Mechanism of Propane Adsorption and the Following NO\textsubscript{x} Reduction over an In/BEA Catalyst: A Computational Study

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ABSTRACT: To expand the knowledge on hydrocarbon selective catalytic reduction (SCR) and follow the research steps of methane-SCR and propane-SCR in our previous work, we studied the characteristics of propane adsorption on In/BEA zeolite, explored the NO and NO\textsubscript{2} activation process on a propane adsorbed catalyst, and calculated the reaction enthalpy of two reaction pathways. Results showed that O site in the L-model (the [InO]\textsuperscript{+}/BEA structure) was the main active site in the adsorption process, and any of the carbon atoms in the propane molecule could react with it, with a lower adsorption energy than methane (−3.20 vs −2.98 eV). Also, NO or NO\textsubscript{2} could not be directly activated on the propane adsorbed catalyst, indicating that the process may be complicated. In addition, propane reduces the NO or NO\textsubscript{2} molecule with two different pathways and the final products were less stable than those of methane (−5.6 vs −20 eV). These results could explain the fact that propane and methane had different reaction temperatures and would further deepen our understanding of the propane-SCR process.

1. INTRODUCTION

The selective catalytic reduction of NO\textsubscript{x} by hydrocarbons (HC-SCR) has been a research focus of environmental catalysis since the 1990s.\textsuperscript{1,2,7} Among the available hydrocarbons, methane was regarded as a special beneficial reducing agent for its cheap cost and abundant resource.\textsuperscript{7} For catalysts in the hydrocarbon SCR, indium-containing zeolites, including ZSM-5,\textsuperscript{9} BEA,\textsuperscript{10} and MOR,\textsuperscript{11} have shown significant activity and resistance to water in the process. In addition, TiO\textsubscript{2} has also been regarded as a promising catalyst with SO\textsubscript{2} tolerance.\textsuperscript{12,13} On the other hand, temperature has been recognized as one important factor in the SCR processes, which can affect the structure of the catalyst and reduce performance.\textsuperscript{14–16} In the studies of optimization of a reducing agent, propane and methane were used as a mixed agent over In zeolites.\textsuperscript{17,18} As one of the results in the experiments, propane exhibited a higher low-temperature reducibility for NO\textsubscript{x}, while methane displayed a greater high-temperature reducibility, and their combined reaction window can cover a relatively wide range and seems ideal for future process control. Thus, NO\textsubscript{x} reduction by a mixture of propane and methane over an In zeolite catalyst reveals a promising industrial application.

We have been studying the detailed mechanism of the methane-SCR and propane-SCR process over an In/BEA catalyst for a deeper understanding of their different reaction windows. In our previous work, the main active sites and detailed catalytic process during the SCR of NO\textsubscript{x} by methane over In/BEA were studied by the density function theory (DFT) using a periodic model.\textsuperscript{19} Geometries of Lewis and Bronsted acid sites have been investigated; adsorption behaviors of CH\textsubscript{4}, NO, NO\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2}O molecules on the acid sites have been studied; and the formation process of key intermediate products during methane-SCR has been identified. However, adsorption behaviors of the propane molecule on the Lewis and Bronsted acid sites have not been studied, and the formation process of intermediate products in propane-SCR has not been compared with that in methane-SCR, without which the mechanism of a broader temperature window in the situation of a mixed agent could not be elucidated.

In this work, we re-construct the [InO]\textsuperscript{+} and [InOH]\textsuperscript{2+} in the channel of BEA zeolite as the Lewis and Bronsted acid sites and proposed six different patterns of adsorption of propane on the two acid sites to explore the most possible adsorbed structures during propane-SCR. In addition, intermediate products of the NO and NO\textsubscript{2} molecule adsorbed to the catalyst in propane-SCR were tried to be learned and compared to those in methane-SCR, aiming to reveal a more
detailed mechanism of different reaction temperatures for propane and methane. Also, reaction enthalpies of propane-SCR processes were also calculated and compared to those of methane-SCR so as to further elucidate the difference and connections of two SCR processes.

