reverse barrier from the HCO intermediate is only 37 kJ/mol and 1 kJ/mol depending on different pathways. This shows that the HCO intermediate is highly endothermic state. Morgan et al. also calculated a reverse barrier of 31 kJ/mol (7.4 kcal/mol) and 17 kJ/mol (4.1 kcal/mole) from different HCO states [26]. Inderwildi et al. predicted an overall barrier of 167 kJ/mol for CO dissociation via the formyl route [21]. However the reverse barrier for the formation of CO + H from the HCO intermediate was only 2 kJ/mol. Interestingly, the barriers for CO

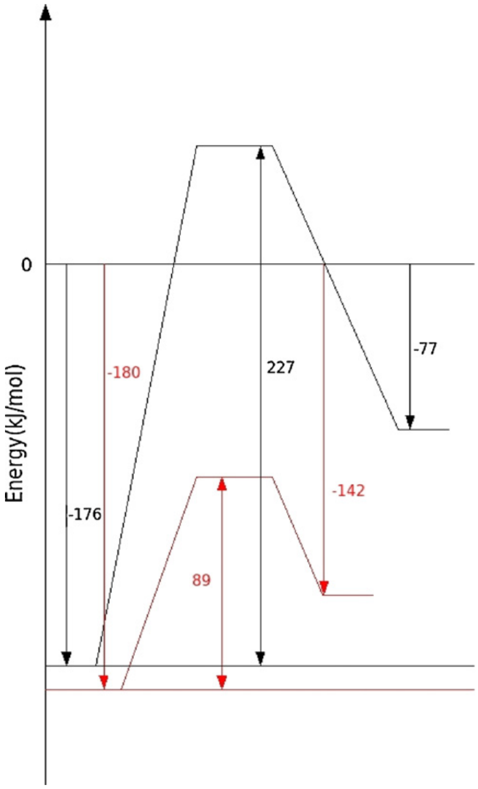

Fig. 1. Energetics of the CO dissociation on Ru(0 0 0 1) (black line) and stepped Ru(1 0 −1 5) (red line) surfaces. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)
Values taken from Ref. [27].

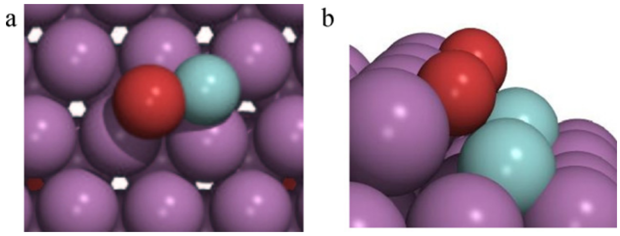

Fig. 2. Transition state geometries of CO dissociation on flat Ru(0 0 0 1) and stepped Ru(1 0 −1 5) surfaces [27]. Purple, blue and red spheres correspond to Ru, C and O atoms, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

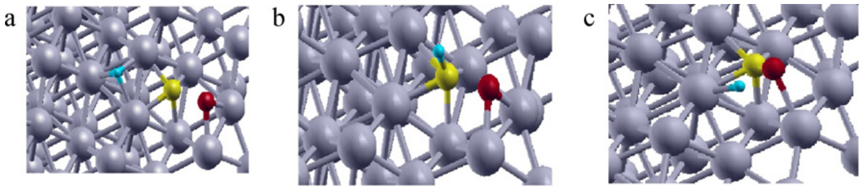

Fig. 3. Transition state geometries of CO dissociation via (a) direct (b) HCO intermediate and (c) COH intermediate on Ru(1 1 −2 1) surface [33]. Grey, yellow, red and blue spheres correspond to Ru, C, O and H atoms, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

dissociation on flat Ru(0 0 0 1) surface reported by Ciobica and van Santen, and Inderwildi et al. via the hydrogen assisted paths are lower than the direct CO dissociation pathway [21,27].

