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Item Type	Article
Authors	Yadav, Manoj Kumar;Vovusha, Hakkim;Sanyal, Biplab
Citation	Adsorption and dissociation of dinitrogen on transition metal (Ta, W and Re) doped MgO surface 2016 Computational and Theoretical Chemistry
Eprint version	Post-print
DOI	<a href="https://doi.org/10.1016/j.comptc.2016.06.019">10.1016/j.comptc.2016.06.019</a>
Publisher	Elsevier BV
Journal	Computational and Theoretical Chemistry
Rights	NOTICE: this is the author's version of a work that was accepted for publication in Computational and Theoretical Chemistry. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Computational and Theoretical Chemistry, 16 June 2016. DOI: 10.1016/j.comptc.2016.06.019
Download date	2024-04-21 22:58:09
Link to Item	<a href="http://hdl.handle.net/10754/614391">http://hdl.handle.net/10754/614391</a>

## Accepted Manuscript

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PII: S2210-271X(16)30225-0  
DOI: <http://dx.doi.org/10.1016/j.comptc.2016.06.019>  
Reference: COMPTC 2170

To appear in: *Computational & Theoretical Chemistry*

Received Date: 13 April 2016  
Revised Date: 15 June 2016  
Accepted Date: 15 June 2016

Please cite this article as: M.K. Yadav, H. Vovusha, B. Sanyal, Adsorption and dissociation of dinitrogen on transition metal (Ta, W and Re) doped MgO surface, *Computational & Theoretical Chemistry* (2016), doi: <http://dx.doi.org/10.1016/j.comptc.2016.06.019>

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# Adsorption and dissociation of dinitrogen on transition metal (Ta, W and Re) doped MgO surface

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## Abstract

The adsorption and dissociation of dinitrogen on transition metal (Ta, W and Re) doped MgO(100) surface has been studied employing density functional theory. It is found that all these transition metals (TM) on MgO(100) surface are capable of adsorbing dinitrogen ( $N_2$ ), however there is no dissociative adsorption of  $N_2$  on single transition metal dopant. When two TM atoms are doped on MgO(100) surface, dissociative adsorption of dinitrogen occurs in all the three cases. Whether the dissociation is spontaneous or is it associated with activation barrier depends on the orientation of  $N_2$  molecule approaching the dopant site.

*Keywords:* Nitrogen fixation, Dissociative adsorption, Transition state, Activation barrier

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## 1. Introduction

Haber process, discovered in early 20th century, is still so far the most efficient method of nitrogen fixation on an industrial scale. In Haber's process, high pressure and high temperature are required for the conversion of atmospheric nitrogen into ammonia. Thus, there is a huge amount of energy consumption to

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maintain high pressure and high temperature. There has been continuous efforts for finding more efficient methods, but without success. Since metalloenzymes that catalyze difficult chemical reactions have been found to consist of clusters containing transition metal atom at their active sites, several studies have been carried out exploring the possibility of breaking the triple bond of nitrogen molecule on transition metal clusters [1, 2, 3, 4]. Roy et al. [3] have studied the adsorption of nitrogen molecule on model lithium clusters employing density functional theory (DFT) method using hybrid-GGA B3LYP functional. They have found that a minimum of 8-atom lithium cluster is required for the complete cleavage of triple bond of dinitrogen. DFT study by Yadav and Mookerjee [4] shows that the global minimum structures of dimer, trimer and tetramer clusters of tantalum adsorb nitrogen molecule in a dissociative manner.

Experimental study by Mitchell et al. [2] shows that nitrogen gets adsorbed on the gas phase clusters of tungsten ( $W_n$ ,  $n < 15$ ) as a precursor state for dissociation. The adsorption of nitrogen on supported metallic clusters is important for the application point of view and as such several reports exist for adsorption on supported clusters as well [5, 6, 7]. Avenier et al. [5] have reported the dissociation of dinitrogen on an isolated tantalum atom supported on a silica surface. As predicted by Mitchell et al. [2], the XPS and XAES studies by Yamaguchi and Murakami [6] show that  $W_5$  cluster supported on HOPG surface indeed adsorbs molecular nitrogen, which is precursor for dissociation. Recently, Murakami and Yamaguchi [7] reported the reduction of  $N_2$  to  $NH_3$  by tungsten clusters supported on graphite surface, and further suggested that such reduction of  $N_2$  to  $NH_3$  via hydrogenation mechanism could mimic the process of nitrogen fixation shown by nitrogenase.