2. RESULTS AND DISCUSSION

2.1. The Re-optimized Structure of In/BEA Models. As we re-constructed the L-model and B-model based on the In/BEA zeolite, we re-optimized the geometry structures of both models. And the result showed two different structures for the models if compared to results in our previous work.19 Thus, both the optimized structures are shown in Figure 1 as other possible configurations. And all following calculations in this work were performed based on the structure shown in Figure 1. The calculated dimensions of the unit cell were $a = 12.661 \text{ Å}$, $b = 12.661 \text{ Å}$, and $c = 26.406 \text{ Å}$, which are more reasonable compared to our previous results of $a = 12.669 \text{ Å}$, $b = 12.675 \text{ Å}$, and $c = 26.781 \text{ Å}$19 because of experimental results of $a = 12.632 \text{ Å}$, $b = 12.632 \text{ Å}$, and $c = 26.186 \text{ Å}$20. In the B-model, the oxygen atom in the BEA zeolite coordinated to the In atom was increased to four from the original two in Gao et al.,19 indicating a more stable structure. The calculated bond lengths and Mulliken charge of the two models are shown in Table 1. The bond length of $[\text{InO}]^+$($d_{\text{In-O}}$) was slightly elongated after a hydroxyl group was modeled (2.004 vs 1.903 Å), and the charge of In and O was remarkably different in the two models ($Q_{\text{In}} = 1.486$ vs 1.218 e, $Q_{\text{O}} = -0.843$ vs $-0.697$ e). The results indicated that the electrons were redistributed after $[\text{InO}]^+$ or $[\text{InOH}]^{2-}$ was anchored on the BEA zeolite, and further discussion of the electronic structure analysis such as the condensed Fukui function and particle density of states (PDOS) of In and O atoms can be seen in our previous work.19

2.2. Interactions of the Propane Molecule to the In/BEA Models. In our previous work,19 we studied the methane adsorption characteristics on the In site and the O site of the L-model and B-model. However, propane is a molecule with less symmetries if compared to methane, and its adsorption characteristics would need further discussion on different possible configurations. In general, these configurations mainly consist of results of different patterns of carbon atoms approaching the In site or the O site. In total, there are six different approaching pathways of the propane molecule to the catalyst: (1) the mid-carbon atom of propane approaching the O site; (2) the mid-carbon atom of propane approaching the In site; (3) the mid-carbon atom of propane approaching the In site, while a side-carbon atom approaches the O site; (4) a side-carbon atom of propane approaching the O site; (5) a side-carbon atom of propane approaching the In site; and (6) a side-carbon atom of propane approaching the In site, while the mid-carbon atom approaches the O site. Each of these six pathways would happen under certain probabilities. Thus, we simulated these six different pathways and optimized their geometries to explore the mechanism involved and figure out the most favorable adsorption configurations. Details are discussed below from Sections 2.2.1 to 2.2.6.

2.2.1. Interaction after the Mid-carbon Atom of Propane Approached the O Site of the L-Model and B-Model. In this section, we proposed a propane molecule whose mid-carbon atom was approaching the O site of the L-model and B-model (Figure 2A,C), and then optimized the total structure of the catalyst model and the gas molecule (Figure 2DB). The result shows that in the L model, the C–H bond of the mid-carbon atom and an adjacent hydrogen atom was easily cleaved. One of the adjacent hydrogen atoms of the mid-carbon atom was moved to the O site, and a C–O bond formed immediately

![Figure 1](https://example.com/figure1.png)

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

![Figure 2](https://example.com/figure2.png)

Figure 2. Comparison of propane adsorption processes of (A) the mid-carbon atom approaching the O site of the L-model; (B) optimized structure of panel A; (C) the mid-carbon atom approaching the O site of the B-model; and (D) optimized structure of panel C.