CO dissociation has been proved to be structure sensitive reaction which depends on the local structure of the active sites [9,10]. Shincho et al. carried out multi-method experimental investigation on the behavior of CO adsorption on Ru(0 0 0 1) and stepped Ru(1 1 1 0) surfaces [28]. They concluded that the CO bond is activated on the stepped surface and not on the flat surface. One should also note that the CO pressure or coverage can have a critical influence on the activation barrier of CO. A high coverage of CO can increase the CO activation barrier. Jacobi et al. have used experimental techniques such as thermal desorption spectroscopy (TDS) and HREELS to investigate the CO dissociation on corrugated Ru(1 1 −2 0) and Ru(1 1 −2 1) surfaces [29]. Their results demonstrated that the CO bond is highly activated on a four-fold hollow (4F) site present on these corrugated surfaces. They showed that the CO dissociation takes place around room temperature unlike that on the flat Ru surface. Yates and co-workers also applied experimental methods such as TPD, infrared reflection-absorption spectroscopy (IRAS) and low energy electron diffraction (LEED) to show that the CO dissociation takes place in the range of 450–500 K on a stepped Ru(1 0 9) surface [29]. This gives ample evidence that there are special active sites present on corrugated and stepped surfaces which are responsible for low barrier CO dissociation. Ciobica and van Santen gave a theoretical proof for the low barrier CO dissociation on Ru surface [27]. In this reaction path, the CO molecule is adsorbed in a hcp site at the bottom of the step. During the dissociation, in the TS (Fig. 2(b)) the C atom stays in the three-fold (3F) hcp site and the O atom moves to a bridge over the step edge. This configuration can be termed as 'B_5' configuration due to the five metal atoms involved in the configuration [30–32]. The C and O atoms do not share the metal atoms (Fig. 2(b)) and have less repulsive interaction [32]. The barrier for the CO bond cleavage along this path corresponds to 89 kJ/mol (red line in Fig. 1).

Shetty et al. showed that the CO dissociation on Ru(1 1 −2 1) surface has a lower barrier than that on the stepped surface proposed by Ciobica and van Santen [33]. This was attributed to the different reaction path for CO dissociation on Ru(1 1 −2 1) surface, where in the TS the C and O atoms are attached to the 4F and bridge sites (Fig. 3(a)) respectively without sharing the metal atoms. This TS is more stable compared to the earlier path because of the stable C and O coadsorption configuration Ru(1 1 −2 1) surface. The barrier for this path was shown to be around 24 kJ/mol lower than that on the stepped Ru surface calculated by Ciobica and van Santen. We now can address the question on the nature of the initial step in the F–T synthesis on corrugated or stepped surface where a low CO dissociation barrier is expected. In a recent study Shetty et al. have resolved the issue of the CO dissociation path on corrugated Ru surface [33]. They showed that the active six-fold sites (combination of 4F and bridge) present on the Ru(1 1 −2 1) surface which are responsible for low CO dissociation barrier of 65 kJ/mol (Fig. 3), the carbide mechanism is the preferred path for CO bond cleavage and not the hydrogen assisted. The TS structures of the three possible reaction paths described in Scheme 1 are shown in Fig. 3. The energy profiles for these paths are shown in Fig. 4. The carbide mechanism (blue line) corresponds to a barrier of 65 kJ/mol. In the TS, C and O atoms are situated in stable co-adsorbed state (Fig. 3(a)) which is not the case on flat Ru(0 0 0 1) surface. The hydrogenation of CO can proceed in two ways. One in which the C can be hydrogenated to form HCO, and in the other path the O of CO can be hydrogenated to form COH (Scheme 1). Let us consider the former path i.e. hydrogenation at the C end of CO to form HCO which requires a barrier of 80 kJ/mol (Green line in Fig. 4). This barrier is 15 kJ/mol higher than the direct dissociation of CO. This state is 75 kJ/mol endothermic with respect to the initial state of CO + H. In the TS, H moves from the three-fold site to form the bond with the C (Fig. 3(b)). These results very well agree with the earlier studies discussed above. If we assume that the HCO state is still formed with a very low reverse barrier. The further step to cleave the HC–O bond has a barrier of 45 kJ/mol (Fig. 4). This shows that the overall barrier for CO bond dissociation via the HCO intermediate is 120 kJ/mol. This barrier is much higher than the direct CO dissociation. Andersson et al. showed that the CO bond dissociation has a low barrier from the COH intermediate on Ni stepped surface [22]. Hence, we also choose this path for our investigation on the Ru(1 1 −2 1) surface. The initial step to hydrogenate the O end to form COH corresponds to a barrier of 149 kJ/mol (red line in Fig. 4).

