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N_2O decomposition on Fe- and Co-ZSM-5: A density functional study

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Abstract

Density functional theory (DFT) calculations are employed to study N_2O decomposition on relaxed $[(SiH_3)_4AlO_4M]$ (where M = Fe, Co) cluster models representing Fe- and Co-ZSM-5 surfaces and Fe-ZSM-5 channel cluster. The catalytic cycle steps are completed both for Fe- and Co-ZSM-5 clusters. It is found that the general trend of the results obtained is in agreement with experimental and theoretical literature: Co-ZSM-5 has a lower activation energy barrier than Fe-ZSM-5 and O_2 desorption step is the rate-limiting step for both clusters. The activation barrier for the decomposition of the first N_2O molecule inside a Fe-ZSM-5 channel cluster increases in comparison with that of the cluster model indicating a channel effect on the activation barrier. The activation barrier reported for the channel cluster is 12.63 kcal/mol. This is also in good agreement with experimental literature.

Keywords: DFT; Fe-ZSM-5; Co-ZSM-5; N_2O decomposition; Channel effect

1. Introduction

Fe-exchanged ZSM-5 is an active catalyst for the stochiometric decomposition of N_2O to N_2 and O_2. It is, therefore, a potentially useful material for the removal of N_2O, a molecule with a high greenhouse potential, from industrial waste streams including nitric acid and adipic acid plants. The postsynthetic introduction of Fe into ZSM-5 generates various Fe species including isolated cations, dimers, oligonuclear clusters and Fe_2O_3 particles. Depending on the preparation and pretreatment method used, one of these species may represent the majority of Fe sites; however, in most cases, mixtures of several species may be present.

Several studies of N_2O decomposition over Co-, Cu-, and Fe-ZSM-5 show that the reaction is first order [1–4] with respect to N_2O concentration. Zhu et al. [5] investigated N_2O decomposition over Fe-ZSM-5 prepared by the sublimation method. They reported that the activity strongly depends on the nature of Fe species inside the zeolite micropores. They showed that the high-temperature calcined and steamed Fe-ZSM-5 shows a good catalytic performance for N_2O decomposition. Nitrous oxide decomposition on Fe-ZSM-5 zeolite was investigated by use of TPD by Wood et al. [4].

Kapteijn et al. [2] made a comparative kinetic analysis of N_2O decomposition over Co-, Cu- and Fe-ZSM-5 zeolite catalysts. They investigated the effect of partial pressure of N_2O, O_2, CO and NO, the space time and temperature. Pirngruber et al. [6] have investigated the mechanism of N_2O decomposition on Fe-ZSM-5 zeolite prepared by ion exchange and chemical vapor deposition methods. They reported two possible mechanisms: (a) a single-site mechanism in which N_2O deposits two oxygen atoms on the same iron site, followed by rapid O_2 desorption, and (b) the ‘‘migration–recombination’’ mechanism, in which two oxygen atoms are deposited on separate iron sites, followed by a slow surface migration and recombination to O_2. It is experimentally reported that O_2 desorption is the rate-limiting step of N_2O decomposition on ZSM-5 [7,8]. N_2O decomposition on Co-ZSM-5 is studied by da Cruz et al. [9] and they reported that Co^{2+} ions are highly active and stable for N_2O decomposition in the presence of oxygen and water.

Yakovlev and Zhidomirov [10,11] investigated the direct N_2O decomposition by 5-coordinated transition metal ions Fe, Co and Rh by using DFT method. The reaction mechanism for nitrous oxide decomposition was studied on hydrated and dehydrated mononuclear iron sites in Fe-ZSM-5 using DFT by Heyden et al. [12]. They used B3LYP formalism with TZVP

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basis set for all atoms and clusters modeled as $[(SiH_3)_4AlO_4FeO]$, $[(SiH_3)_4AlO_4FeO_2]$ and $[(SiH_3)_4AlO_4Fe(OH)_2]$.

Ryder et al. [13] have studied the dissociation of N_2O on Fe- and Co-exchanged ZSM-5 zeolite clusters by use of DFT method. The active center used was taken to be mononuclear $[FeO]^+$ and $[CoO]^+$ and the surrounding portion of the active site was represented by a 24-atom cluster. They reported that Co-ZSM-5 cluster has lower activation energy for N_2O decomposition than that of Fe-ZSM-5 cluster. Yoshizawa et al. [14] researched decomposition of N_2O on neutral $FeAl(OSiH_3)_2(OH)_2$ cluster. They reported that N_2O decomposition occurs easily at a coordinatively unsaturated iron active center supported on zeolite.

