

Article

Identification of Main Active Sites and the Role of NO₂ on NO_x Reduction with CH₄ over In/BEA Catalyst: A Computational Study

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Abstract: The main active sites and the catalytic process in selective catalytic reduction of NO_x by CH₄ (CH₄-SCR) on In/BEA catalyst were investigated by density functional theory (DFT) using a periodic model. The [InO]⁺ and [InOH]²⁺ moieties were constructed in the channel of periodic BEA zeolite representing the Lewis and Brønsted acid sites. The electronic structures [InO]⁺ and [InOH]²⁺ were analyzed, and it was found that the [InO]⁺ group were the main active sites for CH₄ activation and NO/NO₂ adsorption in the CH₄-SCR process. CH₄ molecules could be activated on the O site of the [InO]⁺ group in In/BEA, which was resulted from the strong interactions between the C-p orbital of the CH₄ molecule and the O-p orbital of the [InO]⁺ group. CH₄ activation was the initial step in CH₄-SCR on In/BEA catalyst. NO₂ molecules were essential in the SCR process, and they could be produced by NO reacting with gaseous O₂ or the O atom of the [InO]⁺ group. The presence of NO₂ could facilitate the key intermediate nitromethane (CH₃NO₂) formation and lower the reaction barrier in the SCR process.

Keywords: In/BEA; active sites; CH₄ activation; SCR

1. Introduction

The selective catalytic reduction (SCR) of NO_x by hydrocarbons has attracted much interest in the past years [1,2]. The readily available CH₄ serving as the reducing agent is of great significance from an environmental point of view, because boilers and automobiles fueled by natural gas are important NO_x emission sources [3–5]. A number of zeolite-supported metal oxides (Pt [6], Co [7], Fe [8], Mo [9], In [10–15], etc.) catalysts have been explored, among which the indium-containing zeolites were the prominent one with excellent CH₄-SCR activities. Nevertheless, the main active sites that are responsible for the CH₄-SCR over In-containing zeolites are still up for debate. Maunula et al. [16] proposed that intrazeolitic [InO]⁺ was the active site on In/ZSM-5 catalyst during the process of SCR. However, Lónyiet et al. [12,17] found that [InOH]²⁺ species originated from H₂O dissociation were responsible for initiating the steps of the SCR process. In our previous work, CH₄-SCR activities over In/BEA were measured [18]. The [InO]⁺ group was found to play an important role, but the roles of [InOH]²⁺ have not been identified, because the experimental characterizations usually only provided us with limited information. In comparison, quantum chemistry calculation based on density functional theory (DFT) has been a powerful tool to elucidate details regarding the geometry and electronic structures of the active sites, which are essential to get a deeper understanding of the active sites and the catalytic process.

In this work, the $[\text{InO}]^+$ and $[\text{InOH}]^{2+}$ moieties were constructed to anchor in the channel of the periodic BEA model to represent the Lewis and Brønsted acid sites of In/BEA catalyst, respectively. Moreover, the geometry structures and the electronic structures properties of the two acid sites were extensively investigated, and the main active sites for CH_4 -SCR over In/BEA catalyst were clarified. In addition, the adsorption behaviors of CH_4 , NO, NO_2 , O_2 , and H_2O molecules on the acid sites were carefully studied, because the detailed adsorption characteristics of these reactants and products help to gain insights of the reaction process. The reaction process and the intermediates formed during the process of CH_4 -SCR were fairly complicated. A variety of key surface intermediates such as CH_3 , CH_3NO , CH_3NO_2 species, et al., were reported to be observed on In-containing zeolites [10,14,18]. The formation of these intermediates were all associated with the CH_4 activation process, and it was regarded as the initial step in CH_4 -SCR in spite of the restrictions of C–H bond cleavage [7,10]. Some researchers suggested that the presence of NO and NO_2 was necessary for the CH_4 dissociation process [19,20]. However, this key process has not been fully elucidated for In/BEA catalyst. The key intermediates, CH_3NO and CH_3NO_2 species, which were highly reactive and could quickly convert into N_2 , CO_2 , and H_2O , were considered to originate from the reactions between the activated CH_3 group and NO^+/NO_2 [21–23], but formation processes have not been identified on In/BEA to date. In the present work, the unsolved fundamental questions were carefully explored and the reaction enthalpy was also studied to further illuminate the CH_4 -SCR process over In/BEA catalyst.

2. Results and Discussion

2.1. The Optimized Structures of BEA Zeolite and In/BEA Model

The chemical formula of the BEA unit cell used in this work was $\text{Si}_{64}\text{O}_{128}$ and the calculated dimensions of the unit cell was $a = 12.669 \text{ \AA}$, $b = 12.675 \text{ \AA}$, and $c = 26.781 \text{ \AA}$, which were very close to the experimental values of $a = 12.632 \text{ \AA}$, $b = 12.632 \text{ \AA}$, and $c = 26.186 \text{ \AA}$ [24]. The calculated bond length of CH_4 and NO were 1.097 and 1.164 Å, respectively. The experiment values were reported to be 1.086 Å of gaseous CH_4 molecule [24] and 1.151 Å of NO molecule [25]. The GGA slightly overestimated the bond lengths as expected, but the errors produced are within the acceptable range. Therefore, we assume that the calculation parameters set above were reasonable for further calculations.

The optimized structures of the In/BEA unit cell are shown in Figure 1, and the corresponding bond length and Mulliken charge population are present in Table 1. The bond length of $[\text{InO}]^+$ ($d_{\text{In-O}}$) were slightly elongated after a hydroxyl group was modeled, the value of which increased to 1.954 Å for the B-model, quite longer than that of the L-model (1.872 Å). By contrast, the bond length of In and oxygen atoms coordinated with Al atoms ($d_{\text{In-O1}} = 2.072 \text{ \AA}$; $d_{\text{In-O2}} = 2.106 \text{ \AA}$) of the B-model were shortened compared with that of the L-model ($d_{\text{In-O1}} = 2.249 \text{ \AA}$; $d_{\text{In-O2}} = 2.229 \text{ \AA}$). It can be seen from the results of Mulliken charge populations that the charge of Al, O₁, and O₂ are almost the same between the two models, while the charge between In and O were remarkably different. The q_{In} and q_{O} were 0.978 and −0.608 e for the L-model, and 1.273 and −0.553 e for the B-model, respectively. The total charge of the acid sites of the L-model and B-model were 0.300 and 1.049 e, respectively. This result suggests a quantity of electrons were transferred to the BEA substrate from the $[\text{InO}]^+$ or $[\text{InOH}]^{2+}$ group, and the electrons redistribution would further influence the interactions between the gas molecules and the acid sites.