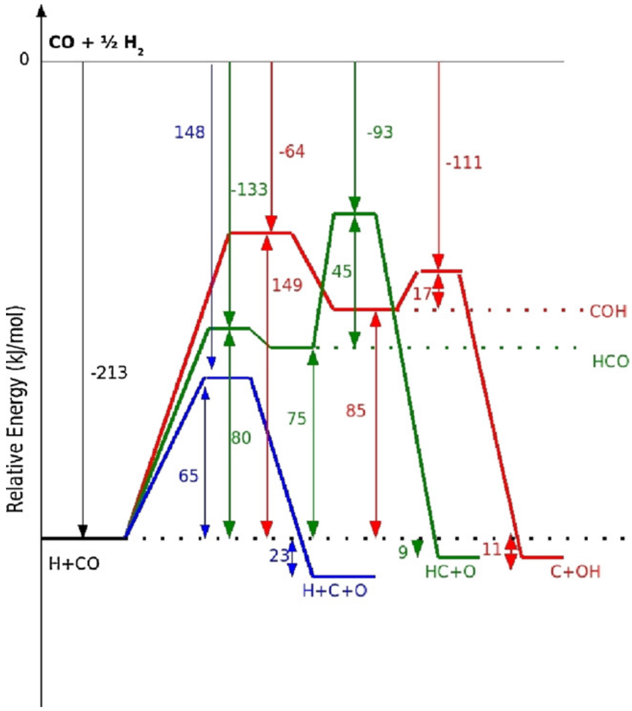

Fig. 4. Energetics of CO dissociation in the presence of co-adsorbed H on Ru(1 1 −2 1) surface. Blue: direct CO dissociation. green: CO dissociation through HCO intermediate. red: CO dissociation through COH intermediate. Energies are with respect to CO + 1/2H_2 in the gas phase [33]. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

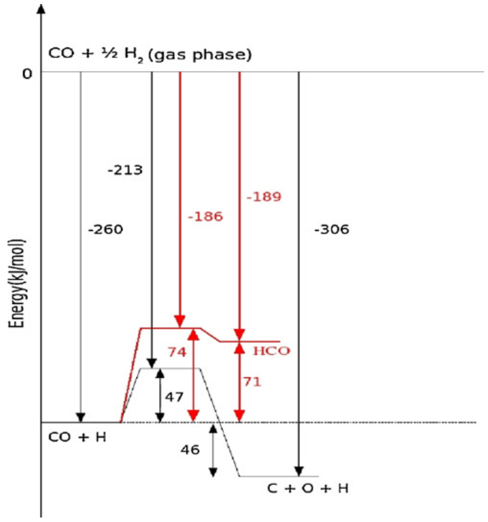

Fig. 5. Black line is the direct CO dissociation and red line is the formation of HCO intermediate on Ru(1 0 −1 0)B surface. Energies are with respect to CO + 1/2H_2 in the gas phase [36]. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

This barrier is much higher than the carbide mechanism. Interestingly, the barrier for CO bond cleavage from the COH intermediate is only 17 kJ/mol. This implies that if one considers the dissociation of CO from the HCO or COH intermediate, the barrier will be lower than the carbide mechanism. This is due to the stretching of the CO bond in these hydrogenated intermediate states which preactivates the CO bond. However, it is important to note that one cannot ignore the initial hydrogenation steps which require high barriers. This interpretation very well agrees with the experimental results of Fan et al., where they demonstrated that co-adsorbed hydrogen eliminates the CO dissociation precursor state on Ru(1 1 −2 1) surface [34]. Ciobica et al. have studied the coadsorption of CO and H on Ru surface [35]. They proposed that increase in the H coverage, the CO adsorption decreases due to the strong repulsive interaction between the coadsorbed CO and H. Hence, increase in the H coverage is not going to stabilize the HCO states instead will desorb the CO through repulsive interaction.