The aim of this study is to identify the nature of the active site for nitrous oxide decomposition and the mechanism via which this reaction occurs for Fe- and Co-ZSM-5 catalysts by use of density functional theory calculations. ZSM-5 clusters used are modeled as $[(SiH_3)_4AlO_4M]$ (M = Fe, Co). DFT calculations with B3LYP formalism using 6-31G** as a basis set are utilized to obtain energy profiles and equilibrium geometries (EG). The initial decomposition mechanism of N_2O molecule inside a Fe-ZSM-5 channel cluster is also investigated.

2. Surface models and calculation method

All calculations in this study are based on DFT [15] as implemented in Gaussian 2003 suit of programs [16]. Becke's [17,18] three-parameter hybrid method involving the Lee et al. [19] correlation functional (B3LYP) formalism using 6-31G** as the basis set is utilized. ZSM-5 surface was modeled as $[(SiH_3)_4AlO_4M]$ (M = Fe, Co) clusters as shown in Fig. 1(a) by using the cartesian coordinates reported by Caho et al. [20]. The dangling bonds of the terminal silicon atoms are terminated with H atoms to obtain a neutral cluster. All of the cluster atoms, the reactant and product molecules were kept relaxed. A 2 layer ONIOM method is used to study decomposition of N_2O molecule on Fe-ZSM-5 channel cluster as given in Fig. 1(b). In this method, the surface is modeled by a channel cluster $[Si_{36}O_{80}AlFe]$ where 2 Si, 10 O, 1 Al and 1 Fe atoms (14 atoms in total) are in high layer DFT region and the rest of the cluster (103 atoms in total) are in low layer molecular mechanics (MM) region utilizing universal force field (UFF). All of the channel cluster atoms are kept fixed except Fe atom in high layer for ONIOM method calculations. The basis sets employed in DFT calculations in high layer of ONIOM channel cluster are 6-31G** for Si, Al, O and N atoms and 6-311++G(3df,3pd) for Fe atom. Energy profile and equilibrium geometry calculations were in general performed for determination of approximate activation barriers and relative reaction energies.

The computational strategy employed in this study is as follows: initially, the correct spin multiplicity of the cluster and adsorbing molecule is determined by single point energy (SPE) calculations. SPE's are calculated with different spin multiplicity numbers for each cluster system and the spin multiplicity number which corresponds to the lowest SPE is accepted as the correct spin multiplicity. The cluster and the adsorbing molecule, N_2O, are then fully optimized geometrically by means of EG calculations.

The adsorbing molecule, N_2O, is first located over the active site of the cluster at a selected distance and a coordinate driving calculation is performed by selecting a reaction coordinate in order to obtain the variation of the relative energy with a decreasing reaction coordinate to get an energy profile as a function of the selected reaction coordinate distance. Single point equilibrium geometry calculations were also performed where necessary by locating the adsorbing molecule in the vicinity of the catalytic cluster. Coordinate driving calculations result in an energy profile. The resulting relative energies for the cluster and reactant molecule complex are plotted against

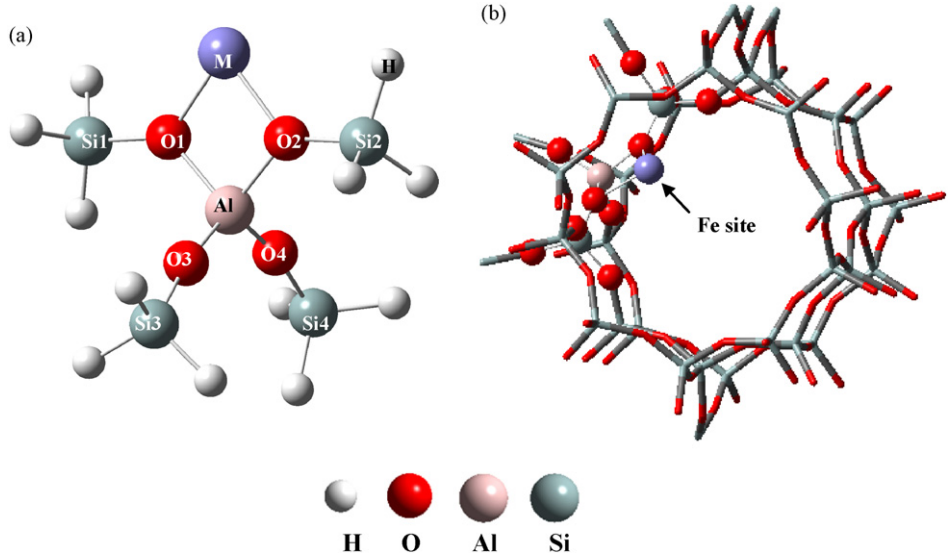

Fig. 1. Optimized geometries (a) M-ZSM-5 cluster (where M = Fe, Co) (b) Fe-ZSM-5 channel cluster: high layer (DFT region) is represented by ball-bond view and low layer (molecular mechanics region) is represented by tube view.