In this paper, we have explored a different approach for nitrogen fixation. Unlike the adsorption by free cluster or supported cluster we have studied adsorption and dissociation by MgO(100) surface doped with 5d transition metals (Ta, W and Re). Due to its favorable properties like high melting point, simple structure and easy preparation in ultra high vacuum, MgO(100) surface is a popular choice as a model catalytic surface [8, 9, 10]. Moreover, MgO is highly

abundant, non toxic and environment friendly.

## 2. Computational Details

The calculations have been carried out using a DFT (density functional theory) based code, Vienna *ab initio* Simulation Package (VASP) [11, 12]. The projector augmented wave (PAW) based potentials with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [13, 14] were used. Our calculated lattice constant of 4.21 Å for bulk MgO and the N-N bond length of 1.11 Å for free nitrogen molecule agree very well with the experimental values (1.10 Å for N<sub>2</sub> and 4.21 Å for MgO). The MgO(100) surface was modeled as a six-layer slab with 36 atoms in each layer (18 atoms each of Mg and O). Thus, the supercell for pure MgO surface consisted of 216 atoms in total. The bottom three layers were fixed to bulk values and the top three layers were allowed to relax in each calculation. A vacuum of 15 Å was created over the surface to avoid the interaction with periodic images. For all the dopants (Ta, W and Re), 5p and 5d electrons were considered in valence states. A plane wave cut off of 500 eV was used with 2×2×1 Monkhorst-Pack sampling of Brillouin zone. A test calculation using 3×3×1 k-point set produced energy difference of less than 1 meV. The geometry optimizations were carried out till the maximum force on each atom became less than 0.01 eV/Å.

## 3. Results and Discussions

Before investigating the case of N<sub>2</sub> adsorption on transition metal (TM) doped MgO surface, we first investigated N<sub>2</sub> adsorption on a clean MgO(100) surface. We considered four different starting geometries as shown in Fig. 1. In none of these cases, chemisorption of N<sub>2</sub> either in molecular or dissociated form was found. This result is contrary to the case of H<sub>2</sub> adsorption on MgO surface[15]. The formation energies for TM (Ta, W and Re) dopants at Mg site on MgO(100) surface were calculated using the relation:

$$E_f = E_{sys} - E_{sub} + \mu_{Mg} - \mu_M, \quad (1)$$

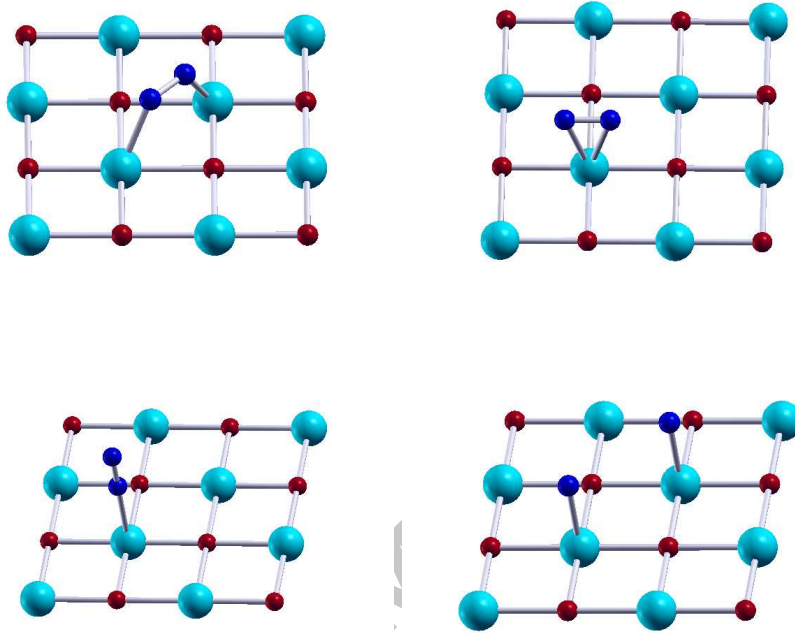


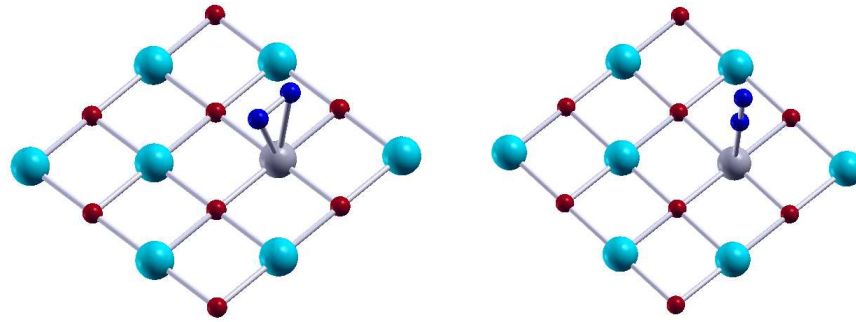
Figure 1: Starting geometries for adsorption of  $N_2$  on clean  $MgO(100)$  surface. Large shaded (cyan), small dark (red) and small lightly shaded (blue) spheres represent Mg, O and N atoms respectively. For the purpose of clarity only a portion of the top layer of the surface is shown.

where  $E_{sys}$  is the energy of the slab with a single dopant atom doped at Mg site,  $E_{sub}$  is the energy of the clean MgO substrate,  $\mu_{Mg}$  is the chemical potential of Mg and  $\mu_M$  is the chemical potential of the dopant. The chemical potential of Mg was calculated using the relation  $\mu_{Mg} = E(MgO) - \frac{1}{2}E(O_2)$ , where  $E(MgO)$  is the total energy of 1 formula unit of bulk MgO and  $E(O_2)$  is the energy of a free oxygen molecule. The chemical potential of dopants were calculated from the energies of their respective bulk phases. The formation energies for Ta, W and Re dopants were found to be -2.10, -0.38 and 0.88 eV respectively indicating reasonably good feasibility for the substitutional doping for Ta and W, however Re doping can only be achieved by non-equilibrium growth technique.

Due to TM doping there is local structural rearrangement around the doping

site. Instead of more or less identical Mg-O bond lengths for O atoms on the surface as well as for O atoms just below the surface, large differences are found between the two types of M-O bond lengths (henceforth we use the symbol M for Ta, W and Re while expressing metal-oxygen, metal-nitrogen and metal-metal bond lengths). The M-O bond lengths on the surface for Ta, W and Re are 2.02, 2.16 and 2.10 Å respectively. Thus, for Ta doping, there is a shortening of bond length compared to Mg-O bond length (2.105 Å) whereas for W doping, the W-O bond length is elongated compared to Mg-O bond length. The Re-O bond length is very much similar close to the Mg-O bond length. However, M-O bond lengths for O atoms just below the surface are 2.84, 2.51 and 2.78 Å respectively. These are much larger compared to corresponding M-O bond lengths on the surface and are responsible for the protrusion of dopant atoms from the surface. The calculated heights of doped TM atoms from the MgO surface are 0.51, 0.36 and 0.44 Å respectively. Interestingly, the height of doped TM atom from the surface is found to be inversely proportional to M-O bond length. It implies that with stronger M-O interaction, O atoms are strongly pulled towards M atom thereby causing the increased height for both M and O atoms.

Next we move on to study the adsorption of N<sub>2</sub> on a single TM atom doped at Mg site on MgO surface. We considered two different orientations of dinitrogen for each TM doped MgO surface: (i) N-N molecular axis parallel to the MgO surface as in Fig. 2(a) and (ii) N-N molecular axis perpendicular to the MgO surface as in Fig. 2(b). Let us first discuss the adsorption of N<sub>2</sub> in the first case. The calculated adsorption energies per N<sub>2</sub> molecule for Ta, W and Re doped cases are 2.09, 2.07 and 1.33 eV respectively. These adsorption energies are larger than N<sub>2</sub> adsorption on Fe (111)[18] and Ru (0001)[19] surfaces ( 0.30 and 0.44 eV/N<sub>2</sub> respectively) but smaller than the case of N<sub>2</sub> adsorption on V (110)[20] surface ( 2.82 eV/N<sub>2</sub>). The large adsorption energies indicate chemisorption of N<sub>2</sub> on all the TM atoms considered here, however in none of the cases there is a dissociative adsorption. The N-N bond lengths for Ta, W and Re doped cases are 1.31, 1.39 and 1.24 Å respectively. Thus, there is an