Table 1. Calculated bond length (d , Å) and Mulliken charge population (q , e) of L-model and B-model.

Models	$d_{\text{Al-O1}}$	$d_{\text{Al-O2}}$	$d_{\text{In-O}}$	$d_{\text{In-O1}}$	$d_{\text{In-O2}}$	$d_{\text{O-H}}$	q_{Al}	q_{In}	q_{O}	q_{H}	q_{O1}	q_{O2}
L-model	1.822	1.827	1.872	2.249	2.229	-	1.445	0.978	−0.608	-	−0.933	−0.933
B-model	1.870	1.872	1.954	2.072	2.106	0.981	1.465	1.273	−0.553	0.329	−0.941	−0.950

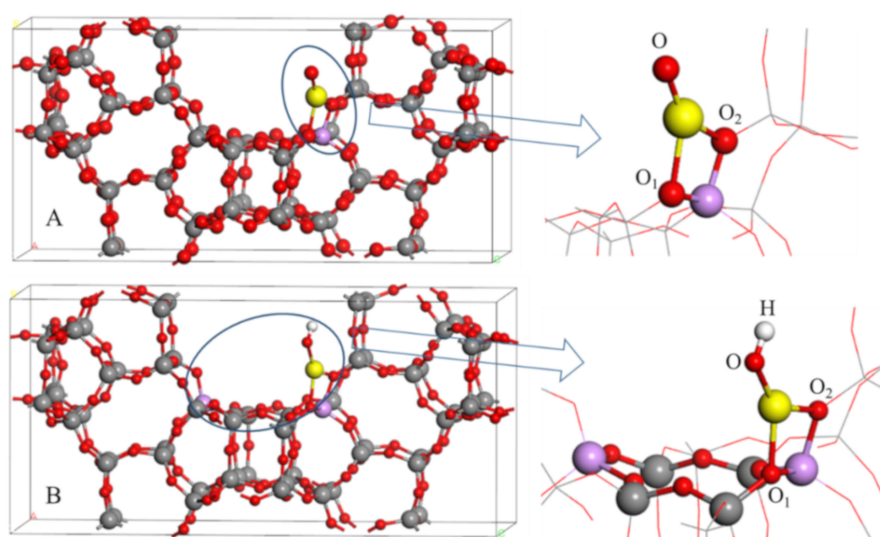


Figure 1. Optimized periodic structure illustrations of In/BEA unit cell. (A) L-model of In/BEA; (B) B-model of In/BEA. Grey, red, purple and yellow balls represent Si, O, Al, and In atoms, respectively, and this color scheme will be used throughout.

2.2. The Electronic Structure Analysis for In/BEA Model

As shown in Figure 2, the energy gap between the Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO) was the largest for the CH_4 molecule, indicating its stronger chemical inertness. Furthermore, based on the frontier molecular orbital theory, it was concluded that the electrons density would be transferred from the HOMO of the CH_4 or NO molecule to the LUMO of the $[\text{InO}]^+$ or $[\text{InOH}]^{2+}$ group due to their lower energy gaps. The energy levels of both the HOMO and LUMO of the L-model were higher than that of the B-model, which suggests that the $[\text{InO}]^+$ group might be more reactive than the $[\text{InOH}]^{2+}$ group for the In/BEA catalyst.

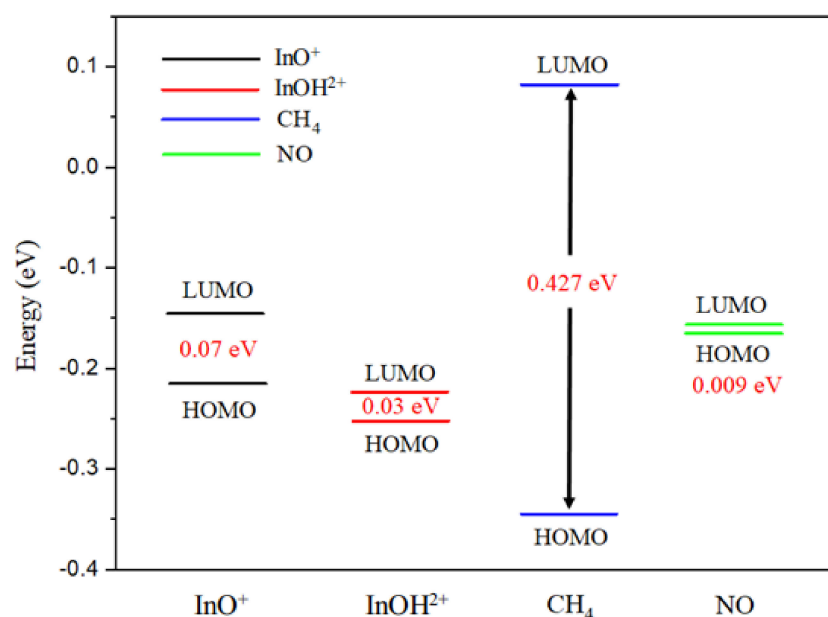


Figure 2. The energy levels of frontier molecular orbitals $[\text{InO}]^+$, $[\text{InOH}]^{2+}$, CH_4 , and NO molecule.

The condensed Fukui function was an effective method to elucidate the ability of a specific atom to gain or lose electrons, and it was defined as [26,27]:

$$f_A^+ = q_A^{n+1} - q_A^n \quad (1)$$

$$f_A^- = q_A^n - q_A^{n-1} \quad (2)$$

The atom with the higher f_A^+ value was prone to accept electrons; otherwise, it was prone to donate electrons. As shown in Table 2, the f_A^+ and f_A^- values of the In atom in the L-model were very close, which indicates that both the electrophilic and nucleophilic adsorptions could possibly occur on the In atom. In the case of O atoms, a much higher value of f_A^- than f_A^+ suggests that it was easier for the O atom of $[\text{InO}]^+$ to donate electrons. As for the B-model, the f_A^- values of both the In and O atoms are negligible when compared with f_A^+ , but f_A^+ values were smaller than that of the L-model. It indicates that the $[\text{InOH}]^{2+}$ group prefers to accept electrons, and its lower f_A^+ and f_A^- values would lead to lower reactivity compared with the $[\text{InO}]^+$ group. In addition, both the f_A^+ and f_A^- values for H atom were much smaller than that of the In and the O atom, which suggests that it would not be easy for a CH_4 or NO molecule to react with an H atom. Therefore, the further adsorption characteristics of the small gases were only considered on In and O atoms.