the reaction coordinate. The relative energy is defined as the following formula:

$$\Delta E = E_{\text{System}} - (E_{\text{Cluster}} + E_{\text{Adsorbate}})$$

where E_{System} is the calculated energy of the given geometry containing the cluster and the adsorbing molecule at any distance, E_{Cluster} is the energy of the cluster, and $E_{\text{Adsorbate}}$ is that of the adsorbing molecule, e.g. N_2O in this case. After obtaining the energy profile for the reaction step, the geometry with the minimum energy on the energy profile is re-optimized by means of EG calculations to obtain the final geometry for the particular reaction step. In this re-optimization calculation, the reaction coordinate is not fixed.

3. Results

3.1. Optimization of clusters and N_2O molecule

EGs for Co- and Fe-ZSM-5 clusters were obtained taking the total charge as neutral, and spin multiplicity as 5 and 6 which have the lowest SPE, respectively. EG for Fe-ZSM-5 channel cluster was obtained taking the total charge as neutral and spin multiplicity of high layer DFT region as 3 which has the lowest SPE. Fig. 1 shows optimized geometries of a ZSM-5 cluster with a single M site (M = Fe, Co), a ZSM-5 channel cluster with a single Fe site. Si–O distances for M-ZSM-5 clusters range from 1.63 A to 1.68 A. The corresponding distances reported in the experimental literature are between 1.55 A and 1.65 A [20]. Similarly M–O (M = Fe, Co) distances are calculated as 2.005 A and 2.006 A for Fe-ZSM-5 cluster and 1.975 A and 1.979 A for Co-ZSM-5 cluster. Average Si–H distance is calculated as 1.485 A for these clusters. Fe–O distances of the Fe-ZSM-5 channel cluster are found to be 2.051 A and 2.054 A.

EG for N_2O as a reactant molecule was obtained by taking the total charge to be neutral and with a singlet spin multiplicity. The optimized linear N_2O molecule has a distance of 1.134 A for N–N length and 1.192 A for N–O length. The corresponding values are reported to be 1.128 A and 1.185 A in the experimental literature [21]. Linear (N–N–O) N_2O molecule was used for decomposition reaction calculations on all clusters.

3.2. N_2O decomposition on M-ZSM-5 (M = Fe, Co) clusters

The cycle of decomposition of N_2O on a mononuclear site on M-ZSM-5 has the following sequence of steps [12];

$$\text{M-cluster} + N_2O \rightarrow \text{MO-cluster} - N_2$$
(Step 1) First N_2O Decomposition (1)

$$\text{MO-cluster} - N_2 \rightarrow \text{MO-cluster} + N_2$$
(Step 2) N_2 Desorption (2)

$$\text{MO-cluster} + N_2O \rightarrow MO_2\text{-cluster} - N_2$$
(Step 3) Second N_2O Decomposition (3)

$$MO_2\text{-cluster} - N_2 \rightarrow MO_2\text{-cluster} + N_2$$
(Step 4) N_2 Desorption (4)

$$MO_2\text{-cluster} \rightarrow \text{M-cluster} + O_2$$
(Step 5) O_2 Desorption (5)

3.2.1. N_2O decomposition on Co-ZSM-5 cluster

For decomposition of the first N_2O molecule, step 1, a reaction coordinate is selected as the distance between the