(a)

(b)

Figure 2: Adsorption of  $N_2$  on a single W atom. Large dark shaded spheres (cyan) represent Mg atoms, small dark (red) spheres O atoms, large gray (gray) sphere TM atom and small lightly shaded (blue) sphere N atoms.

elongation of N-N bond lengths in each case caused by transfer of electron from TM d states to the anti-bonding orbitals ( $\sigma^*$  and  $\pi^*$ ) of  $N_2$ . For Ta and W doping, the N-N bond length lies between N-N single bond length (1.49 Å) and N-N double bond length (1.25 Å)[16], however for Re doping the N-N bond length lies between N-N triple (1.10 Å)[17] and N-N double bond lengths. The M-N distances for Ta, W and Re doping are 1.98, 1.87 and 2.0 Å respectively. The smallest M-N distance for W doping implies the strongest bonding between W and N atoms thereby causing larger separation between the two N atoms. In none of the cases,  $N_2$  dissociates into N atoms.

Now we discuss the adsorption of  $N_2$  in the second case [Fig. 2(b)]. The adsorption energies per  $N_2$  molecule for Ta, W and Re doped cases are 1.74, 1.69 and 2.11 eV respectively. Clearly, the adsorption of parallel configuration is favored for Ta and W doped cases whereas for the Re doped case, the adsorption in perpendicular configuration is favored. It is known that the adsorption of  $N_2$  in perpendicular configuration is the least favored on V (110) surface[20] whereas it is the most favored on Fe (111) surface[21]. The N-N bond lengths for Ta, W



and Re doped cases are 1.19, 1.18 and 1.17 Å respectively. Thus, in all the cases, the N-N bond lengths are close to N-N triple bond length and the N<sub>2</sub> adsorption is more or less like adsorption in molecular form. Unlike in the case of parallel N-N, less transfer of electrons from TM d states to anti-bonding orbital of N<sub>2</sub> is expected for end-on N-N on TM atoms, and hence the elongation of N-N bond length is smaller for end-on adsorption.

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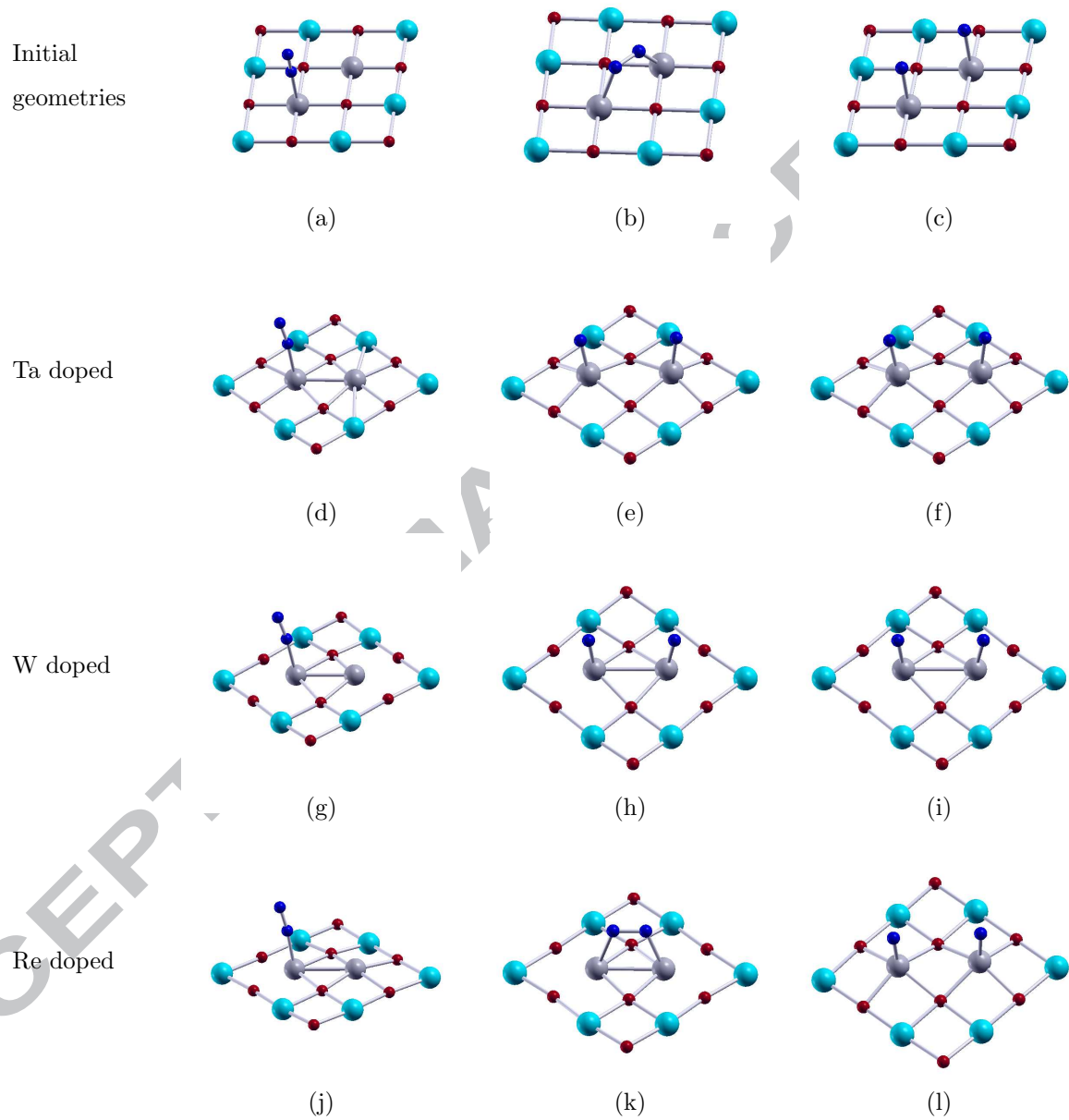


