

Site Structure Sensitivity Differences for Dissociation of Diatomic Molecules

Sharan Shetty · Rutger A. van Santen

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Abstract A review on the analysis based on our recent theoretical results on the site specific activation of CO, N₂ and NO on corrugated Ru surface is presented. We discuss the issues such as what should be the configuration of the active site for the optimum dissociation of the diatomic molecules?, How is the barrier dependent on the structure of the reaction path?, Whether the further steps involved in the reaction sequence dependent on the activation of the diatomic molecules?

Keywords Structure sensitivity · FT synthesis · Diatomic · DFT · Catalysis

1 Introduction

Recent developments in the field of heterogeneous catalysis has made it possible to probe the surface chemical reactions at a molecular level with the use of state-of-the-art experimental and theoretical techniques. This has not only helped us to understand the fundamental issues in the surface science, but have proved to be important for the technological advancement. The three surface catalyzed reactions which have drawn a considerable attention in the

past decade are the Fischer–Tropsch (F–T) synthesis to produce liquid hydrocarbons from the syngas, three-way catalytic (TWC) process to convert the harmful gases such as CO and NO into CO₂ and N₂ in the automobile exhaust, and the ammonia synthesis via the Haber–Bosch (H–B) process [1–5]. A significant experimental and theoretical work has been devoted to investigate the elementary steps involved in the above mentioned reactions [6–13]. These studies have concluded that the factors such as the surface topology, electronic structure and geometry of the intermediate states, influence the reaction mechanisms. They have also shown that the reactions can be categorized as structure sensitive and insensitive. The rates of the structure sensitive reactions depend on the geometry of the local active sites, while the structure insensitive reactions are independent of the surface topology. The structure sensitive reactions related to the above mentioned reactions viz F–T, TWC and H–B processes are the CO, NO and N₂ activation respectively. These reactions are not only structure-sensitive but are also considered to be the initial steps in the reaction sequences [14]. Hence, an appropriate active site for a low barrier activation of these diatomic molecules on the transition metal (TM) surfaces and nanoparticles is an important issue in the field of heterogeneous catalysis.

In the present review we briefly discuss the recent issues related to the structure sensitivity of the active sites involved in the activation of CO, NO and N₂ on corrugated Ru surface.

2 Methodology

The calculations presented in this work have been performed by the Vienna ab-initio simulation package (VASP)

S. Shetty (✉) · R. A. van Santen
Schuit Institute of Catalysis, Eindhoven University
of Technology, P.O. Box 513, 5600 MB Eindhoven,
The Netherlands
e-mail: s.g.shetty@tue.nl

R. A. van Santen
e-mail: r.a.v.santen@tue.nl

code [15, 16]. This is based on the periodic density functional theory (DFT) which uses the plane wave basis set for the valence electrons in conjunction with the projector augmented-wave (PAW) potentials for the core [17, 18]. This combination significantly decreases the computational time and not ignoring the chemical characteristics of the system. The Kohn–Sham equations are solved self-consistently with an iterative matrix diagonalization scheme. The mixing of the charge density is done by the Broyden method. The kinetic energy cut-off for the plane wave basis set is setup to 400 eV. The exchange-correlation functional is expressed by the generalized gradient approximation (GGA) with Perdew–Becke–Ernzerhof (PBE) [19]. The k-point sampling was generated following the Monkhorst–Pack procedure with a $5 \times 5 \times 1$ mesh. The ionic relaxation has been carried by the conjugate gradient method. During the optimization all the degrees of freedom of the system i.e. slab and adspecies are relaxed. The reaction paths to determine the transition state (TS) have been computed using the nudged elastic band (NEB) method developed by Jónsson et al. [20]. The initial images between the optimized initial and the final state structures are obtained from the linear interpolation. These images are optimized simultaneously by the program. The TS is confirmed by the saddle point obtained from the additional frequency calculations. The open Ru(1121) surface is cut from the HCP Ru bulk which is initially optimized. The calculated bulk Ru–Ru distance is 2.70 Å and the binding energy is -6.699 eV/atom. These are in agreement with the experimental values which are reported as Ru–Ru distance of 2.71 Å and binding energy of -6.615 eV/atom [21]. The optimized Ru(1121) surface is shown in Fig. 1. The possible adsorption sites are also represented. We have used a 2×2 supercell consisting of 12 layers of slab and 16 layers of vacuum between the slab along the *c* axis. For the experimental work on the characterization of Ru(1121) surface we refer to the work by Jacobi and coworkers [22].