Table 2. Values of condensed Fukui function for In, O, and H atom in L-model and B-model based on Hirshfeld charge population.

Models	In		O		H	
	f_A^+	f_A^-	f_A^+	f_A^-	f_A^+	f_A^-
L-model	0.425	0.411	0.155	0.310	-	-
B-model	0.391	0.003	0.120	0.001	0.059	0.003

The partial (PDOS) of the In and O atom of the L-model and B-model were calculated to elucidate electronic structure and bonding mechanism. The results are presented in Figure 3. The orbital energy levels were quite different between the $[\text{InO}]^+$ and $[\text{InOH}]^{2+}$ group, but the density of states (DOS) of both In and O atom were mainly donated by the p-orbital. The hybridizations between O-p and In-s, p at around -2.5 , 0 , and 2.0 eV for the L-model were clearly observed, so were the O-p and In-s at around -7.5 and 3.0 eV for the B-model. This suggests that there were strong covalent interactions between the In and O atom for both the $[\text{InO}]^+$ and $[\text{InOH}]^{2+}$ groups, in other words, the active site models used in our work were stable and could reasonably represent the active sites. The Fermi level was set to zero and is represented with a dotted line in this work. It can be clearly seen that the PDOS intensities at the Fermi level of $[\text{InO}]^+$ was greatly stronger than that of $[\text{InOH}]^{2+}$, which indicates that the In and O atoms are more active in the L-model compared with that in the B-model. This result corresponds well to the Fukui function calculations that the $[\text{InO}]^+$ group exhibited greater electrophilic and nucleophilic abilities than $[\text{InOH}]^{2+}$ group.

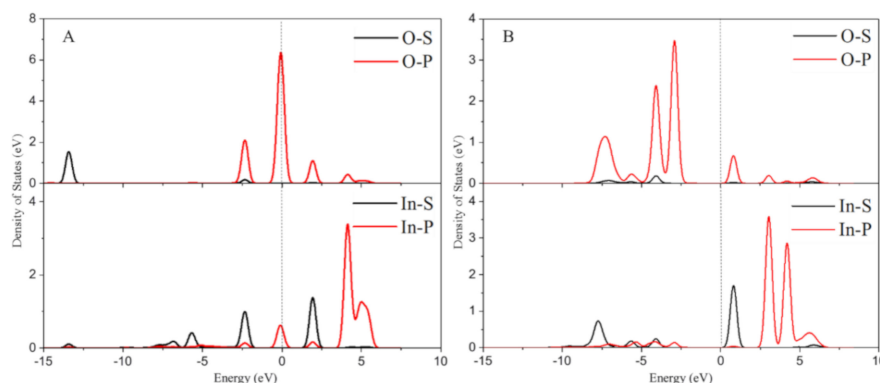


Figure 3. The partial density of states (PDOS) of the In and O atom of (A) $[\text{InO}]^+$ and (B) $[\text{InOH}]^{2+}$ group.

2.3. CH₄ Adsorption Characteristics

The adsorption characteristics of CH₄ on the In and O site of the L-model and B-model were carefully explored in this section, and the most favorable adsorption configurations are shown in Figure 4. All the four adsorption processes were found to be exothermic, but CH₄ adsorption characteristics varied greatly at different sites. It is interesting to note that the C–H bond was easily cleaved without an energy barrier when it was initially absorbed on the O site of the L-model (Figure 4A2). One of the H atoms of CH₄ moved to the O site, and a C–O bond formed simultaneously. This result was similar to the findings of Sinev et al. [28] that an H atom abstraction was energetically favorable with an O atom. It means that the CH₄ activation could occur on the O site of [InO]⁺ group in In/BEA catalyst without the assistance of an NO or NO₂ molecule. By contrast, the [InOH]²⁺ group had very weak affinity with the CH₄ molecule, whether on the In site or the O site. CH₄ would move away from the active site after geometry optimization with the $d_{\text{In-C}}$ and $d_{\text{C-O}}$ equaling 2.469 and 4.358 Å, respectively (Figure 4B1,B2). In addition, the interactions between CH₄ and the In site of the [InO]⁺ group was also very weak, and the corresponding In–C bond length was 3.360 Å (Figure 4A1). The binding energies were −0.15, −2.98, −0.48, and −0.10 eV for configuration in Figure 4A1, the configuration in Figure 4A2, the configuration in Figure 4B1, and the configuration in Figure 4B2, respectively. The interactions between the CH₄ molecule and substrates were much weaker when it was adsorbed on the In site of the L-model and the O site of the B-model, and it would move away after geometry optimization (Figure 4A1,B2).

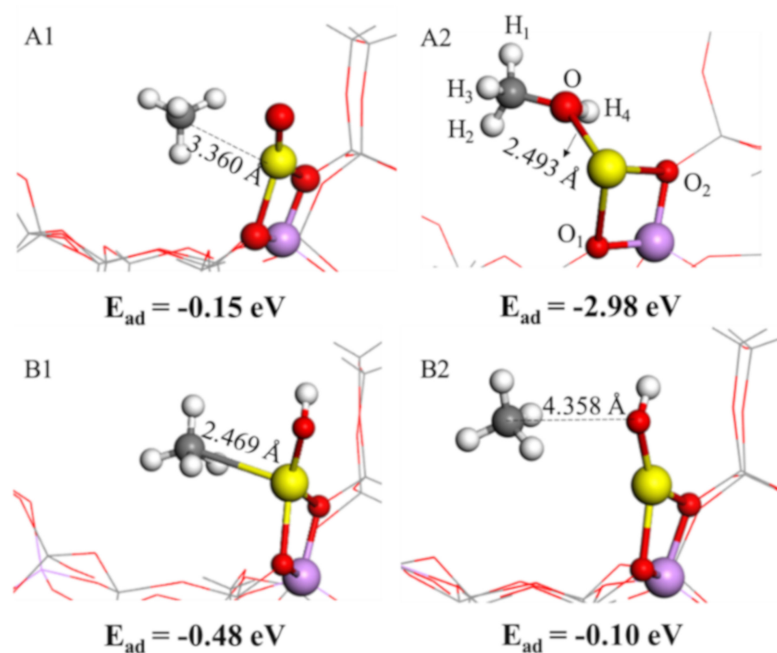


Figure 4. Optimized structures of CH₄ adsorption on (A1) In site of L-model; (A2) O site of L-model; (B1) In site of B-model; (B2) O site of B-model.