Figure 3: Adsorption of  $N_2$  on two TM atoms. First row: Initial starting configurations, Second row: Ta doped cases, Third row: W doped cases and Fourth row: Re doped cases. Color codes for atoms are same as in Fig. 2.

With the presence of a single TM dopant, the  $N_2$  molecule lacks the favorable situation for dissociation. Thus, we aim to explore  $N_2$  adsorption on MgO surface doped with two TM atoms. At first we examined energetics of two different geometries of doping 2 TM atoms at Mg sites on the MgO(100) surface: (i) M-O-M making an angle of  $90^\circ$  and (ii) M-O-M making an angle of  $180^\circ$ . It turns out that the former configuration is energetically more favorable than the latter for all the three dopants. The difference in energies between the two geometries for Ta, W and Re doped cases are 1.33, 2.46 and 1.79 eV respectively. Thus, we have considered only the first case for studying adsorption of  $N_2$  on MgO surface doped with two TM atoms. Three different initial configurations for adsorption at the TM dopant sites on the MgO surface were considered: (i)  $N_2$  placed perpendicular to the MgO surface and on top of a dopant atom, as in Fig. 3(a) (vertical configuration), (ii)  $N_2$  placed parallel to the MgO surface and in between the two dopant atoms as in Fig. 3(b) (horizontal configuration) and (iii) a nitrogen atom placed on top of each of the two dopant atoms as in Fig. 3(c) (dissociated configuration). The corresponding optimized final geometries for the three configurations for the three types of TM dopants are shown in the lower three panels of Fig. 3. The adsorption energies and local geometries along with N-N bond lengths are presented in Table I.

Clearly, there is no dissociative adsorption for any of the TM doped case when  $N_2$  approaches the metal site in a vertical configuration. The nitrogen molecule gets adsorbed on a single TM dopant with its molecular axis slightly tilted. The calculated M-N and N-N bond lengths for Ta, W and Re doped cases are 1.99, 1.92, 1.87 Å and 1.17, 1.17 and 1.16 Å respectively. Thus, N-N bond lengths are elongated in all cases, but these are still very close to N-N single bond length and hence the adsorption can be considered as molecular adsorption as seen in the cases of single TM dopants. The calculated adsorption energies per  $N_2$  molecule for Ta, W and Re doped cases are 1.74, 1.69 and 2.14 eV respectively.