| models | $d_{\text{In-O}}$ (Å) | $d_{\text{In-O1}}$ (Å) | $d_{\text{In-O2}}$ (Å) | $d_{\text{In-O3}}$ (Å) | $d_{\text{In-O4}}$ (Å) | $d_{\text{O-H}}$ (Å) | $Q_{\text{In}}$ | $Q_{\text{O}}$ | $Q_{\text{H}}$ | $Q_{\text{O1}}$ | $Q_{\text{O2}}$ | $Q_{\text{O3}}$ | $Q_{\text{O4}}$ |
|--------|----------------|----------------|----------------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| L-model | 1.903 | 2.345 | 2.392 | 2.188 | 2.212 | 0.985 | 1.218 | $-0.697$ | $-0.939$ | $-0.916$ | $-0.986$ | $-0.976$ | $-0.987$ |
| B-model | 2.004 | 2.225 | 2.188 | 2.212 | 2.422 | 0.985 | 1.486 | $-0.843$ | 0.452 | $-0.997$ | $-0.986$ | $-0.867$ | $-0.987$ |
model, the In–O bond was greatly elongated after adsorption of the propane molecule (1.903 vs 2.452 Å). Table 2 also shows that a large portion of electron was transferred from the mid-carbon atom to the In atom, indicating that propane interacted strongly with the catalyst model, which could also be confirmed from the very low adsorption energy of −3.20 eV of the process. On the contrary, in the B-model, the bond length of I–O (2.004 and 2.004 Å) and O–H (0.985 and 0.982 Å) and the Mulliken charge of In (1.486 and 1.480 e) and O atom (−0.843 and −0.848 e) almost remained unchanged when the mid-carbon atom of the propane molecule was adsorbed on the O site, indicating a very weak interaction between propane and the catalyst model, which is consistent with the previous result and a high adsorption energy of −0.42 eV. These results confirm that the [InO]+ group might serve as a major active site in this situation, which is consistent with our previous study.19

Furthermore, the projected density of states (PDOS) of the carbon atom and O atom was calculated to clarify the bonding mechanism of propane adsorption in Figure 3. In both models, the PDOS of C-p overlapped with the O-p orbital to some extent whether before and after adsorption, even in the B-model whose adsorption energy was relatively high, indicating that a C–O bond was easy to form in both models, and the propane molecule moved away from the B-model maybe due to space obstruction of hydrogen atom. These PDOS results are different than those in Gao et al.,19 which may come from the different geometry configurations of the B-model used and different properties of propane and methane. Also, the peak of the O-p orbital near the Fermi level in the L-model moved slightly away, accompanied with PDOS split at lower energy levels after adsorption, with a quantity of electron transferred from the C-p orbital at higher energy levels. The electron outflow from the C-p orbital still happened in the B-model, yet the PDOS of O-p remained largely unchanged, indicating a weak interaction between C-p and O-p in the B-model, confirming that the B-model is not a good active site.

2.2.2. Interaction after the Mid-carbon Atom of Propane Approached the In Site of the L-Model and B-Model. In this section, we proposed a propane molecule whose mid-carbon atom was approaching the In site of the L-model and B-model (Figure 4A,C), and then optimized the total structure of the catalyst model and the gas molecule (Figure 4DB). In Figure 4, both [InO]+ and [InOH]2+ in the L-model and B model had a very weak affinity to the propane molecule in this situation, indicating that the In site was not a good active site for the mid-carbon atom of propane. After geometry optimization, the d_{In–O} equals 3.630 and 4.154 Å for the L-model in Figure 4A and the B-model in Figure 4B, respectively, which shows that the interaction between the catalyst and propane was slight in this situation. However, both processes could be regarded as adsorption, as they are found to be exothermic. Specifically, in the L-model, d_{In–Al} was elongated from 2.839 Å (Figure 4A) to 3.071 Å (Figure 4B), while in the B-model, the transfiguration of the catalyst model was found to be small, in which the torsion of the O–H bond was the only obvious one (Figure 4DC).