Another example where the CO dissociation follows the carbide mechanism is illustrated in Fig. 5. In this figure the carbide (black line) and the hydrogen assisted (red line) paths for CO dissociation are shown on the Ru(1 0 −1 0)B surface [36]. The CO dissociation via the carbide mechanism has a barrier of 47 kJ/mol. It is worth to mention that the Ru(1 0 −1 0)B surface does not have the 'B_5' site which have been suggested to be active for CO dissociation on stepped Ru surface and Co nanoparticles [7,16]. Surprisingly, the barrier on Ru(1 0 −1 0)B surface is lower than that on the stepped and corrugated Ru(1 1 −2 1) surface possessing the B_5 active sites. This implies that the six-fold (F_6) sites present on the Ru(1 0 −1 0)B surface are more active than the B_5 sites for CO dissociation. The barrier for the formation of HCO from the CO + H is 74 kJ/mol. Moreover, the reaction energy corresponds to 71 kJ/mol (Fig. 5). This is higher than the barrier required for the direct CO dissociation. The COH intermediate is unstable on the surface and we could not locate minima for this intermediate. Hence, we disregard the formation of COH intermediate on this surface [36].

In summary, the CO dissociation on flat Ru surface is via the hydrogen assisted pathway. However, on corrugated and stepped Ru surfaces and also nanoparticles possessing B_5 and F_6 sites for low barrier CO dissociation, the carbide mechanism is the dominant route. It is worth to mention that as the particle size decreases below ~1 nm the stabilization and coverage of the active sites is less and hence the activity for the formation of hydrocarbons is less. However, as the particle size increases the distribution of the number of active sites increases for the formation of active C1 species for the chain propagation. Consequently, the activity as well as the turn over frequency for the hydrocarbon formation is maximum in a certain particle size regime [6–8].

3. CO dissociation on cobalt surfaces

Since Co is less expensive than Ru, it is more attractive for industrial applications of the F–T synthesis [4]. Hence, along with Ru, many studies have been devoted to understand the F–T reactions on Co surfaces and nanoparticles. Similar to flat Ru(0 0 0 1) surface, the CO molecularly adsorbs on the flat Co(0 0 0 1) surface [23]. Geerlings et al. studied experimentally the F–T reaction on Co(0 0 0 1) surface under industrial conditions with temperatures around 500 K and at a total pressure of 1 bar with H_2:CO ratio of 2:1 [37]. They suggested from the post-reaction spectroscopic analysis that the carbon is deposited from the CO dissociation during the formation of hydrocarbons. This carbon formation is also responsible for self-poisoning the surface resulting into the deactivation of the catalyst. Tommes and King performed TDS and RAIRS analysis on the CO adsorption on low index plane of Co(1 0 −1 0) surface [38]. They concluded that CO does not dissociate on this surface. Gong et al. calculated a CO dissociation barrier of 260 kJ/mol on Co(0 0 0 1) surface [15]. Ge and Neurock studied in detailed the CO dissociation on several Co surfaces [39]. They reported a barrier of 232 kJ/mol for CO dissociation on Co(0 0 0 1) surface. They attributed the high CO dissociation barrier on the flat Co to the repulsive interaction between the C and O adatoms in the TS and also in FS. They calculated repulsive energy of 65 kJ/mol between the C and O adatoms in the FS. This leads to high endothermic FS which increases the dissociation barrier. On corrugated Co(1 1 −2 0) surface which consists of 'zig-zag' rows, they calculated a barrier of 200 kJ/mol with respect to the adsorbed state. This barrier is 32 kJ/mol lower than that on the Co(0 0 0 1) surface. This was due to the strong coadsorption of the C and O atoms in the FS along the under coordinated sites on the Co(1 1 −2 0) surface resulting into less endothermic FS unlike that on the flat Co surface.