In the case of horizontal configuration, the  $N_2$  molecule gets completely dissociated and gets adsorbed as atomic nitrogen on the two TM atoms for Ta

Table 1: Adsorption energy,  $E_{ad}$  in eV, M-M, M-N and N-N bond lengths in Å.

Configuration	Dopant	$E_{ad}/N_2$	M-M	M-N	N-N
Vertical	Ta	1.60	2.59	1.99	1.17
	W	2.08	2.53	1.92	1.17
	Re	1.85	2.60	1.86	1.16
Horizontal	Ta	3.78	3.22	1.74	dissociated
	W	4.94	2.77	1.70	dissociated
	Re	1.54	2.57	1.99	1.26
Dissociated	Ta	3.78	3.22	1.74	dissociated
	W	4.94	2.77	1.70	dissociated
	Re	3.16	3.13	1.67	dissociated

and W doped cases. Thus, there is a spontaneous dissociative adsorption of  $N_2$  on Ta and W doped cases. The spontaneous dissociative adsorption has also been found for Fe(111) surface[21]. However, in the case of Re doping,  $N_2$  gets adsorbed without a complete cleavage as shown in Fig. 3(k). The N-N bond length is 1.26 Å which is slightly larger than N-N double bond. Thus, the N-N triple bond is now activated to N-N double bond and can be considered as a precursor state for the dissociation of  $N_2$ . For all the three TM dopant cases, there are structural rearrangements around the doping sites after the adsorption of  $N_2$ . The M-M bond lengths before and after adsorption of  $N_2$  for Ta, W and Re doped cases are 2.49, 2.44, 2.44 Å and 3.22, 2.77, 2.56 Å respectively. Thus,  $N_2$  adsorption causes elongation of M-M bonds in all the three cases. The M-N bond lengths for Ta, W and Re are 1.74, 1.70 and 1.99 Å respectively. Clearly, for the complete cleavage cases (bidoped Ta and W) of  $N_2$ , the M-N bond lengths are significantly smaller than their corresponding values as seen above in the cases of adsorption of  $N_2$  on single TM atoms. However, in the case of bidoped Re, the Re-N distance is still comparable to the case of monodoped Re. The adsorption energies per N atom are 1.89, 2.47 and 1.58 eV respectively for Ta, W and Re doping. Thus, in all the cases the dissociative adsorption energy is

large.

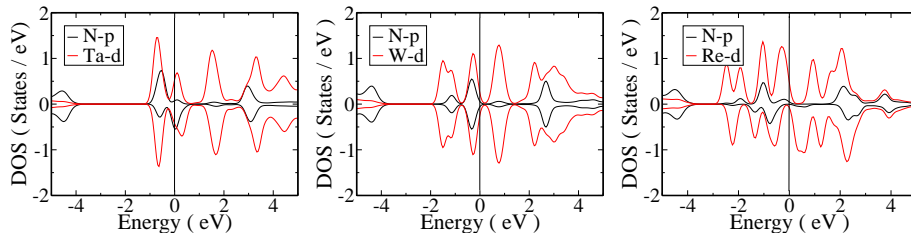


Figure 4: Atom and orbital projected density of states (DOS) for Ta, W and Re doped cases.

In order to understand why dissociative adsorption occurs for horizontal configuration in the cases of Ta and W, but not in the case of Re, we carried out Bader charge analysis of the optimized horizontal configuration for Re doping. We then carried out self consistent static calculations for Ta and W doped cases with the final geometries identical to the case of Re doping [as in Fig. 3(k)] followed by Bader charge analysis for each case. We have found charge transfer from TM atoms to N atoms in all the cases. The average electronic charges received by each N atom for Ta, W and Re-doped cases are 1.18, 1.02 and 0.48 respectively. Clearly for the cases of dissociative adsorption, the charge transfer is more than twice of non-dissociative adsorption case of Re. The large amount of charge transfer in Ta and W doped cases causes weakening of N-N triple bond and thus leads to dissociative adsorption. Since the charge transfer in Re doped case is not sufficient to weaken the N-N bond, there is no dissociative adsorption for Re doping. We further attempt to understand the reason behind varying amount of charge transfer in terms of electronic configurations and hybridization between orbitals near the top of the valence bands. The trend of the amount of charge transfers from TM atoms to the nitrogen antibonding states is not necessarily proportional to the number of valence electrons of the TM atoms. Therefore, with the valence configurations of  $5d^36s^2$ ,  $5d^46s^2$  and  $5d^56s^2$  for Ta, W and Re respectively, one may not expect increasing order of charge transfers on moving from Ta to Re. The charge transfer is rather dependent on the hybridization between orbitals. The densities of states for