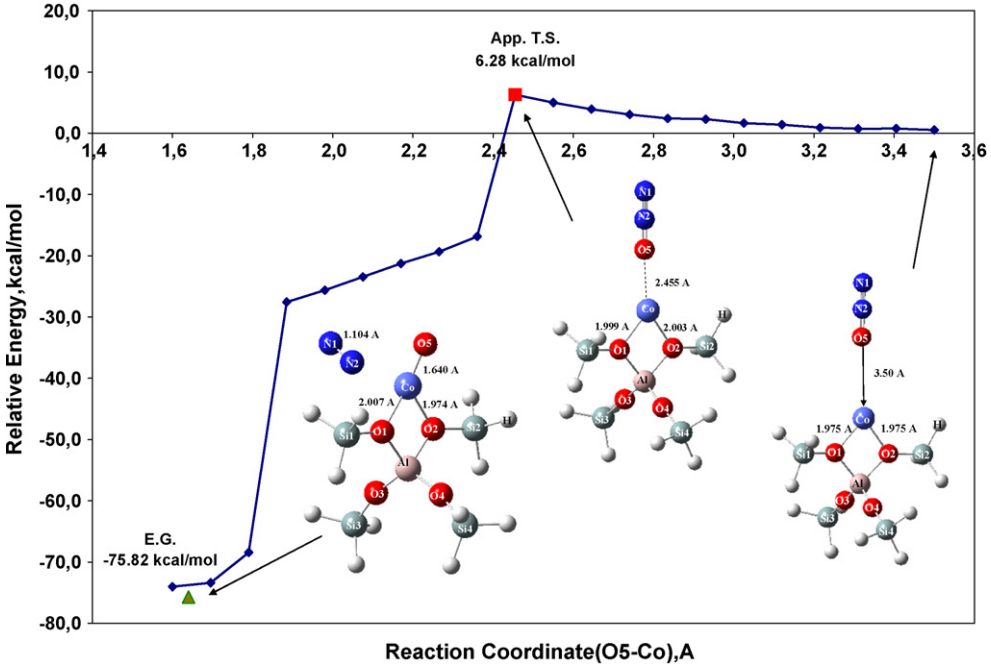

Fig. 2. Relative energy profile for first N_2O decomposition (step 1) on Co-ZSM-5 cluster.

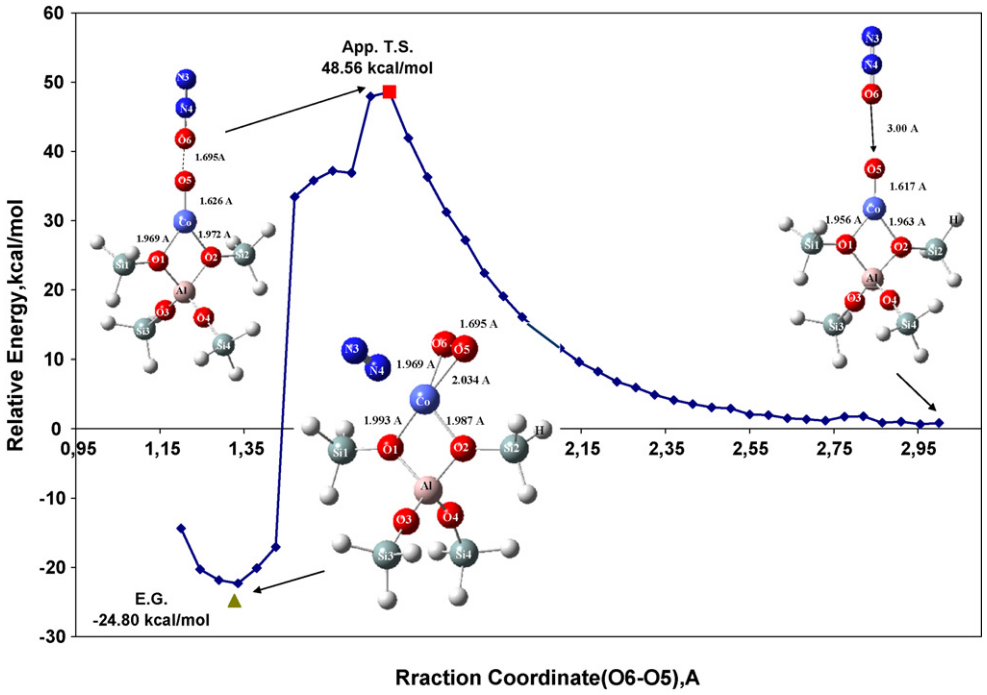

Fig. 3. Relative energy profile for decomposition of second N_2O molecule (step 3) on CoO-ZSM-5 cluster.