3 Results and Discussion

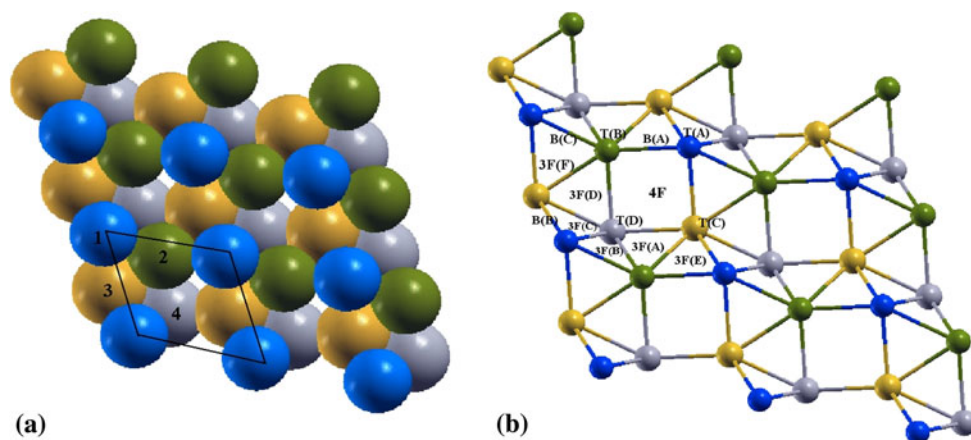
In this section we present a brief analysis on the role of active sites on the activation of diatomic molecules on the corrugated Ru surface in relation to the technological important reactions viz. F–T synthesis, H–B process and the TWC process.

3.1 CO Activation and F–T Process

F–T process uses syngas ($\text{CO} + \text{H}_2$) to produce liquid hydrocarbons via complex surface reactions. The process includes three primary steps, initiation, propagation and termination. The initiation step consists of the adsorption and dissociation of CO and H_2 molecules. Although the H_2 dissociates at a low barrier, the critical issue is to activate the CO bond which is also considered to be the rate-limiting step in the F–T process. The CO molecule in the gas phase has a triple bond with a bond energy of 1,079 kJ/mol. On the late transition metal surfaces e.g. Ni, Rh, Ru, Co etc this energy is around 200–400 kJ/mol [23]. The next crucial step includes the chain propagation through C–C coupling. The selectivity and activity of the catalyst strongly depends on the balance between CO dissociation and C–C bond association according to the Sabatier's principle [23]. This balance is achieved by Ru and Co catalysts and hence are considered to be the efficient catalysts for the F–T process.

The adsorption of CO on TM surfaces has been well explained by the Blyholder model. CO molecule in the gas has a non-bonding 5σ HOMO which arise from C lone pair. The LUMO has two antibonding $2\pi^*$ degenerate states. The removal of the density from the HOMO does not act the CO bond due to the non-bonding nature of HOMO [24]. However, the filling of the LUMO results into the decrease in the bond order of CO. Blyholder model propose that the CO molecule linearly adsorbs on the metal

Fig. 1 **a** Ru(1121) surface blue, green, yellow and grey spheres correspond to the 1st, 2nd, 3rd and 4th layer atoms respectively. **b** Different active sites possible on the Ru(1121) surface: four-fold hollow (4F), three-fold hollow (3F), top (T), bridge (B). The different possibilities for each site are represented in the parenthesis by A, B etc. [13, 28]