Ta, W and Re doped cases in the above mentioned configurations are shown in Fig.5. First of all, one does not observe a rigid band filling going from Ta to Re with increasing number of d electrons. It is clear that a significant amount of rearrangement in distribution of electronic states takes place and hence, the amount of hybridization between TM-d and N-p strongly varies. This affects the amount of charge transfer to the antibonding p-orbital states of nitrogen. It is observed that for Re doping, the hybridization is minimal and so is the charge transfer.

The third dissociated configuration turns out to be the ground state configuration for all TM doped cases. The adsorption energy per  $N_2$  molecule for Ta, W and Re doped cases are 3.78, 4.94 and 3.16 eV respectively. The M-N bond lengths for Ta, W and Re doped cases are 1.74, 1.70 and 1.67 Å respectively. For the cases of Ta and W, the optimized dissociated configurations are exactly identical to the optimized horizontal configurations as evidenced by the identical M-M and M-N bond lengths (Table I). However, Re doped case has now dissociated N-N bond unlike the undissociated N-N bond in the case of horizontal configuration.

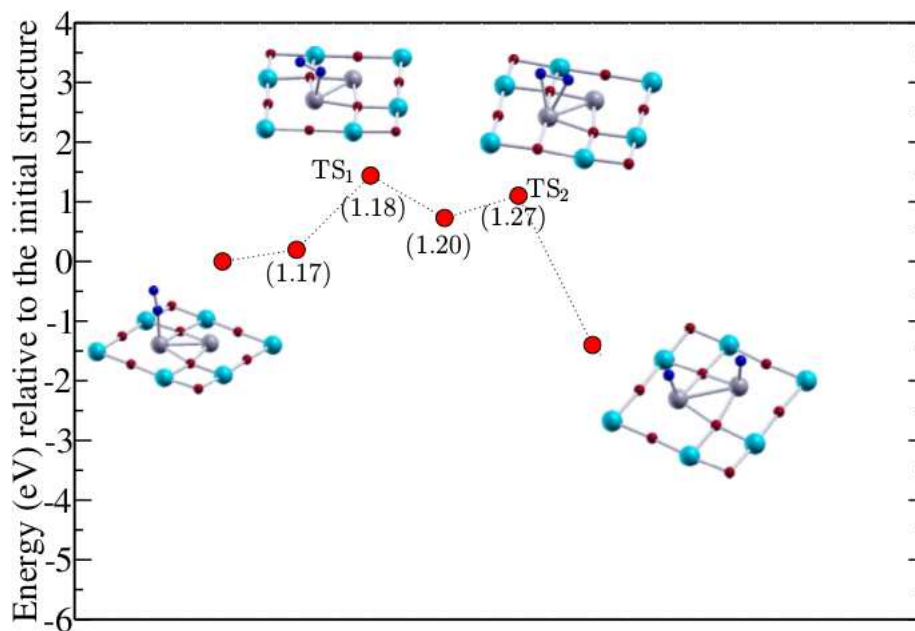


Figure 5: Minimum energy path for the dissociative adsorption of  $N_2$  on MgO surface doped with two W atoms. The figures in the brackets represent N-N bond lengths in Angstrom for the corresponding images. The dotted line between the points are drawn for the sake of better visualization.

One of the paths for the N-N dissociation could be adsorption of  $N_2$  on one of the TM atoms (vertical configuration) followed by the dissociative adsorption with single N atom adsorbed on each TM atom (dissociated configuration). Certainly there is a possibility of intermediate transition state with associated barrier. In order to investigate whether the dissociative adsorption is easily viable or not, we have attempted to calculate the activation barrier for the dissociation using climbing image nudged elastic band method. Since the calculation is computationally expensive we performed the calculation only for the case of nitrogen dissociation on W as W lies in between Ta and Re. The calculations were carried out considering 4 images between the initial configuration (almost molecularly adsorbed  $N_2$ ) as in Fig. 3(g) and final configuration (with dissociated  $N_2$ ) as in Fig. 3(i). The minimum energy path for  $N_2$  dissociation is shown in Fig. 4. The main transition state  $TS_1$  has almost molecularly ad-

sorbed  $N_2$  with elongated N-N bond length of 1.18 Å. The activation barrier for dissociation on W-doped surface is found to be 1.43 eV [Fig. 4]. There is another intermediate transition state  $TS_2$  with a barrier height of 0.41 eV. The N-N bond length in  $TS_2$  is 1.27 Å, which eventually gets completely dissociated on reaching the final ground state.