Recently, in an interesting study, Inderwildi et al. established an alternative path for CO dissociation on Co(0 0 0 1) surface [20]. They used periodic DFT as implemented in CASTEP to propose that the CO dissociation occurs via the formaldehyde (CH_2O) intermediate which is formed from two successive hydrogenation steps. In the initial path, CO was hydrogenated to form HCO which requires a barrier of 126 kJ/mol. However, the HCO intermediate was shown to be 96 kJ/mol endothermic [21]. The CO bond cleavage from this formyl intermediate corresponds to a barrier of 96 kJ/mol. Hence the overall barrier from the IS i.e. coadsorbed CO + H can be calculated to be 192 kJ/mol. This is higher than the desorption energy of CO shown to be 172 kJ/mol. The other option was to hydrogenate the C or O end of the HCO intermediate to form CH_2O or HCOH intermediates, respectively. The former path was proposed to have a lower barrier than the later [20]. In a similar study, Cheng et al. also found a barrier of 126 kJ/mol and with a reaction energy of 116 kJ/mol for the HCO formation. Furthermore, they proposed that the HCOH formation (119 kJ/mol) has a higher barrier compared to the CH_2O formation (53 kJ/mol) and discarded the former path [41]. Inderwildi et al. showed that the CO bond cleavage from the CH_2O intermediate corresponds to 82 kJ/mol which is lower than the direct CO dissociation of 272 kJ/mol. In a recent work Zhuo et al. suggested a CO insertion path for the C–C coupling reactions [40]. For the initial step of CO dissociation, their results were in agreement with the proposition of Inderwildi et al. [20], Ojeda et al. in a combined experimental and theoretical study suggested that the CO dissociation on Co(0 0 0 1) with a 50% coverage proceeds via

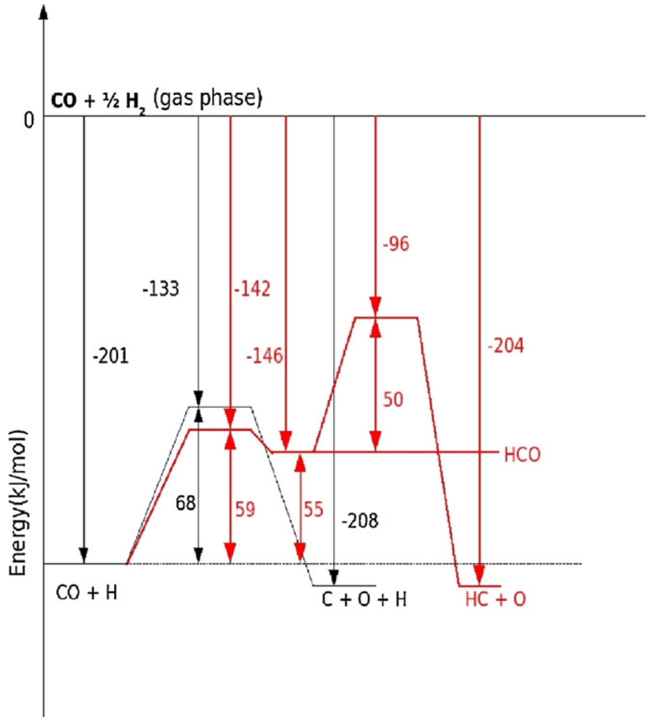

Fig. 6. Black line is the direct CO dissociation and red line is the CO dissociation via the HCO intermediate on Co(1 0 −1 0)B surface. Energies are with respect to CO + 1/2H_2 in the gas phase [36]. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

the HCOH intermediate [23]. The barrier for the formation of HCO of 138 kJ/mol is similar to the one proposed by the earlier studies on Co(0 0 0 1) surface. Surprisingly, the barrier for the formation of COH (125 kJ/mol) is lower than the HCO formation (138 kJ/mol) and also exothermic by 55 kJ/mol with respect to the CO + H, however the HCO route was proposed to be favorable. The authors argue that, since COH formation is more exothermic, it will not equilibrate under normal F–T conditions. Although the CH_2O formation is shown to be only 14 kJ/mol compared to a barrier of 90 kJ/mol for the formation of CHOH from the CHO intermediate. The proposed path was shown to be via the CHOH intermediate and not the CH_2O. This analysis contradicts to the reaction path proposed by Inderwildi et al. and Cheng et al. which may be due to the differences in the CO coverage used. Nevertheless, the barriers calculated for CO activation on Co(0 0 0 1) via hydrogen assisted paths were lower compared to the direct CO dissociation.