surface with the σ donation into the d-orbital of the TM and a back-donation from the d-orbitals into the antibonding $2\pi^*$ orbital of CO. Contrary to this, there have been two other propositions for the adsorption of CO by Bagus et al. and Föhlisch et al. [25, 26]. Bagus et al. showed that CO interaction with the Na, Mg and Al metal atoms is through the π to $2\pi^*$ transition, while the 5σ has a Pauli repulsive interaction. Föhlisch et al. showed that the stretching of the CO bond on the TM surfaces results from the internal mixing of 1π and $2\pi^*$ orbitals similar to the Bagus model. However, in the model proposed by Föhlisch et al., interaction with the d-orbital is explicitly considered. In general these models have proved that the CO molecular orbitals undergo rehybridization after the adsorption on the TM surfaces. Filling of the anti-bonding $2\pi^*$ orbital of CO varies with respect to the site preference on the surface. Hence, the adsorption of CO is strongly dependent on the site. On the stepped surfaces the adsorbed CO molecule has tilted configuration due to the corrugation of the surfaces unlike the flat surfaces. In these configurations CO is pre-activated and consequently lowers the activation barrier.

In an experimental work Zubkov et al. [9] showed that the CO dissociation on stepped Ru(109) surface occurs at low temperature (450–500 K) compared to the flat Ru(0001) surface. Followed by this in a theoretical study, Ciobica and van Santen [12] proved that the CO dissociation barrier on stepped Ru surface is reduced by 120 kJ/mol compared to that on the flat Ru(0001) surface. This clearly implies that there are special active sites present on the stepped surface which facilitate the activation of CO. In another experimental work, Fan et al. [27] examined the CO dissociation on corrugated Ru(1121) surface. Their results demonstrated a lower temperature CO activation compared to the stepped surface. This manifests the sensitivity of the CO activation on the local structure of the active sites. Shetty et al. [13, 28] recently showed in a theoretical work that the CO on Ru(1121) surface is activated along a six-fold coordinated Ru site. The CO is located in a four-fold site as predicted by the experimental studies. The CO molecule adsorbed in this site is pre-activated due to low CO frequency ($1,339\text{ cm}^{-1}$) as a result of bond stretched [28]. In this configuration C and O are

attached to the 4F and 2F sites. This is not the situation when the CO molecule is aligned perpendicular to the surface normal, for e.g. on the flat Ru(0001) surface. During the CO dissociation on the flat Ru(0001) surface in the TS the CO molecule has to bend and the C and O atoms share the metal atom [12, 14]. In this configuration there is strong repulsive interaction due to the sharing of the metal atom. Consequently the activation barrier increases. Moreover the C and O atoms have to diffuse in the final state to reduce the repulsive interaction which also contributes to the barrier. Contrary to this the dissociation path on a corrugated surface is quite different. Geometrical description of the dissociation path of CO on corrugated Ru(1121) surface is shown in Fig. 2. In the TS, the C and O atoms do not share the metal atoms which reduce the repulsive interaction. The configuration in the final state (FS) is similar to the TS. This indicates that the similar structure of TS and FS and non-sharing of the metal atoms in the TS lowers the activation barrier. For a detailed illustration on the behavior of barrier on the structure of the reaction path, we refer to a recent review by van Santen et al. [14]. The barrier corresponding to the CO dissociation along the six-fold site on Ru(1121) surface is 65 kJ/mol. This barrier is 24 kJ/mol lower than the Ru stepped surface. One should note that on the stepped Ru surface the dissociation was along a combination of three-fold and 2F sites which can be described as a ‘B₅’ site. Interestingly, we also showed that the dissociation along this ‘B₅’ site on the Ru(1121) surface the barrier increases by 48 kJ/mol [28]. This was due to the local reconstruction of the 3F site onto a 4F site. This suggests that the CO dissociation is more favorable on a six-fold site.