Bond length changes and the Mulliken charge before and after interaction of the mid-carbon atom of propane approaching the In site are compiled in Table 2. In the L-

| bonds | L-model | B-model |
|-------|---------|---------|
| before | after | before | after |
| In–O | 1.903 | 2.452 | 2.004 | 2.004 |
| C–O | 1.473 | 0.985 | 0.982 |
| O–H | 1.218 | 0.642 | 1.486 | 1.480 |
| q_{In} | −0.300 | 0.001 | −0.300 | −0.724 |
| q_{C} | −0.697 | −0.752 | −0.843 | −0.848 |
| q_{O} | −3.20 | 0.42 |

Adsorption on In/BEA with the Mid-carbon Atom of propane molecule (d_{C–O} = 1.473 Å in Figure 2B). This indicates that the adsorption could easily happen under this pathway for the L-model. And this result is similar to the findings of one of the methane adsorption situations in Gao et al.19 and Sinev et al.21 except that the [InO]+ moiety was isolated from the BEA zeolite for going too far away from the O atom and Al atom in the zeolite. However, in the B-model, the propane molecule seemed to be moved away from the catalyst (d_{C–O} = 4.157 Å in Figure 2D), suggesting that the O site of the B-model had very weak interaction with the propane molecule in this situation, which also means that the B-model is not a good active site in this pathway.

Bond length changes and the Mulliken charge before and after interaction of the mid-carbon atom of propane approaching the O site are compiled in Table 2. In the L-
NO or NO₂ molecule. In the meantime, the In site was reduced into the In atom, and In−O bonds before adsorption disappeared. Note that the In atom was not a usual phenomenon; the most common form of In that appeared in such SCR process was [InO]⁺, while it could be explained that the In atom was not stable and could be further oxidized back into [InO]⁺. Results also showed that d_{In−O} was elongated from 1.903 to 2.785 Å, which broke the [InO]⁺ group into two parts if compared with the situation of the mid-carbon atom approaching the O site of the L-model as discussed in Section 2.2.1. By contrast, the [InOH]²⁺ group in the B-model had little affinity with the propane molecule in this situation; except for the torsion of the O−H bond, little structure change was observed. The closest distance between the propane molecule and [InOH]²⁺ group was d_{C1−O} = 3.476 Å.

Bond length changes and the Mulliken charge before and after interaction of the mid-carbon atom of propane

Figure 3. The PDOS of C and O atoms when the mid-carbon atom of propane approaches the O site of the In/BEA zeolite for the (A) L-model and (B) B-model.

Figure 4. Comparison of propane adsorption processes of (A) the mid-carbon atom approaching the In site of the L-model; (B) the optimized structure of panel A; (C) the mid-carbon atom approaching the In site of the B-model; and (D) the optimized structure of panel C.

Table 3. Bond Length (d, Å), Mulliken Charge Population (q, e), and Adsorption Energy (E_{ads}, eV) of Propane Adsorption on In/BEA with the Mid-carbon Atom of Propane Approaching the In Site

| bonds | L-model before | L-model after | B-model before | B-model after |
|-------|----------------|---------------|----------------|---------------|
| In−O  | 1.903          | 1.901         | 2.004          | 2.004         |
| O−H   | 0.985          | 0.985         | 1.485          | 1.485         |
| q_{In} | 1.218          | 1.220         | 1.486          | 1.485         |
| q_C   | −0.300         | −0.481        | −0.300         | −0.476        |
| q_O   | −0.697         | −0.705        | −0.843         | −0.843        |
| E_{ads} | −0.45        | −0.44         |                |               |
approaching the In site and a side-carbon atom approaching the O site are compiled in Table 4. In the L-model, the In−O bond was greatly elongated and broken after the adsorption. Quite an amount of electron was transferred from the C1 atom to C2 atom to In atom, indicating strong interaction between the gas molecule and catalyst model. However, in the B-model, the bond length of In−O (2.004 and 2.006 Å) and O−H (0.985 and 0.983 Å) and the Mulliken charge of \( q_{\text{In}} \) (1.486 and 1.497 e) and \( q_{\text{O}} \) (−0.843 and −0.847 e) largely remained unchanged after adsorption. These results are consistent with the adsorption energy calculated (−2.74 eV for the L-model and −0.43 eV for the B-model) and structure change discussed in the previous paragraph.