oxygen atom (O5) of the N_2O molecule and Co atom of the cluster. This step occurs on Co-ZSM-5 cluster with an exothermic relative energy difference of −75.82 kcal/mol through a small activation barrier. An approximate transition state (ATS) is found to be 6.28 kcal/mol. The relative energy profile obtained is shown in Fig. 2. The second step is desorption of N_2 formed on cluster. For this step, a reaction coordinate is selected as the distance between the nitrogen atom (N2) of the N_2 molecule and Co atom of the cluster. A small barrier of 5.6 kcal/mol is required for desorption of N_2. For decomposition of a second N_2O molecule (third step), a reaction coordinate is selected as the distance between the oxygen atom (O6) of the second N_2O molecule and O atom (O5) adsorbed on the cluster during the first step. This reaction occurs on CoO-ZSM-5 cluster with an exothermic relative energy difference of −24.8 kcal/mol through a higher activation barrier (ATS) of 48.56 kcal/mol as compared to that of the first step. The relative energy profile obtained is shown in Fig. 3. The fourth step is desorption of the second N_2 molecule formed on the cluster. For this reaction, a reaction coordinate is selected as the distance between the nitrogen atom (N4) of the second N_2 molecule and Co atom of the cluster. This step has a very small barrier of 1.61 kcal/mol. And finally the last step is desorption of O_2 formed on the cluster. For this step, a reaction coordinate is selected as the distance between the oxygen atom (O6) of the O_2 molecule and Co atom of the cluster. This step is found to be the rate-limiting step for N_2O decomposition cycle on Co-ZSM-5 cluster since it has relatively a much higher activation barrier (64.95 kcal/mol) when compared with the other reaction steps. Fig. 4 summarizes the energy diagram of reaction steps of N_2O decomposition cycle for Co-ZSM-5 cluster.

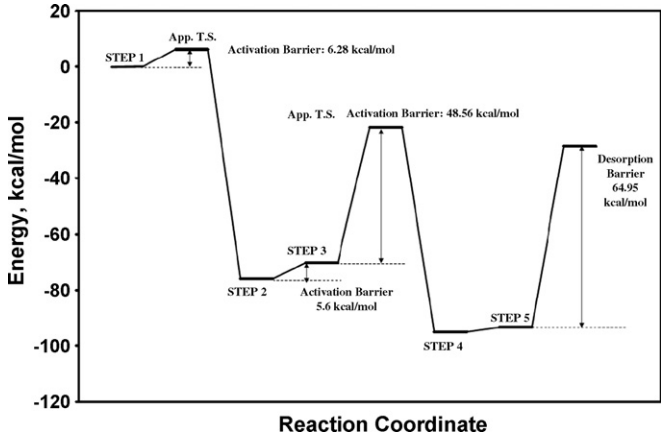

Fig. 4. Energy diagram of N_2O decomposition cycle on Co-ZSM-5 cluster.

3.2.2. N_2O decomposition on Fe-ZSM-5 cluster

For N_2O decomposition on Fe-ZSM-5 cluster, steps 1 and 2 occur simultaneously. Initially a reaction coordinate is selected as the distance between the oxygen atom (O5) of the N_2O molecule and Fe atom of the cluster for this reaction. This step occurs with an exothermic relative energy difference of −75.63 kcal/mol through a small activation barrier (ATS) of 4.41 kcal/mol. The relative energy profile obtained is shown in Fig. 5. For steps 3 and 4, a reaction coordinate is selected as the distance between the oxygen atom (O6) of the second N_2O molecule and O atom (O5) adsorbed on the cluster for this step. This reaction has an exothermic relative energy difference of −19.92 kcal/mol through a higher activation barrier (ATS) of