#### 4. Summary

From detailed DFT calculations, we have found that both monodoped and bidoped MgO surface with TM atoms (T, W and Re) are capable of chemisorbing  $N_2$ . In none of the monodoped cases, dissociative adsorption of  $N_2$  is observed. However, in the bidoped cases, dissociative adsorption occurs for all the three dopants. However, whether the dissociation is associated with or without barrier depends on the orientation of the approaching  $N_2$  molecule. Spontaneous (barrierless) dissociative adsorption occurs in the cases of Ta and W doping when a  $N_2$  molecule approaches the dopant site with its axis parallel to the axis of M-M dopant. For non-spontaneous dissociative adsorption, an activation barrier height of 1.43 eV was found in the case of bidoped W. We hope that our theoretical prediction of conditions for  $N_2$  dissociation will boost the experimental efforts along this direction.

#### Acknowledgements

BS acknowledges Swedish National Infrastructure for Computing (SNIC) for the allocation of super- computing time.

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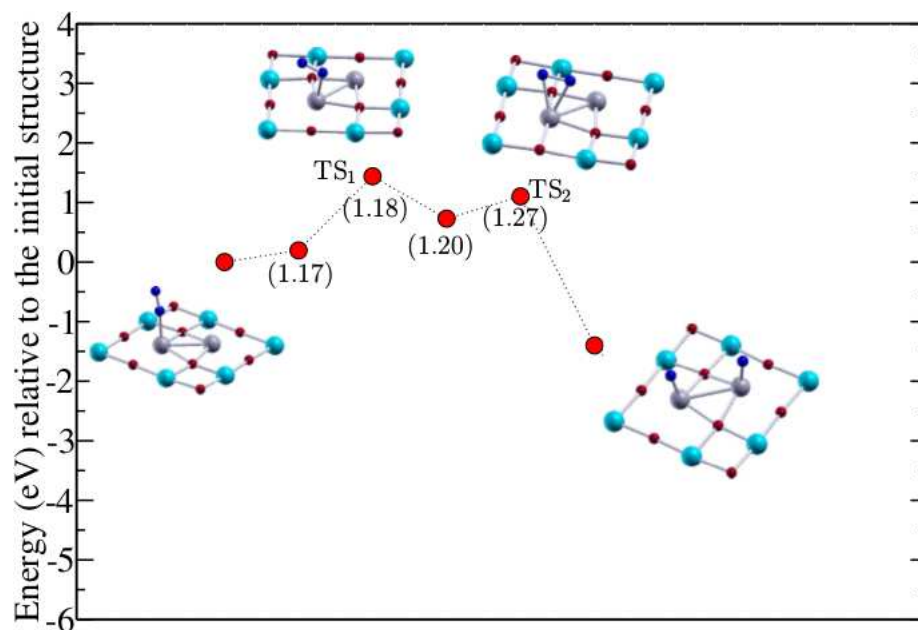
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Minimum energy path for the dissociative adsorption of N<sub>2</sub> on MgO surface doped with two W atoms. The figures in the brackets represent N-N bond lengths in Angstrom for the corresponding images. The dotted line between the points are drawn for the sake of better visualization.

Dinitrogen adsorbed almost molecularly (non-dissociative) in the first figure has to overcome the activation barrier of 1.43 eV for the dissociative adsorption shown in the last figure.

1. Dissociative adsorption of dinitrogen on Ta, W and Re doped MgO surface.
2. Activation barrier for dissociative adsorption of dinitrogen on W doped MgO surface is 1.43 eV.
3. The TM (Ta,W,Re) doped MgO surface is found to be suitable candidate for dinitrogen activation and adsorption.

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