Table 4. Bond Length (\( d \), Å), Mulliken Charge Population (\( q \), e), and Adsorption Energy (\( E_{\text{ads}} \), eV) of Propane Adsorption on In/BEA with the Mid-carbon Atom of Propane Approaching the In Site and a Side-Carbon Atom Approaching the O Site

| bonds | L-model before | L-model after | B-model before | B-model after |
|-------|---------------|---------------|----------------|---------------|
| In−O  | 1.903         | 2.004         | 2.006          |
| C−O   | 1.439         | 1.486         |                |
| O−H   | 0.985         | 1.497         |                |
| \( q_{\text{In}} \) | 1.218         | 0.741         | 1.486          |
| \( q_{\text{C1}} \) | −0.300        | −0.489        | −0.300         |
| \( q_{\text{C2}} \) | −0.483        | −0.230        | −0.843         |
| \( q_{\text{O}} \) | −0.697        | −0.700        | −0.843         |
| \( E_{\text{ads}} \) | −2.74 eV      | −0.43 eV      |                |
The projected density of states (PDOS) of the C1, C2, O, and In atoms was calculated to clarify the bonding mechanism of propane adsorption, whose results are shown in Figure 7. For the In site of the L-model, although the PDOS of C1-p, In-s, and In-p had little overlaps as C1, In atoms did not form any bond in the optimized structure, and the electron outflow for the C1 atom, shift of the electron in In-s, and enhancement of the peak in the In-p orbital indicate that the two atoms might have interacted with each other in the adsorption process. For the O site of the L-model, the PDOS of C2-p and O-p had a large portion of overlaps from −8 eV to the Fermi level, and electrons in O-p orbital split and moved from the Fermi level to lower energy levels, suggesting that a C2−O bond in this situation is easily formed. As to both the In site and O site in the B-model, although electron outflow in C1-p and C2-p orbitals was obvious, the PDOS of In-s, In-p, and O-p orbitals did not change obviously before and after the adsorption process, and in both sites, overlaps of PDOS of orbitals were very small, which are consistent with previous discussions about the little structure change and a high adsorption energy.

2.2.4. Interaction after a Side-Carbon Atom of Propane Approached the O Site of the L-Model and B-Model. In this section, we proposed a propane molecule, one of whose side-carbon atom was approaching the O site of the L-model and B-model (Figure 8A,C), and then optimized the total structure of the catalyst model and the gas molecule (Figure 8D,B). In Figure 8, we could see that in the L-model, the C−H bond was easily cleaved when it adsorbed on the O site just like the situations in Sections 2.2.1 and 2.2.3. Similarly, one adjacent hydrogen atom was moved to the O site, with a C−O bond formed simultaneously. It means that the side-carbon atom of the propane molecule could be activated on the O site of the L-model despite the position and configuration of the propane molecule may vary. In the meantime, the In site was also reduced in the In atom, and In−O bonds before adsorption disappeared, which also need more experimental confirmation. In this situation, the distance between the In atom and O atom, \( d_{\text{In−O}} \), was elongated from 1.903 to 2.563 Å, and other In−O bonds also disappeared. This result showed the great reduction ability of the propane molecule at the O site of the L-model again, if compared to the adsorption process of the methane molecule to the O site of the L-model as discussed in Gao et al.19 By contrast, the propane molecule and B-model of the catalyst showed little structure change and no new bond was formed in the process. The closest distance between the side-carbon atom in the propane molecule and O atom in the
adsorption has a large portion of overlaps from −9 to 0 eV, indicating that a C–O bond was easily formed. As to the B-model, although the outflow of electron in the C-p orbital was obvious, the PDOS of the O-p orbital remained largely unchanged, and they only had small overlaps after adsorption, which were consistent with previous results of very little interaction between the gas molecule and catalyst model.

2.2.5. Interaction after a Side-Carbon Atom of Propane

Approached the In Site of the L-Model and B-Model. In this section, we proposed a propane molecule, one of whose side-carbon atom was approaching the In site of the L-model and B-model (Figure 10A,C), and then optimized the total structure of the catalyst model and the gas molecule (Figure 10D,B). In Figure 10, we can see that for both the L-model and B-model, the catalyst model and gas molecule had some torsion in configuration, yet no obvious structure change was found and no new bond was formed. The closest distances between the propane molecule and catalyst model after optimization were $d_{\text{In-C}}$ for the L-model (3.624 Å) and $d_{\text{In-O}}$ for the B-model (3.532 Å), indicating that the adsorptions were weak.