The bond length changes of the active sites are compiled in Table 3. The bond length of In–O (1.872; 1.873 Å), In–O₁ (2.249; 2.247 Å), In–O₂ (2.229; 2.241 Å), and Al–O₁ (1.822; 1.824 Å), and Al–O₂ (1.827; 1.824 Å) almost remained unchanged when the CH₄ was adsorbed on the In site of the L-model, indicating weak interactions between the CH₄ molecule and In atom. In the case of CH₄ bonding with the O site of the L-model, the bond length of In–O (1.872; 2.493 Å), In–O₁ (2.249; 2.596 Å), and In–O₂ (2.229; 3.246 Å) greatly increased, by contrast, the bond length of Al–O₁ (1.822; 1.794 Å) and Al–O₂ (1.827; 1.786 Å) slightly decreased. Additionally, it is noted that the net charge of CH₄ was positive except for the O site of the B-model, which indicates the electrons were transferred from the CH₄ molecule to the catalyst as CH₄ was adsorbed, and the values are 0.034, 0.305, 0.052, and −0.002 e

for the configuration in Figure 4A1, the configuration in Figure 4A2, the configuration in Figure 4A3, and the configuration in Figure 4A4, respectively. The net charge value was the highest when CH₄ was adsorbed on the O site of the L-model, in accordance with its lowest adsorption energy.

Table 3. Bond length (d , Å), Mulliken charge population (q , e), and adsorption energy (E_{ads} , eV) of CH₄ adsorption on In/BEA.

Bonds	L-model		B-model	
	In site	O site	In site	O site
In–O	1.873	2.493	1.986	1.954
In–O ₁	2.247	2.596	2.118	2.072
In–O ₂	2.241	3.246	2.124	2.106
Al–O ₁	1.824	1.794	1.854	1.870
Al–O ₂	1.824	1.786	1.860	1.873
O–H	-	0.975	0.980	0.981
C–O	-	1.445	-	4.358
C–H ₁	1.098	1.096	1.096	1.097
C–H ₂	1.098	1.098	1.105	1.097
C–H ₃	1.097	1.100	1.109	1.098
C–H ₄	1.099	-	1.102	1.098
q_{CH_4}	0.034	0.305	0.052	−0.002
E_{ads}	−0.15	−2.98	−0.48	−0.10

Furthermore, the projected density of states (PDOS) of C-p and In-s, p was calculated to clarify the bonding mechanism of CH₄ adsorption and dissociation, the results of which are shown in Figure 5. The PDOS of C-p scarcely overlaps with the orbitals of the In atom (In-s, p), thus a new chemical bond would not be easily formed. However, the PDOS of C-p and O-p are strongly overlapped at around Fermi level, which indicates that the new formed C–O bond was contributed by the interactions between the C-p orbitals of CH₄ and the O-p orbitals of the [InO]⁺ group in this configuration. Moreover, a mass of electron densities was transferred from C-p orbitals of CH₄ to O-p after adsorption, and the C-p moved to lower energy levels accompanied with its PDOS split. Therefore, CH₄ activation resulted from the strong interactions between C-p and O-p orbitals when it was adsorbed on the O site of the L-model. In the case of CH₄ interacting with the B-model, the electron densities of C-p of CH₄ were redistributed owing to the weak interactions between C-p and In-s, and the energy level of C-p also become lower after adsorption. There were only tiny overlapped DOS bands when CH₄ molecule was adsorbed on the B-model, which indicates that CH₄ could not be easily activated on Brønsted acid sites due to their relatively weaker interactions.

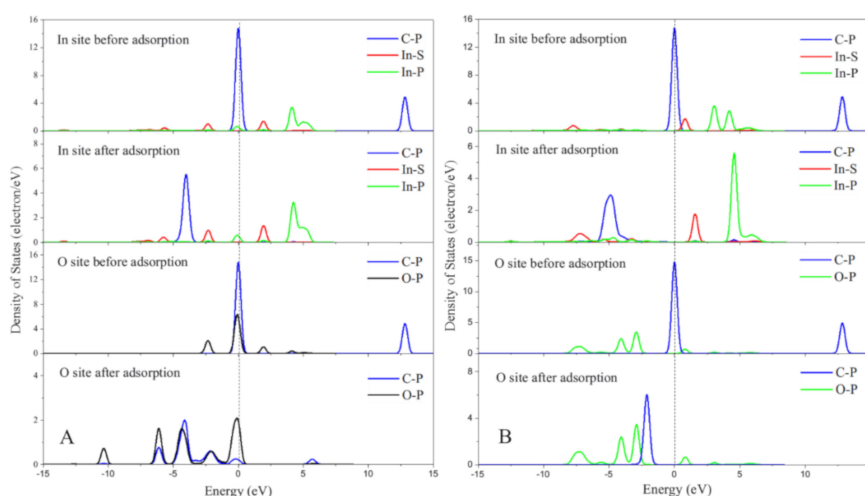


Figure 5. The PDOS of CH₄ before and after adsorption on In and O site of L-model (A) and B-model (B).

2.4. NO and NO₂ Adsorption Characteristics

It was reported that NO₂ was more important than NO in the CH₄-SCR process, because NO₃[−] species would be easily produced when an NO₂ molecule was coordinated with the [InO]⁺ group. Some researchers proposed that NO₃[−] could facilitate CH₄ activation and active intermediates formation [12,29]. However, it was found that CH₄ molecules can be easily activated on the O site of the InO⁺ group of the In/BEA catalyst in Section 2.2. As key reactants, the adsorption characteristics of NO and NO₂ on the L-model and B-model of In/BEA required further explorations and comparisons.