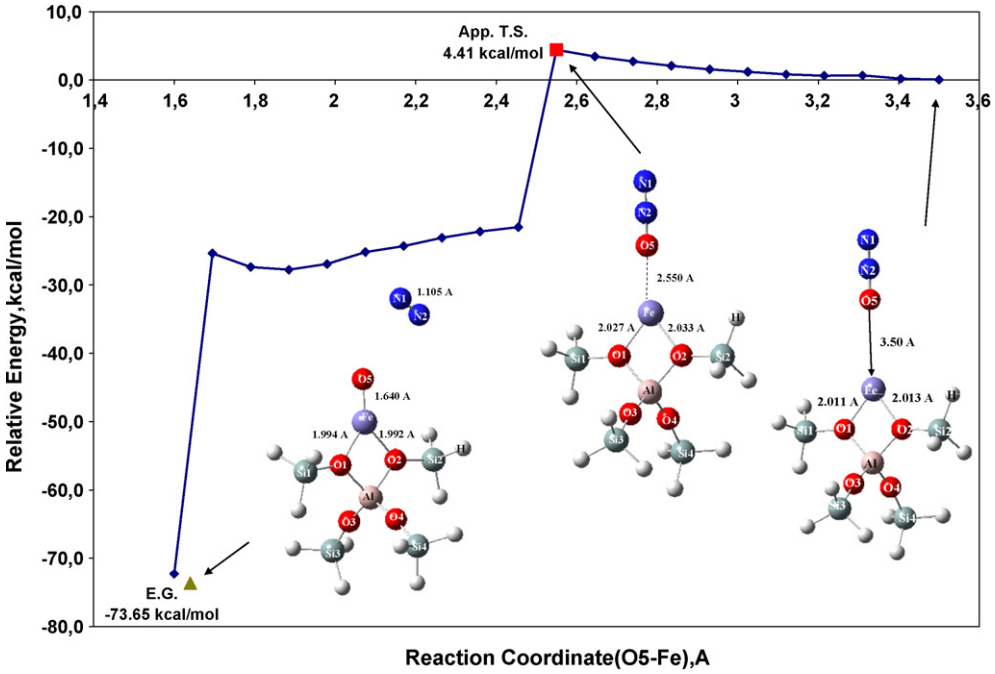

Fig. 5. Relative energy profile for decomposition of first N_2O molecule (steps 1 and 2) on Fe-ZSM-5 cluster.

58.13 kcal/mol when compared with that of the first step for Fe-ZSM-5 cluster. The relative energy profile obtained is shown in Fig. 6. The final step to complete the cycle is desorption of O_2 formed on the cluster. The reaction coordinate for this reaction is selected as the distance between the oxygen atom (O6) of the O_2 molecule and Fe atom of the cluster. This step has a very high barrier (ATS) of 67.3 kcal/mol indicating that it is the rate-limiting step for the N_2O decomposition cycle on Fe-ZSM-5 cluster.

3.3. Decomposition of the first N_2O molecule in Fe-ZSM5 channel cluster

Decomposition of the first N_2O molecule, step 1, occurs inside the channel along a reaction coordinate selected as the distance between the oxygen atom (O) of the N_2O molecule and Fe atom of the channel. The relative energy profile obtained is shown in Fig. 7. This step has an exothermic relative energy difference of −37.58 kcal/mol through a relatively higher

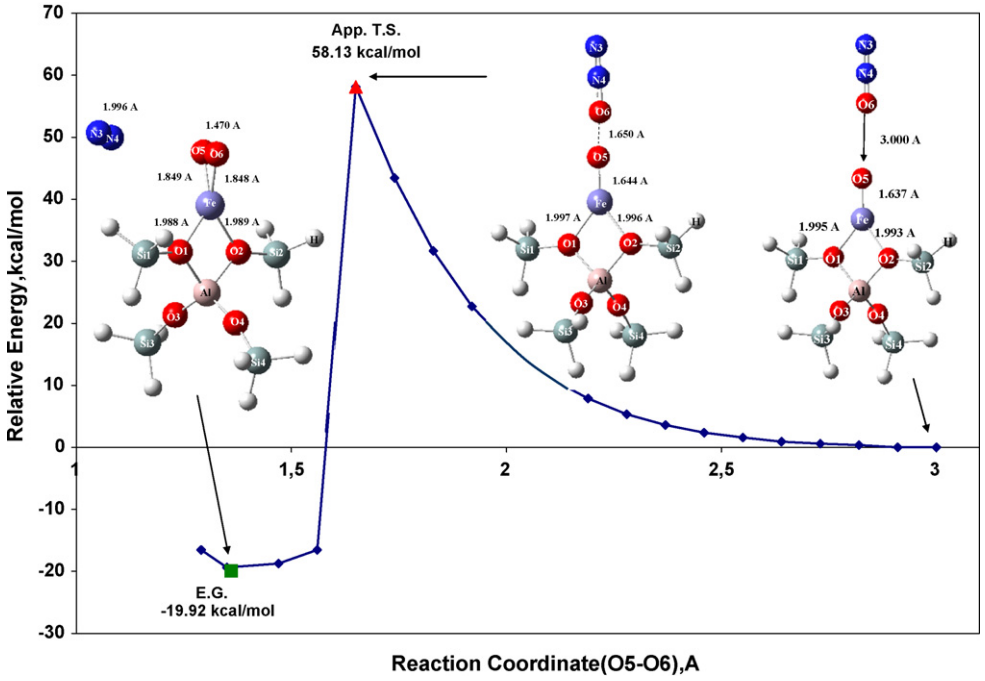

Fig. 6. Relative energy profile for decomposition of second N_2O molecule (steps 3 and 4) on FeO-ZSM-5 cluster.