Considering this aspect we examined several open Ru surfaces which would have a six-fold site where the CO molecule can be pre-activated. Interestingly, such six-fold sites are present on Ru(1010)B surface. A detailed explanation on the structure of Ru(1010)B surface is given elsewhere [29]. The reaction path is shown in Fig. 3. The CO molecule in the adsorbed state is pre-activated and is in a six-fold configuration. Interestingly, the CO molecule maintains this six-fold configuration in the complete dissociation path. The dissociation barrier from the adsorbed

Fig. 2 a, b and c correspond to the initial, transition and final state structures respectively, of CO dissociation along six-fold site on Ru(1121) surface. Grey, yellow and red spheres correspond to Ru, C and O atoms respectively. The six-fold site is highlighted in green color. The bond lengths are in Å [13]

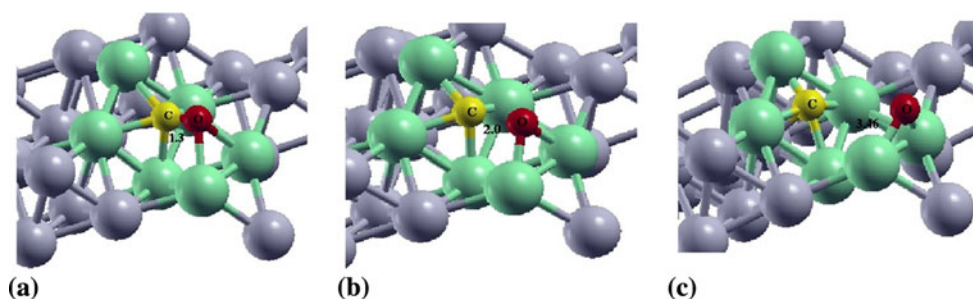
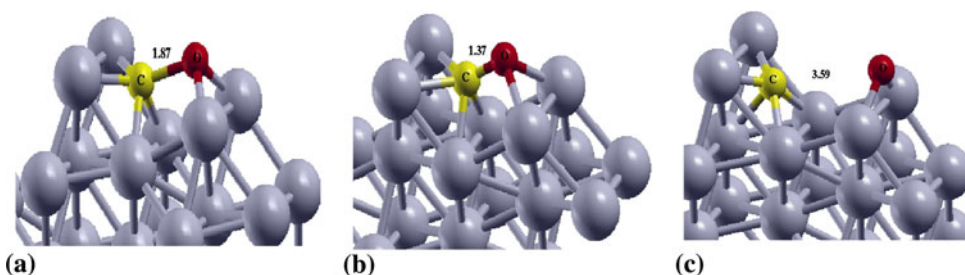


Fig. 3 **a, b** and **c** Correspond to the initial, transition and final state structures respectively, of CO dissociation along six-fold site on Ru(1010)B surface. Grey, yellow and red spheres correspond to Ru, C and O atoms respectively. The bond lengths are in Å [29]



state corresponds to only 47 kJ/mol. This is around 18 kJ/mol lower than the one reported on Ru(1121) surface. This justifies the strong dependency of the CO dissociation barrier on the local structure of the active site.

Although the above analysis shows that a specific site for a low dissociation of CO has been suggested. The critical issues which need to be addressed are; whether the low CO dissociation barrier poisons the active sites with coke formation? what are the structure insensitive reactions? What size of nanoparticles would have these six-fold active sites? and whether the further reaction steps are affected due to low CO dissociation barrier?

3.2 N₂ Activation and H–B Process

Experimental and theoretical studies have proposed that the N₂ activation is the rate limiting step in the ammonia synthesis via the Haber–Bosch process. Hence, in the past, enormous research has been devoted to the adsorption and activation of N₂ on metal surfaces. It is interesting to note that N₂ and CO are isoelectronic. However, their properties on the metal surface is distinct. This is due to the difference in their molecular orbitals.

For an elaborate analysis of the bonding nature of N₂ adsorption on metal surfaces we refer to a recent article by Nilsson and Pettersson [30]. The explanation is based on the N₂ adsorption on Ni cluster using the X-ray emission spectroscopy and DFT calculations. They proposed that the inter and intra orbital mixing of the N₂ and metal orbitals give rise to three rehybridized allylic orbital configurations i.e. bonding, non-bonding and antibonding. The weakening