The adsorption configurations of NO and NO₂ coordinated with the In or O sites of the L-model and B-model are displayed in Figure 6. Interestingly, NO was inclined to coordinate with the O atom rather than the In atom of [InO]⁺. However, NO₂ was inclined to coordinate with the In atom of [InOH]²⁺. Generally, the NO molecule has stronger affinities with the L-model than the B-model, the binding energy of which was −1.84 and −1.07 eV, respectively. This result is in agreement with the Fukui function results that the activity of the [InO]⁺ group is higher than the [InOH]²⁺ group. The adsorbed NO₂[•] species was produced simultaneously when NO interacts with the L-model regardless of the adsorption sites (Figure 6A1,B1), and a similar phenomenon was observed by Huang et al. [30]. In the case of NO₂ adsorption, NO₂ molecule also had stronger interactions with the L-model than the B-model (−1.93 eV vs. −0.56 and −0.42 eV). In addition, NO₃[−] species could be produced as the NO₂ molecule interacts with the L-model, and the adsorption energy was similar to that of the NO adsorbed on the L-model. Therefore, it is concluded that [InO]⁺ groups serve as major active sites for CH₄ activation, NO and NO₂ adsorption in the CH₄-SCR process.

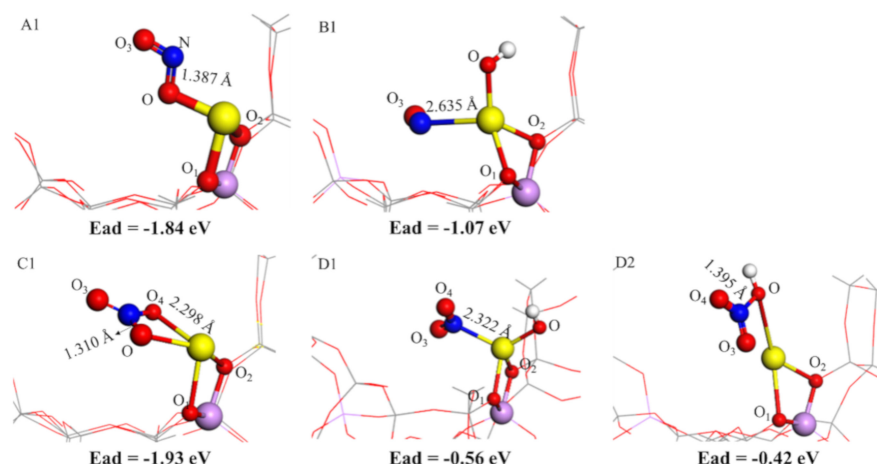


Figure 6. Structures of NO adsorption on Lewis and Brønsted acid sites of In/BEA: NO on In and O site of L-model (A1); NO on In and O site of B-model (B1); NO₂ on In and O site of L-model (C1); NO₂ on In site of B-model (D1); NO₂ on O site of B-model (D2).

The bond length and Mulliken charge population of NO and NO₂ adsorption are compiled in Table 4. Compared with other adsorption configurations, the In–O bond was greatly elongated as NO was adsorbed on the L-model (1.872; 2.169 Å) and NO₂ was adsorbed on the O site of the B-model (1.872; 2.183 Å) due to the much stronger interactions. Meanwhile, the bond length of the NO molecule also became larger (1.164; 1.197 and 1.171 Å), indicating an active status for the adsorbed NO. The negative net charge of NO and NO₂ adsorbed on the L-model suggests that NO and NO₂ molecules have accepted electrons from the catalyst, and the values were −0.267 and −0.248 e, respectively (Figure 6A1,C1). As for NO and NO₂ adsorbed on the B-model, the positive net charge suggests that the electrons were transferred from NO and NO₂ to the catalyst. The net charge values were 0.120, 0.122, and 0.037 e for the configurations in Figure 6B1,D1,D2, respectively. The higher electrons transfer amounts for NO and NO₂ on the L-model corresponded to their lower binding energies.

Table 4. Bond length (d , Å), Mulliken charge population (q , e) and adsorption energy (E_{ads} , eV) of NO and NO₂ adsorption on In/BEA.

	L-Model		B-Model		
	NO-In and O site	NO ₂ -In and O site	NO-In and O site	NO ₂ -In site	NO ₂ -O site
d_{In-O}	2.169	2.330	1.995	1.990	2.183
d_{In-O1}	2.332	2.324	2.158	2.159	2.375
d_{In-O2}	2.345	2.298	2.204	2.187	2.453
d_{Al-O1}	1.813	1.818	1.840	1.833	1.811
d_{Al-O2}	1.814	1.817	1.832	1.846	1.811
d_{In-N}	-	-	2.635	2.322	-
d_{N-O}	1.387	1.310	-	-	1.395
d_{N-O3}	1.197	1.210	1.171	1.224	1.209
d_{N-O4}	-	1.304	-	1.220	1.234
d_{O-H}	-	-	-	0.976	1.008
q_{In}	0.859	0.917	1.072	1.132	0.816
q_O	-0.422	-0.407	-0.609	-0.613	-0.333
$q_{NO/NO2}$	-0.267	-0.248	0.120	0.122	0.037
E_{ads}	-1.84	-1.93	-1.07	-0.56	-0.42

2.5. O₂, H₂O and CO₂ Adsorption Characteristics

The detailed adsorption characteristics of O₂, H₂O, and CO₂ were also investigated, because O₂ was the reactant and H₂O and CO₂ were products in the flue gas. Based on the above results, it was concluded that the [InO]⁺ group rather than the [InOH]²⁺ group plays the dominant role in CH₄ activation and the NO/NO₂ adsorption process. Therefore, only the adsorption characteristics on the L-model were calculated and discussed. The optimized structures and their corresponding adsorption energies are displayed in Figure 7, and the bond lengths and Mulliken charge population are shown in Table 5. O₂ and CO₂ molecules were more likely to coordinate with the O site, while H₂O molecule prefers the In site (Figure 7A2,B2,C1), the corresponding energy was -0.49, -0.86, and -0.29 eV, respectively. Therefore, the O₂ adsorption process would be less favorable on the active sites. Therefore, it is deduced that activation of CH₄ on the O site of [InO]⁺ would be the initial steps on the In/BEA catalyst. Interestingly, the CO₂ molecule has a strong affinity with the O site of the [InO]⁺ group, with a carbonate formed, yielding the adsorption energy of -0.86 eV (Figure 7B2). Meanwhile, there is a mass of electrons transferred from the CO₂ molecule to the catalyst, the quantity of which is equal to 0.215 e. The adsorption configurations of H₂O are shown in Figure 7C1,C2. It is noted that the H₂O molecule interacted weakly with the [InO]⁺ group and the adsorption energy on the In site and O site were -0.29 and -0.05 eV, respectively. The d_{In-O} bond length for H₂O interacting with the In and O site were 2.430 and 3.430 Å, respectively, and there was only a small quantity of electrons transferred between the H₂O molecule and the catalyst. This result suggests that the In/BEA catalyst has excellent water vapor durability in the process of CH₄-SCR.