Geerlings et al. proposed that the CO dissociation is more facile on the stepped Co(1 0 1 2) surface compared to that on the Co(0 0 0 1) surface [13]. Their spectroscopic data revealed a very low frequency CO on the stepped Co(1 0 −1 2) surface which was assigned to the CO adsorbed in a step site. This was theoretically confirmed by Ge and Neurock [39]. They examined two paths for the CO dissociation and reported barriers of 161 and 123 kJ/mol. The barrier corresponding to 161 kJ/mol was 19 kJ/mol higher, while the later was 29 kJ/mol lower than the desorption energy of CO. Furthermore they also carried out CO dissociation on stepped Co(1 1 −2 4) surface. Gong et al. also showed that the sites present on the stepped Co surface are active for CO dissociation compared to that on the flat Co(0 0 0 1) surface [15]. Beitel et al. observed from PM-RAIRS that around 490 K at 300 mbar the CO molecule disappears at the defect site and hydrocarbon formation takes place. In our earlier discussion on flat Ru surface we showed that the HCO state is highly unstable above 200 K and dissociates into CO and H. Now the question is, whether the HCO state on Co(0 0 0 1) can be stabilized at or above 300 K?

Recently, we performed a study of CO dissociation on the corrugated Co(1 0 −1 0)B surface [36]. We considered the paths described in Scheme 1 similar to the paths discussed on Ru(1 1 −2 1) and Ru(1 0 −1 0)B surface in the earlier section. The energy diagram for the direct CO dissociation and hydrogen assisted pathways are shown in Fig. 6. The direct CO dissociation in the presence of coadsorbed H corresponds to a barrier of 68 kJ/mol. In the hydrogen assisted path we consider the formation of HCO from the coadsorbed CO and H. This path requires a barrier of 59 kJ/mol. The HCO intermediate is 55 kJ/mol endothermic with respect to the CO + H coadsorbed state. The barrier to form HCO is lower than the direct CO dissociation unlike on the corrugated Ru surfaces. A barrier of 50 kJ/mol is found for the CO bond cleavage from the HCO intermediate. The overall barrier with respect to the IS of CO + H is 105 kJ/mol to dissociate CO via the hydrogen assisted path. One can clearly see that this barrier is 37 kJ/mol higher than direct CO dissociation. We also checked the COH path. However, the COH intermediate is highly unstable and do not exist on this surface. Hence, we disregard this path for CO dissociation.

4. Conclusion

CO dissociation is considered to be the crucial step in the F–T synthesis to produce 'clean' fuel from syngas. Hence, predicting the appropriate mechanism for CO dissociation is of utmost importance. Here, we have presented a short review on the CO dissociation pathways suggested in recent years based on experimental and theoretical studies. The fundamental question on the initial step in the F–T synthesis which has been debated is, whether adsorbed CO directly dissociates or first is activated through hydrogenation? Our analysis indicated that:

- On flat Ru and Co surfaces the CO bond cleavage from the HCO intermediate corresponds to a lower barrier than the direct CO dissociation. However, the formation of HCO is an endothermic process. The experiments on Ru surface show that the HCO state can be stabilized around 100 K. However, above 200 K this state will be unstable and will readily form CO + H. The effect of coverage can also influence the hydrogen assisted paths. High coverage of H can be responsible for CO desorption due to repulsive interaction between the coadsorbed H and CO.
- Analysis from the theoretical data clearly indicate that the corrugated and stepped Ru and Co surfaces consisting of active sites for low barrier CO dissociation, the carbide mechanism will be the preferred path over the hydrogen assisted. We also believe that the deactivation of the catalyst due to the carbide formation from the adsorbed C_1 species manifest the direct CO dissociation pathway. Since within the carbide F–T mechanism, the activation energy to form active CH_x adsorbed intermediates from adsorbed CO has to be low compared to that of the chain growth termination reaction, the F–T reaction will have to take place on the corrugated sites as we discussed. The requirement of low barrier CO dissociation is consistent with the often used kinetic assumption in F–T that CO dissociation is equilibrated with its dissociated fragments.

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