Bond length changes and the Mulliken charge before and after interaction of a side-carbon atom of propane approaching the In site are compiled in Table 6. In both models, except for an obvious electron outflow at the carbon atom, most of the bond length and Mulliken charge remained largely unchanged, which also indicated weak adsorption processes involved. Overall, these results were consistent with the high adsorption energy of $-0.49$ and $-0.41$ eV for the L-model and B-model, respectively.

Furthermore, the projected density of states (PDOS) of the C and In atom was calculated to clarify the bonding mechanism of propane adsorption, whose results are shown in Figure 11. In Figure 11, we can see that the PDOS graph was very similar to that of Section 2.2.2. In both models, the PDOS of C-p, In-s, and In-p orbitals only slightly overlapped; the outflow of electron in the C-p orbital happened in both the L-model and B-model, while the PDOS of In-s and In-p orbitals mainly remained unchanged. Together with the results in Section 2.2.2, such PDOS results confirm that the In site might be a poor active site for the adsorption of propane.

2.2.6. Interaction after a Side-Carbon Atom of Propane

Approached the In Site While the Mid-carbon Atom Approached the O Site of the L-Model and B-Model. In this section, we proposed a propane molecule, one of whose side-carbon atom was approaching the In site while the mid-carbon atom was approaching the O site of the L-model and B-model (Figure 12A,C), and then optimized the total structure of the catalyst model and the gas molecule (Figure 12B,D). In Figure 12, we could see that in both the L-model and B-model, the propane molecule had some movement and configuration change during the adsorption process. In addition, for the L-model, the distance between the In and Al atom was shortened a little bit (from 2.839 to 2.837 Å) and an In–Al bond was suggested to be formed, while for the B-model, the [InOH]$_2^+$ group remained largely unchanged. Overall, results showed that the two adsorption processes were weak on both the In site and O site, suggesting that these two situations were not favorable configurations of propane approaching the catalyst model.

Bond length changes and the Mulliken charge before and after interaction of a side-carbon atom of propane approaching the In site and the mid-carbon atom approaching the O site are compiled in Table 7. From Table 7, we can see that in the L-
model, the distance between the In and Al atom was shortened to 2.837 Å, as discussed previously. And electron outflow for the C₁ and C₂ atom in both the L-model and B-model was quite significant. Except for these, no obvious change for bond length and atom charge was discovered. Adsorption energies for both models in this situation were also small, which equal −0.44 and −0.44 eV, indicating that the interaction between the gas molecule and catalyst model was weak.

In addition, the projected density of states (PDOS) of the C, In, and O atom was calculated to clarify the bonding mechanism of propane adsorption, whose results are shown in Figure 13. In Figure 13, we can see that for both the L-model and B-model, electron outflow at the C₁ and C₂ atom was quite significant during the adsorption processes. However, the PDOS of the In and O atom remained largely unchanged, which can be also confirmed from their high

**Table 6. Bond Length (d, Å), Mulliken Charge Population (q, e), and Adsorption Energy (E_{ads}, eV) of Propane Adsorption on In/BEA with a Side-Carbon Atom of Propane Approaching the In Site**

| bonds | L-model before | L-model after | B-model before | B-model after |
|-------|----------------|--------------|----------------|--------------|
| In−O  | 1.903          | 1.898        | 2.004          | 2.005        |
| O−H   | 0.985          | 0.986        |                |              |
| q_{In}| 1.218          | 1.191        | 1.486          | 1.494        |
| q_{C₁}| -0.300         | -0.714       | -0.300         | -0.691       |
| q_{O₂}| -0.697         | -0.686       | -0.843         | -0.855       |
| E_{ads}| -0.49          | -0.41        |                |              |

Figure 9. The PDOS of C and O atoms when a side-carbon atom of propane approached the O site of the In/BEA zeolite for the (A) L-model and (B) B-model.