The PDOS of O₂, CO₂, and H₂O before and after adsorption were also compared to obtain insights into the bonding mechanism (Figure 8). The distinct bands at the Fermi level could be observed for the free O₂, CO₂ and H₂O molecules, and they overlapped with the In-p and O-p orbitals of the [InO]⁺ group. It is noted that the shape and intensity of free O₂ were greatly changed within the range of -8 to 2 eV after adsorption. The electron density depletion indicates that the O₂ molecule donated electrons to the catalyst. As for the CO₂ adsorption on the In site, the PDOS bands shifted to a lower energy level, but the intensity did not change distinctly. This indicates that the adsorption caused CO₂ electron redistribution while only a few electrons were transferred to the catalyst. By contrast, the electron density depletion was obvious as CO₂ was adsorbed on the O site but there were almost no PDOS band shifts. The situation was similar for H₂O adsorption on the In and O sites.

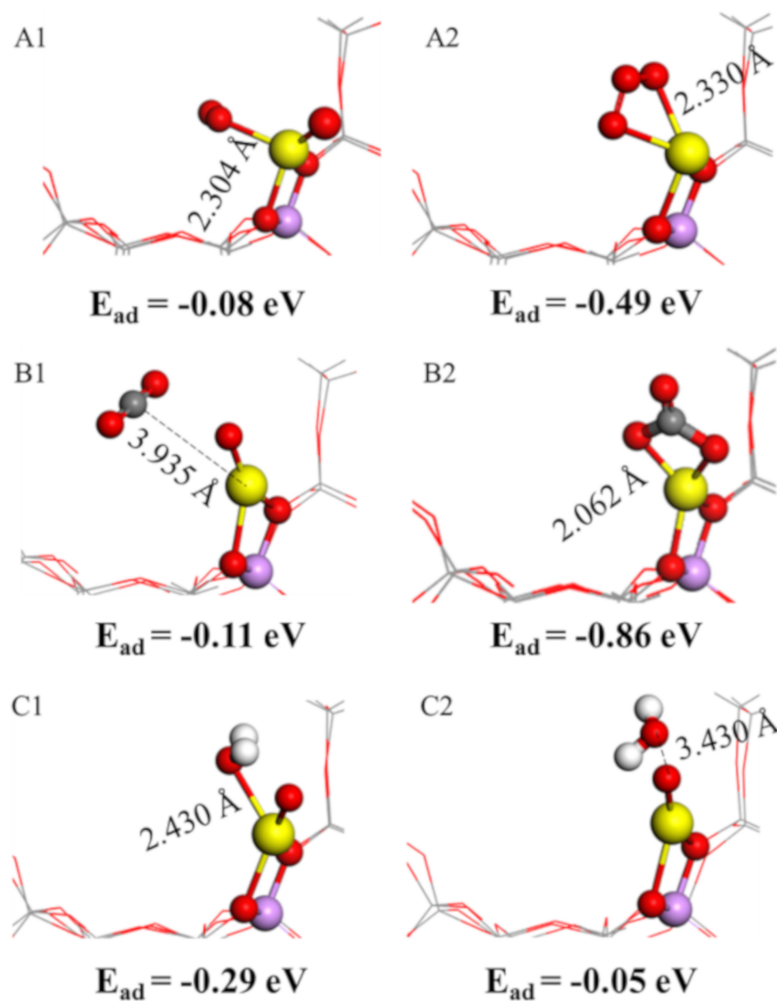


Figure 7. Optimized structures of O_2 , CO_2 , and H_2O molecules adsorbed on L-model of In/BEA: O_2 molecule on In site (**A1**); O_2 molecule on O site (**A2**); CO_2 molecule on In site (**B1**); CO_2 molecule on O site (**B2**); H_2O on In site (**C1**); H_2O on O site (**C2**).

Table 5. Bond length (d , Å), Mulliken charge population (q , e) and adsorption energy (E_{ads} , eV) of O_2 , H_2O , and CO_2 adsorption on L-model.

	O_2		CO_2		H_2O	
	In site	O site	In site	O site	In site	O site
d_{In-O}	1.933	2.330	1.874	2.058	1.897	1.894
d_{In-O1}	2.235	2.336	2.255	2.178	2.279	2.335
d_{In-O2}	2.234	2.368	2.200	2.166	2.244	2.196
d_{Al-O1}	1.828	1.813	1.822	1.840	1.817	1.801
d_{Al-O2}	1.824	1.811	1.835	1.845	1.823	1.836
$d_{O_2/H_2O/CO_2}$	1.269	1.346	1.174, 1.175	1.380, 1.209	0.995, 0.980	0.964, 0.967
$q_{O_2/H_2O/CO_2}$	0.092	0.094	0.077	0.215	0.027	0.016
E_{ads}	-0.08	-0.49	-0.11	-0.86	-0.29	-0.05