of the N₂ bond is attributed to the mixing of bonding 1π and antibonding $2\pi^*$ orbitals. The in-phase mixing of 1π and $2\pi^*$ orbitals and interaction of this state with the d-orbital give rise to a bonding $\tilde{\pi}$ with metal orbitals and the out-phase mixing give rise to a non-bonding lone-pair $d\tilde{\pi}$ orbital. N₂ dissociation has been shown to be sensitive to the geometry of the local site. Dahl et al. [31] in an interesting work showed that the activation of N₂ is enhanced on the sites present along the steps of Ru(0001) surface. Their theoretical results showed that the barrier for N₂ dissociation along the steps is reduced by 145 kJ/mol compared to the terrace sites. It was evident from these results that the N₂ molecule in the active sites have different configuration which pre-activates the N₂ bond to lower the dissociation barrier. Hence, understanding the properties of these active sites is an important issue from the synthesis point of view. In the past Van Hardeveld and van Montfort [32] suggested that a combination of 3F and 2F ('B₅') sites for the activation of N₂ on Ni metal particles. Recently, these sites were also shown to be active for N₂ activation on Ru nanoparticle [7]. In an experimental work, Kim et al. [33] demonstrated that the sites present on a double-stepped Ru surface are relatively more active than the single stepped surface. In a theoretical study, Shetty et al. [34] showed that on a corrugated Ru surface there are two kinds of 'B₅' sites which can be active for N₂ dissociation.

The reaction path for the N₂ dissociation on corrugated Ru(1121) surface is shown in Fig. 4. In the initial state the N₂ is in a 4F coordination with the Ru atoms. Interestingly, this configuration is similar to the one observed by Morgan et al. [35] on a double stepped Ru(109) surface. In this

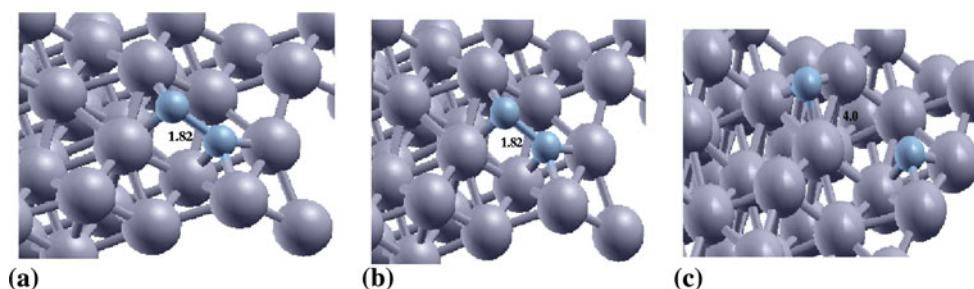


Fig. 4 **a, b** and **c** Correspond to the initial, transition and final state structures respectively, of N₂ dissociation on Ru(1121) surface. The grey and the blue spheres represent the Ru and N atoms respectively. The N–N bond lengths are given in Å [34]

state the N–N bond length is 1.25 Å which indicate that the N₂ molecule is preactivated. In the transition state one N atom is in a 3F and the other is in a 2F coordination attaining a ‘B₅’ configuration. In the final stable state the two N atoms are adsorbed in 3F hollow sites. The reaction is 20 kJ/mol exothermic with respect to the adsorbed state. It is interesting to note that the two N atoms in the TS do not share the metal atoms unlike in the case on flat Ru(0001) surface. This reduces the repulsive interaction and contributes to the stabilization of the TS. The additional stability is due to the configuration where the TS of N₂ is close to the FS. The dissociation of N₂ molecule in another ‘B₅’ site has a higher barrier because the TS structure where the N₂ molecule attains a 4F coordination and remains distant from the FS. This implies that the dissociation barrier depends on the structural connection between the initial, transition and final states. Deviation between these structures due to diffusion of the atoms in the FS, reconstruction of the active site or repulsive interaction between the adspecies will increase the barrier. Contrary to this if the dissociating species have the same coordination in the IS, TS and FS then the barrier for activation can be extremely low.

Although the CO and N₂ are isoelectronic in nature, the adsorption and dissociation behavior of these molecules on the same surface is different. It is worth to note that the number of Ru atoms involved in the complete dissociation path of CO and N₂ are six. This can be attributed to the valence of the C, O and N atoms. In analogy we would expect that the NO dissociation would require five Ru atoms. This will be discussed in the next section.