Figure 10. Comparison of propane adsorption processes of (A) a side-carbon atom approaching the In site of the L-model; (B) the optimized structure of panel A; (C) a side-carbon atom approaching the In site of the B-model; and (D) the optimized structure of panel C.
adsorption energy discussed previously. In addition, there are some overlaps in the PDOS of the C2 and In atom at the In site for the L-model and in those of the C1 and O atom at the O site for both the L-model and B-model. However, there was no new bond formed, which may be due to the lack of interaction between the gas molecule and catalyst model.

Thus, from Sections 2.2.1 to 2.2.6, we examined all six possible configurations of propane molecules adsorbing on the In/BEA zeolite and checked the change of bond length, charge, and PDOS of involved atoms during the adsorption processes. To summarize, the propane adsorption process had a lot in common with that of methane in the SCR process.

Figure 11. The PDOS of C and In atoms when a side-carbon atom of propane approached the In site of the In/BEA zeolite for the (A) L-model and (B) B-model.

Figure 12. Comparison of propane adsorption processes of (A) a side-carbon atom approaching the In site and the mid-carbon atom approaching the O site of the L-model; (B) the optimized structure of panel A; (C) a side-carbon atom approaching the In site and the mid-carbon atom approaching the O site of the B-model; and (D) the optimized structure of panel C.

Table 7. Bond Length (d, Å), Mulliken Charge Population (q, e), and Adsorption Energy (E_{ads}, eV) of Propane Adsorption on In/BEA with a Side-Carbon Atom of Propane Approaching the In Site and the Mid-Carbon Atom Approaching the O Site

| bonds    | L-model before | L-model after | B-model before | B-model after |
|----------|----------------|---------------|----------------|---------------|
| In−O     | 1.903          | 1.905         | 2.004          | 2.004         |
| In−Al    | 2.837          |               | 0.985          | 0.984         |
| O−H      |                |               | 1.486          | 1.499         |
| q_{In}   | 1.218          | 1.224         | 1.486          | 1.499         |
| q_{C1}   | −0.300         | −0.449        | −0.300         | −0.449        |
| q_{C2}   | −0.483         | −0.683        | −0.483         | −0.714        |
| q_{O}    | −0.697         | −0.701        | −0.843         | −0.846        |
| E_{ads}  | −0.44          | −0.44         | −0.44          | −0.44         |
the O site in the L-model was the main active site. Specifically, both the mid-carbon atom and side-carbon atom can react with the O site of the L-model without an energy barrier (Sections 2.2.1, 2.2.3, and 2.2.4), and the adsorption energy was lower than that of methane adsorption in their most favorable configurations (−3.20 eV in Section 2.2.1 vs −2.98 eV19), which could explain why propane exhibited a higher low-temperature reducibility if compared to methane.18

2.3. Interaction of the NO and NO2 Molecule to Propane Adsorbed the In/BEA Zeolite. It is reported that NOX molecules, especially NO2, could coordinate with the [InO]+ group in the In/BEA zeolite and produce NO3− to facilitate methane activation and formation of active intermediates.22,23 Thus, we explored the adsorption characteristics of NO and NO2 on the L-model and B-model of the In/BEA zeolite in our previous work.19 However, whether NO and NO2 could be activated on the gas-adsorbed In/BEA zeolite as a second step of the SCR process still requires further exploration and comparisons. Considering that the situations of the L-model in Section 2.2.1 and B-model in Section 2.2.2 had the lowest adsorption energy (−3.20 and −0.44 eV, respectively), NO and NO2 adsorption tests were conducted on the structures in Figures 2B and 3D, which were the most favorable configurations of propane adsorptions.

In Figure 14, we could see that all of the adsorption processes did not involve much configuration change, indicating that the interaction was weak. The closest distance between the C and N atom was 3.886, 4.571, 4.062, and 4.032 Å for Figure 14A, B, C, D, respectively, which were too far to form any bond. These results indicated that NO and NO2 molecules were not easy to be activated on the propane adsorbed In/BEA zeolite, suggesting that the interaction mechanism might not be a simple step-by-step adsorption process.