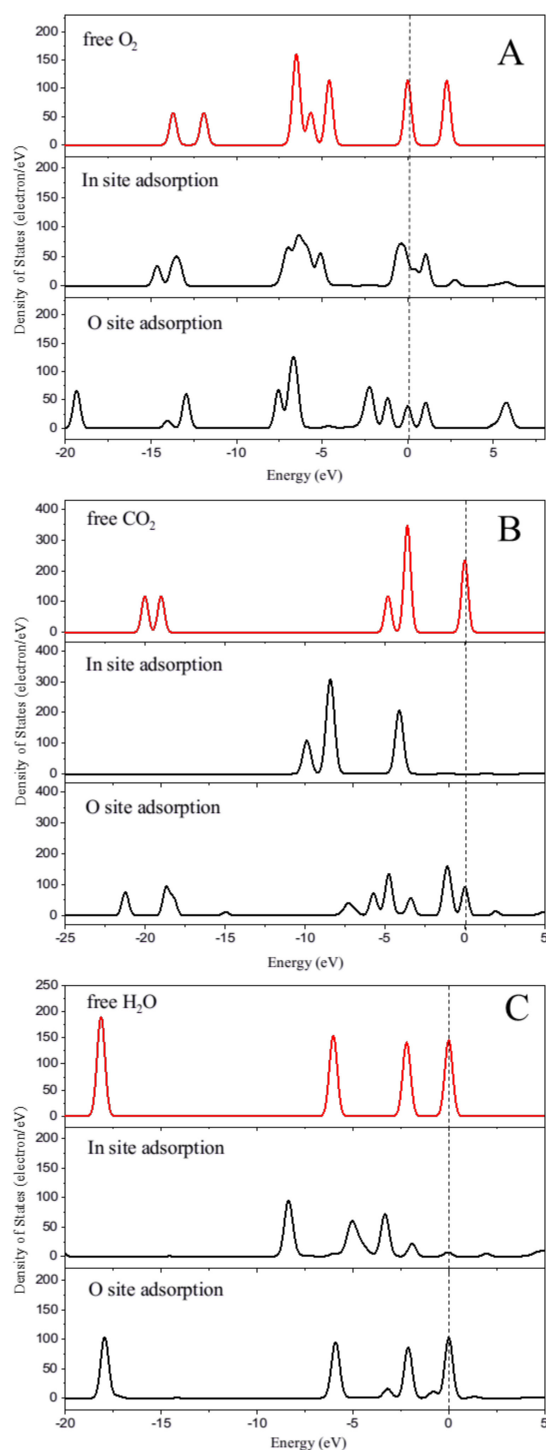


Figure 8. The PDOS before and after O₂ (A), CO₂ (B), and H₂O (C) adsorption on In and O site of L-model.

2.6. Nitromethanes' Formation and Reaction Enthalpy

It was reported by many researchers that nitromethanes (CH₃NO and CH₃NO₂) are the key intermediates involved in N₂ formation [22,31–33]. As shown in Section 2.3, CH₃ formation on the O site of the [InO]⁺ species was the initial step. Therefore, the formation process of nitromethanes was considered as the CH₃ group further reacting with gaseous NO or NO₂ molecules. It is interesting to find that the adsorption behaviors of NO and NO₂ on the CH₃ group were entirely different. Figure 9 shows that the NO molecule would move away from the CH₃ group whether the NO

molecule was placed on the C site or the O site at the beginning, with the N–C bond length equaling 3.707 Å. This indicates that there was a strong repulsion between the NO molecule and the CH₃ group, and CH₃NO intermediates were not easily produced on the In/BEA catalyst. In comparison, when the NO₂ molecule was placed near the CH₃ group, the C–O bond broke immediately and CH₃NO₂ was formed simultaneously. Subsequently, CH₃NO₂ rotated to a tilted position with the N–C bond and C–O length equaling to 3.707 and 1.498 Å, respectively. As a result, it was concluded that CH₃NO₂ rather than CH₃NO species could be formed on the catalyst, and this key intermediate would facilitate the following catalytic process. This result also indicates that NO₂ plays a key role in the CH₄-SCR process for the In/BEA catalyst, in accordance with previous research [13,34].

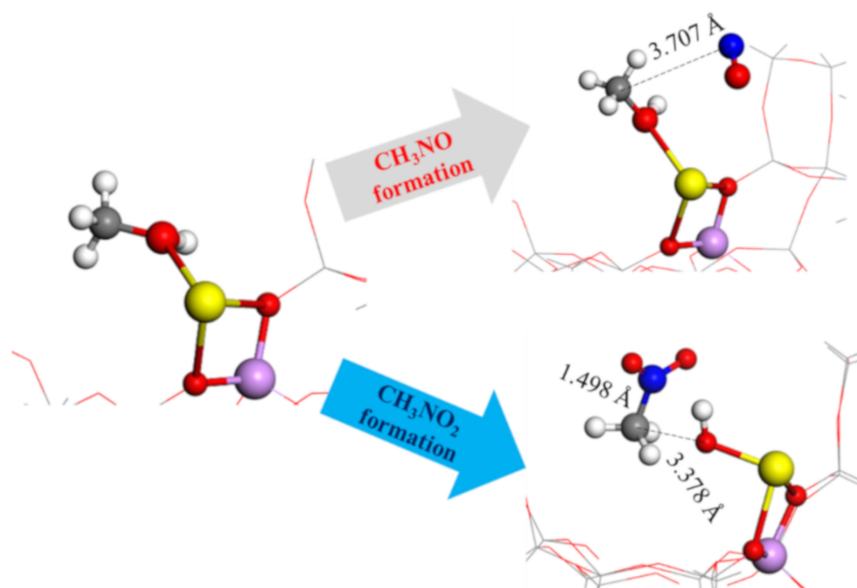


Figure 9. The scheme of CH₃NO and CH₃NO₂ formation pathway and the optimized geometry structure of CH₃NO₂.

There are mainly two reaction pathways in the CH₄-SCR process: (1) CH₄+O₂+2NO→CO₂+2H₂O+N₂; (2) CH₄+2NO₂→CO₂+2H₂O+N₂ [34,35]. In this regard, co-adsorption characteristics of multiple species of the reactants (IS1-NO, CH₄, O₂; IS2-2NO₂, CH₄) and products (CO₂, N₂, H₂O) were studied. As shown in Figure 10, it is noted that a NO molecule was inclined to coordinate with an O₂ molecule in IS1, and an NO₂^{*} was formed. The formed NO₂^{*} was necessary for the CH₃NO₂ formation. This result is in line with the findings in Section 2.4 and it also suggests that IS2 might be the subsequent status of IS1 in the SCR process, because CH₃NO could not be easily produced. Additionally, the two reaction routes occurred using the same catalyst. Thus, it is assumed that the status of transition state was the same for the two reaction pathways. It can be seen that both reaction pathway 1 and 2 were exothermic but the energy of IS1 was 3.03 eV lower than that of IS2, suggesting that the total energy barrier E_{a2} of reaction 2 should be smaller than E_{a1}. Therefore, it is concluded that NO₂ molecules were essential in the SCR process, and they could be produced by NO reacting with gaseous O₂ or the O atom of the [InO]⁺ group. In this case, on one hand, the formation of key intermediate CH₃NO₂ could be facilitated, on the other hand, the reaction rates would be much higher due to the lower reaction barrier in the presence of NO₂.