The further steps involved in the ammonia synthesis are the hydrogenation of the atomic N to form NH₃. One could ask then how structure sensitive these steps are? Interestingly in an experimental work Jacobi et al. [36] showed that the Ru(1121) surface is active for NH₃ decomposition. They found that the intermediate species NH and NH₂ are more stable on the open Ru(1121) surface than the flat Ru(0001) surface. A detailed analysis of the reaction barrier for the hydrogenation of the atomic N to form NH₃ is required. This will explain whether only the N₂ dissociation or the complete reaction sequence is structure sensitive.

3.3 NO Activation and TWC Process

The TWC process is considered to be one of the important catalytic reactions in removing the three harmful components viz. CO, NO and hydrocarbons from the automobile exhaust [8]. Basically the main focus in the TWC converter is to reduce NO and oxidize CO to less harmful N₂ and CO₂ respectively. The critical issue concerns the dissociation of NO molecule which is the rate determining step.

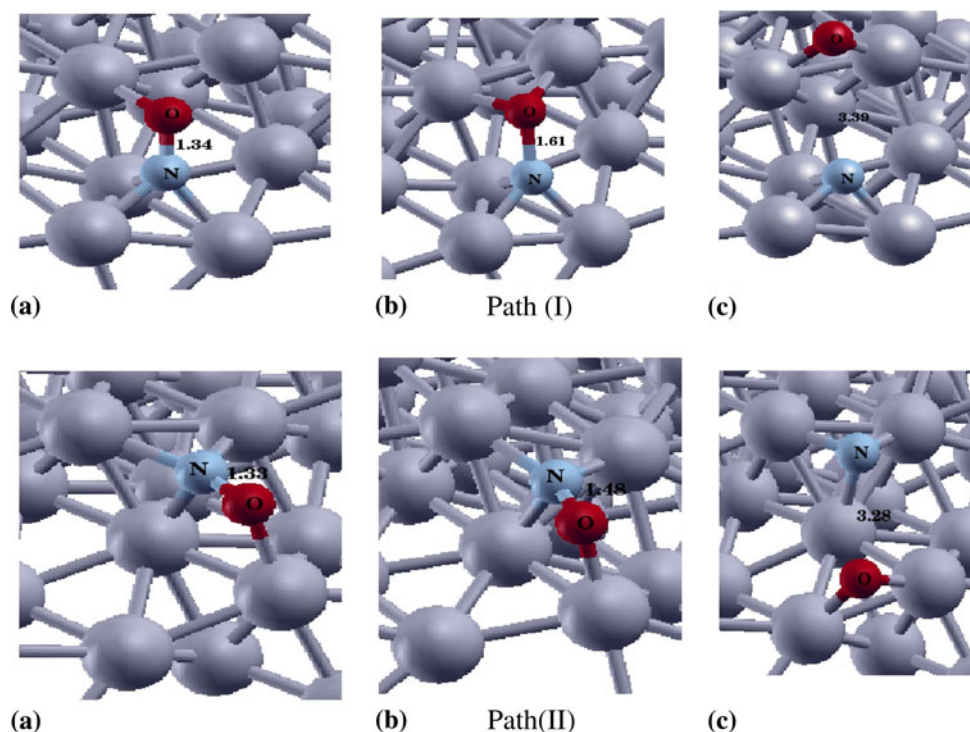
Ruthenium has been proposed to be selective towards the reduction of NO. Zambelli et al. [6] employed scanning tunneling microscopy to demonstrate that special sites present on monoatomic steps of Ru(0001) surface are more active for NO activation compared to that on the terrace. This interpretation was theoretically proved by Hammer.

He showed that the NO is highly activated on the stepped Ru surface due to the local geometry of the active sites present along the edge of the steps. One reason for high barrier for NO dissociation on the Ru(0001) surface is that the NO molecule bends and shares the metal atoms in the TS which increase the repulsive interaction. Compared to CO, the barrier required for the dissociation of NO is less. This is due to the one unpaired electron in the antibonding state. Consequently, less energy is required to populate the antibonding state.