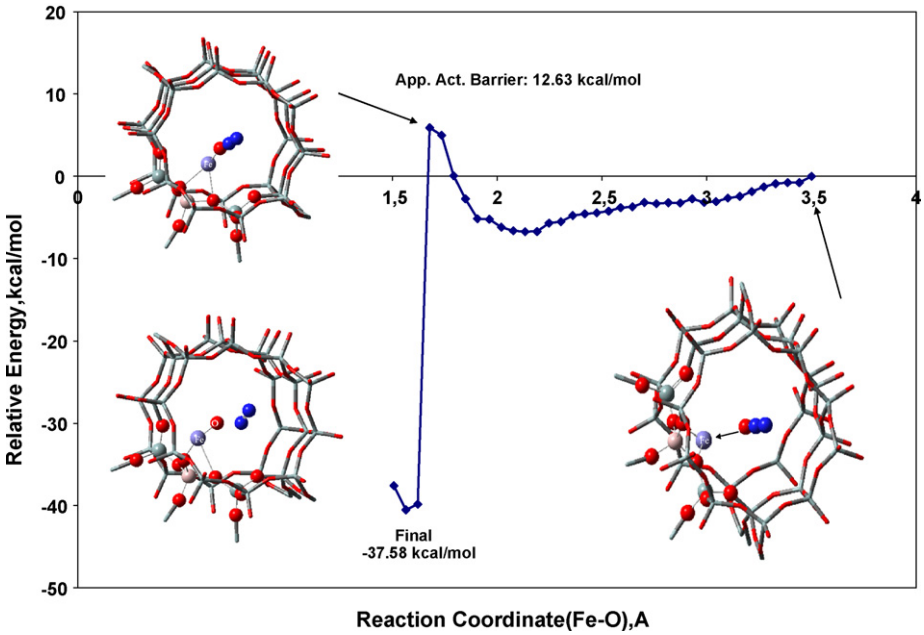

Fig. 7. Relative energy profile for decomposition of first N_2O molecule (step 1) on Fe-ZSM-5 channel cluster. High layer (DFT region) is represented by ball-bond view and low layer (molecular mechanics region) is represented by tube view.

activation barrier (ATS) of 12.63 kcal/mol in comparison to that of the first step for Fe-ZSM-5 cluster (4.41 kcal/mol). Therefore, it is observed that the activation barrier for first N_2O decomposition increases inside the Fe-ZSM-5 channel cluster. This value is now in more reasonable agreement with the reported experimental value of 16.8 kcal/mol for step 1 on Fe-ZSM-5 in the literature [4].

4. Discussion

A comparison of the activation energy barriers of the N_2O decomposition cycle steps on all clusters with available experimental and theoretical literature is given in Table 1. Activation barrier of N_2O decomposition for Fe-ZSM-5 cluster was computed as 4.41 kcal/mol which is close to value of 2.4 kcal/mol reported theoretically by Yoshizawa et al. [14]. Decomposition of a single N_2O molecule may proceed with the vibrational preactivation. It may lead to the significant bending of the adsorbed molecule that results in the modification of the electron energy levels.

Activation barrier for step 3 for Fe-ZSM-5 cluster was calculated to be 58.13 kcal/mol which seems to be higher than the experimental (44.2 kcal/mol) value reported in the literature [4]. There may be several reasons for this discrepancy: (1)

Table 1
The comparison of the activation energy barriers of the N_2O decomposition cycle steps on Fe- and Co-ZSM-5 with literature values

	Activation barrier (kcal/mol)					
	Fe-ZSM-5			Co-ZSM-5		
	This study	Experimental	Other theoretical	This study	Experimental	Other theoretical
Step-1 (First N_2O decomposition)	4.41	16.8[a]	2.4[b]	6.28		
Step-1 (Channel effect for First N_2O decomposition)	12.63					
Step-2 (N_2 desorption)				5.60		
Step-3 (Second N_2O decomposition)	58.13	44.2[a]	37.6[c]	48.56		32.9[c]
Step-4 (N_2 desorption)				1.61		
Step-5 (O_2 desorption)	67.30	45.7[a]	94.9[c]			
			54.2[d]	64.95		85.6[c]
Global (Experimental)		39.4[e]				
		45.4[f]			26.3[e]	
		42.4[g]			26.5[f]	

[a] Wood et al. [4].
[b] Yoshizawa et al. [14].
[c] Ryder et al. [13].
[d] Heyden et al. [12].
[e] Kapteijn et al. [1].
[f] Kapteijn et al. [2].
[g] Wood et al. [22].