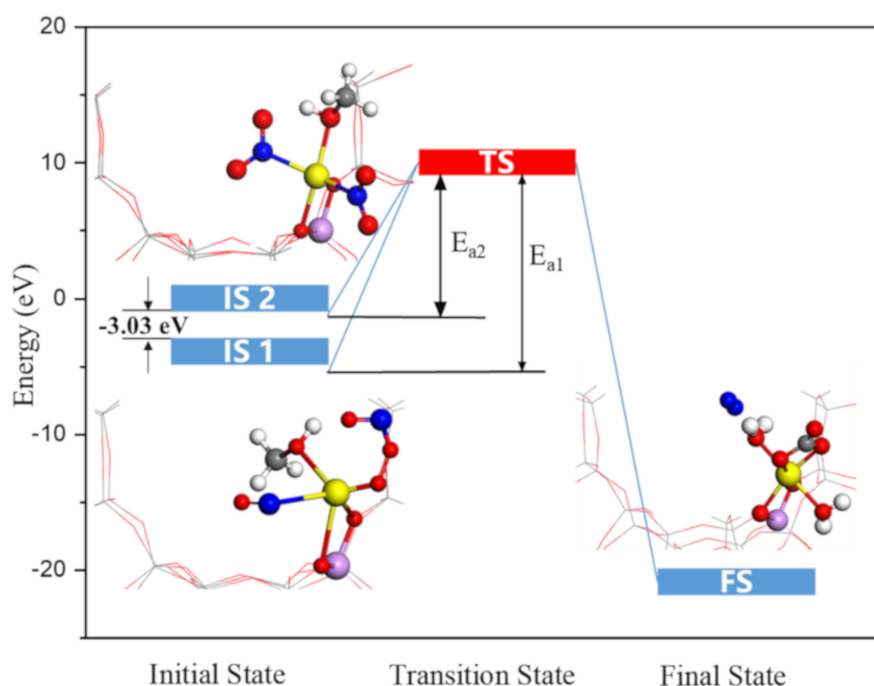


Figure 10. Energy profile of the reactants (NO or NO₂), undetermined transitional state, and the products (N₂, H₂O and H₂O).

3. Computational Methods

There were several DFT calculations concerning zeolites conducted based on a simplified cluster model in order to save calculation time [8,9,36]; the accuracy of the computational results was therefore usually less accurate. In this regard, all DFT calculations were performed on a periodic boundary BEA zeolite model for the first time to achieve results with higher reliabilities (Figure 11).

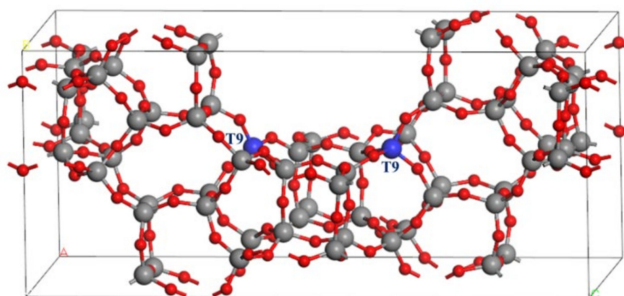


Figure 11. Optimized periodic structure illustrations of BEA zeolite labeled with blue T9 sites.

All calculations were performed based on DMol³ implemented in Materials Studio 2017R2 [37], in which the Perdew–Burke–Ernzerhoff (PBE) [38] functional in the generalized gradient approximation (GGA) [39] was used to calculate the exchange–correlation potential. The following three convergence criteria were used for the geometry optimization and energy calculation: SCF tolerance (1.0×10^{-6}), the atomic forces (2.0×10^{-3} Hartree/Å), maximum displacement (5.0×10^{-3} Å), and total energy variation (1.0×10^{-5} Hartree). The molecular orbitals were expanded using a double numerical basis set with polarization functions (DNP), which is equivalent to 6-31 G^{**}. The range of integration for charge density and functional was confined within a global orbital cutoff value of 3.5 Å. The core electrons were treated using the DFT semicore pseudo potentials (DSPP) method. A $(3 \times 3 \times 3)$ Monkhorst–Pack k-point grid was used for In/BEA unit cell optimization. All the atoms in the model were allowed to be relaxed during the calculation.

The $[\text{InO}]^+$ and $[\text{InOH}]^{2+}$ moiety introduced one and two positive charges, respectively, which were compensated by substituting one Si^{4+} with Al^{3+} to keep the charge balance. In the unit cell of BEA, there are nine distinct Si sites denoted as T sites for Al cation substitution, among which T1 and T9 sites substitution were suggested to be relatively stable [36]. Based on the parameters set in our calculations, we found that the structure of Al^{3+} substituting on the T9 site is more energetically favorable, and the energy is 0.08 eV lower than that on T1 site. Similar substitution methods were suggested by Yan [9] and Zhou [19]. For the sake of simplicity, the formed $[\text{InO}]^+/\text{BEA}$ model was denoted as the L-model, and the $[\text{InOH}]^{2+}/\text{BEA}$ model was denoted as the B-model. The $[\text{InO}]^+$ species was placed in the five-member ring, six-member ring and 12-member ring and optimized at the beginning, among which InO^+ in the 12-member ring has the lowest energy after geometry optimizations. Therefore, further calculations were performed based on this model.

Adsorption energy (E_{ad}) denotes the interaction between the surface and the adsorbate, which is defined as:

$$E_{\text{ad}} = E_{\text{sub}} + E_{\text{x}} - E_{\text{total}} \quad (3)$$

where E_{total} is the total energy of the catalyst model and gas molecule; E_{sub} and E_{x} are the energy of catalyst model and gas molecule, respectively. A smaller value indicates a stronger adsorption.

4. Conclusions

The geometry and electronic structure of the $[\text{InO}]^+$ and $[\text{InOH}]^{2+}$ groups were quite different, and the $[\text{InO}]^+$ group was more reactive and served as the main active site in the In/BEA catalyst. Furthermore, CH_4 could be easily activated on the L-model to form a CH_3 group in the absence of NO or NO_2 , while the B-model was inactive in this process. NO_2 plays a more important role than NO in the SCR process, because it could react with the activated CH_3 to form the key intermediate CH_3NO_2 and lower the total reaction barrier.

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