In this section we discuss the role of the active sites for NO dissociation on corrugated Ru surface. There are two active ‘B₅’ sites where the NO molecule is preactivated. The dissociation paths on these sites are shown in Fig. 5. In the first path (Path I) the NO molecule in the IS has N and O coordinated to 3F and top sites respectively. The NO bond length is stretched to 1.34 Å. In the TS the N and O atoms attain 3F and 2F coordination with a bond length of 1.61 Å. This configuration is also maintained in the FS. In the second dissociation path (Path II) the difference with earlier path is only in the TS where NO has 4F coordination with N and O attached to 3F and top sites respectively. The dissociation barrier corresponding to path (I) and (II) are 13 and 18 kJ/mol respectively. These barriers are similar to the one reported on stepped Ru surface i.e. 16 and 17 kJ/mol. This proves that the active B₅ sites on open Ru(1121) and stepped Ru surfaces for NO dissociation have similar geometries. The question is whether the two sites described are equally probable to activate NO? Our results indicate that the NO in the IS of path (II) is 43 kJ/mol more stable than the IS of path (I) [37]. This energy is higher than the difference in the energy barrier between the two paths. Hence, at low NO coverage, path (II) is active for NO dissociation due to strong adsorption compared to path(I). The dissociation along the path (I) will proceed at higher coverages once the ‘B₅’ sites of path(II) are occupied by the N and O adspecies.

The next critical step after the NO dissociation in the TWC process is the removal of N and O adspecies to avoid the poisoning of the active sites. This is carried out by the formation of N₂ formation and oxidation of CO to form CO₂. From the above discussion on CO and N₂ dissociation we can interpret the formation of CO₂ and N₂ on the corrugated Ru surface. From our recent results we can deduce that the CO and O are strongly adsorbed with energy around –160 to –200 and –500 to –600 kJ/mol respectively with respect to the gas phase CO and O [28]. This

Fig. 5 **a, b** and **c** Correspond to the IS, TS and FS structures respectively, of NO dissociation along two different ‘B₅’ sites Path (I) is along 3F(B) and B(A) sites and Path (II) is along on 3F(F) and B(A) sites on Ru(1121) surface. Grey, blue and red spheres correspond to Ru, N and O atoms respectively. The NO bond lengths are in Å [37]



strong adsorption on the corrugated Ru surface creates difficulty in inserting the O atom in the C–Ru bond to form CO₂. Comparatively the formation of N₂ is feasible with a barrier of 115 kJ/mol [29]. This analysis shows that there are two steps which are contrary to each other. One is the bond breaking of NO and the other are the bond association reactions to form CO₂ and N₂. Metals such as Rh and Pd have high barriers to dissociate NO but the formation of CO₂ is easier. On the other hand Ru is more active for NO dissociation rather than CO₂ formation. Moreover, an active site such as ‘B₅’ lowers the barrier for NO and CO dissociation. However, these sites are inactive for CO oxidation. Hence a balance between the bond breaking and bond forming reactions is necessary for an optimum path.

4 Conclusion

The present analysis provides a brief discussion on the role of the active sites for the dissociation of CO, N₂ and NO on corrugated Ru surface. The main conclusions are as follows;

- Dissociation of diatomic molecules is dependent on the local active sites such as six-fold for CO and five fold (‘B₅’) for N₂ and NO in a specific configuration on stepped or open surfaces and nanoparticles. Deviation from these configuration can affect the dissociation

barrier. Moreover, the barrier also depends on which TM these active sites are present. For e.g. the six-fold active site for CO dissociation on Ru and Co can have different reactivity.

- The dissociation barrier is related to the structures involved in the reaction path. More closely the IS, TS and FS are related, lower is the barrier for the activation. Sharing of the metal atoms in the TS by the adspecies increases the repulsive interaction and can destabilize the TS. This repulsive interaction is immensely reduced on the corrugated surfaces and lowers the barrier.
- The stability of the active site is also an important factor during the dissociation. The metal atoms on the corrugated surfaces are lower coordinated compared to the flat surfaces. Hence, the interaction of the atomic species can reconstruct the active site and can hinder the further reaction steps.
- A balance between the dissociation of the diatomic molecules and the further steps such as the hydrogenation in the F–T and H–B or oxidation of CO in the TWC processes is necessary.

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