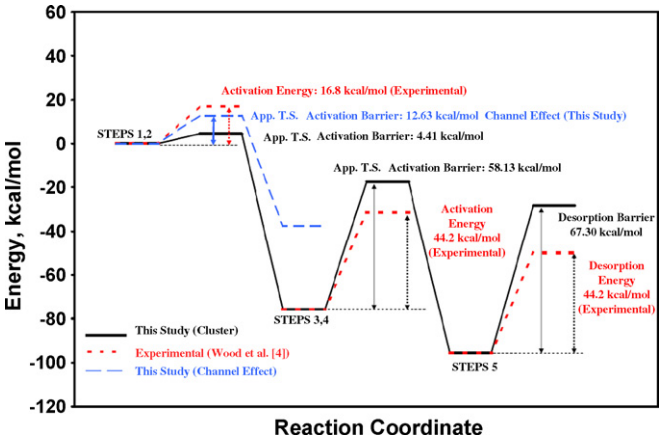

Fig. 8. A summary energy diagram showing a comparison of all the steps of N_2O decomposition cycle on Fe-ZSM-5 cluster with the experimental energy values.

isolated cations, dimers, and oligonuclear clusters may be present in the Fe-ZSM-5 catalyst as opposed to our single site model; (2) our model for this step does not include the effect of the zeolite channel; (3) the actual transition state will be somewhat lower as compared to the approximate barrier peak value reported in this study. The activation barrier calculated for this step is also somewhat higher than the value of 37.6 kcal/mol reported by Ryder et al. [13] in the theoretical literature. The reason for this discrepancy here may be that Ryder et al. obtain a transition state where the bending of the N–N–O bond angle 150.6 as opposed to 180 at the adsorbed state. O_2 desorption step (step 5) is calculated to be 67.30 kcal/mol which is comparable to the reported theoretical values of 54.2 kcal/mol [12] and 94.9 kcal/mol [13]. Although the experimental value of 45.7 kcal/mol reported for step 5 by Wood et al. [4] is lower, the experimental conditions of the catalyst surface can be quite different than the single site model as described above. However, as a summary it can be concluded from our study and from both experimental and theoretical literature that O_2 desorption step is the rate-limiting step for N_2O decomposition on Fe-ZSM-5. The same trend can also be observed in Table 1 for the global activation barriers of 39.4 kcal/mol [1], 45.4 kcal/mol [2] and 42.4 kcal/mol [21] reported in the experimental literature for N_2O decomposition on Fe-ZSM-5. Fig. 8 is a summary energy diagram where these comparisons are made for all the steps of the cycle for N_2O decomposition on Fe-ZSM-5 cluster and Fe-ZSM-5 channel cluster.

Similar discussion would be valid for the entire cycle step results for Co-ZSM-5 cluster given in Table 1, and as a summary, O_2 desorption is the rate-limiting step for Co-ZSM-5 cluster consistent with other theoretical literature [13]. However, the experimentally reported global activation barriers for N_2O decomposition on Co-ZSM-5 are lower (26.3 kcal/mol [1] and 26.5 kcal/mol [2]), and the reasons for this discrepancy may again be due to a very different surface construction for Co atoms, such as dimers, isolated cations or oligonuclear clusters. In general, however, it can also be concluded from Table 1 that for all of the cycle steps calculated and experimental results reported indicate somewhat lower activation barrier values for Co-ZSM-5 in comparison to Fe-ZSM-5 catalysts.

5. Conclusions

The steps for the catalytic cycles of N_2O decomposition on Fe- and Co-ZSM-5 clusters modeled as $[(SiH_3)_4AlO_4M]$ (M = Fe, Co) are calculated using DFT. According to the results obtained, Co-ZSM-5 cluster has a lower activation barrier than that obtained for Fe-ZSM-5 cluster and O_2 desorption step is the rate-limiting step for both clusters. This trend is in agreement with both the experimental and theoretical literature. It is also concluded that the activation barrier for decomposition of first N_2O molecule (12.63 kcal/mol) increases inside the Fe-ZSM-5 channel cluster in reasonable agreement with the reported experimental value of 16.8 kcal/mol for step 1 on Fe-ZSM-5 in the literature [4]. The subject of our next study is to further see the effect of the channel in all of the cycle steps for Fe- and Co-ZSM-5 channel clusters.

Acknowledgments

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