On the other hand, propane may react with the −CH2COO− group, which is the oxidation product of propane and intermediate products in a typical propane and methane mixed SCR reaction considering that there is also oxygen in the process.18,24,25 Thus, to explore other possible mechanisms of the activation process of propane on the In/BEA zeolite, we further replaced one of those −CH3 of the propane molecule with −COOH in the structures in Figures 2B and 3D and then tested NO and NO2 adsorption on the oxidated form of the propane-adsorbed In/BEA zeolite. Results are shown in Figure 15. We could see that all the four catalyst
models did not have much change in configuration, and the propane molecule was kind of far away. The closest distance between the C and N atom was 5.753, 4.122, 1.739, and 3.932 Å for structures in Figure 15A−D, respectively. Except for the structure in Figure 15C, the N atoms were too far away to form any bond. These results indicate that interactions between NO and NO$_2$ molecules and the oxidated form of propane adsorbed In/BEA zeolite were quite weak, and the activation of NO and NO$_2$ molecules on the catalyst may require a more complicated process other than a direct reaction.

Thus, in Section 2.3, we checked the reaction ability of the NO or NO$_2$ molecule on the propane adsorbed In/BEA zeolite. To summarize, the reaction process might be complicated, as neither NO nor NO$_2$ could be directly activated on the propane adsorbed catalyst or its oxidated product. Further studies are needed to illustrate details of the activation stage of NO or NO$_2$ with the catalyst.

2.4. Propane-SCR Reaction Enthalpy for the NO and NO$_2$ Pathways. While the key intermediate product in the propane-SCR was not able to be inferred from consequent adsorption processes of propane and NO$_x$, here we proposed two structures as the initial states of propane-SCR similar to those of methane-SCR in our previous work$^{19}$ for both NO and NO$_2$ pathways to estimate the reaction enthalpy and check their transition states. Transition state search indicated that although both reaction routes shared the same product and catalyst, they had two different transition states, as shown in Figure 16. This was a different finding if compared to methane-SCR as discussed in our previous work.$^{19}$ Also, in Figure 16, we can see that both reactions were exothermic; however, the route for the reduction of NO$_2$ (initial state 1−transition state 1−product) had a much lower energy barrier (6.3 vs 14.9 eV), suggesting that NO$_2$ is also an important molecule in propane-SCR as it was in methane-SCR, and the reaction would be much faster if there is NO$_2$ in the reaction instead of NO.

Thus, in Section 2.4, we showed that propane-SCR for NO and NO$_2$ has two entirely different transition states and routes, which are different than those of methane-SCR, yet NO$_2$ was again the more important molecule in the SCR process, as it was in methane-SCR. In addition, methane-SCR was very likely to have a lower energy of optimized final products, if comparing Figure 16 with Figure 10 in our previous work$^{19}$, which was in the form of a complex compound and 20 eV lower than the initial state. This could explain the fact that methane had a high-temperature reducibility.$^{18}$

3. CONCLUSIONS

To conclude, we studied the adsorption characteristics of the propane molecule on the L-model and B-model of In/BEA zeolite, explored the possibilities of NO and NO$_2$ activation on the propane adsorbed catalyst, and calculated the reaction enthalpy and compared the two reaction routes for NO and NO$_2$ in propane-SCR. In general, both the mid-carbon atom and side-carbon atom can react with the O site of the L-model

Figure 14. Optimized structures of the NO and NO$_2$ molecule adsorbed on the propane adsorbed In/BEA zeolite: (A) NO adsorbed on the most favorable L-model; (B) NO$_2$ adsorbed on the most favorable L-model; (C) NO adsorbed on the most favorable B-model; and (D) NO$_2$ adsorbed on the most favorable B-model.

Figure 15. Optimized structures of the NO and NO$_2$ molecule adsorbed on the oxidated form of propane adsorbed In/BEA zeolite: (A) NO adsorbed on the oxidated form of the most favorable L-model; (B) NO$_2$ adsorbed on the oxidated form of the most favorable L-model; (C) NO adsorbed on the oxidated form of the most favorable B-model; and (D) NO$_2$ adsorbed on the oxidated form of the most favorable B-model.

Figure 16. Energy profile of the reactants (NO$_2$ for initial state 1, NO for initial state 2), transition state, and products (N$_2$, H$_2$O, CO$_2$, etc.) in a propane-SCR.
easily, and the adsorption energy was lower than that of methane adsorption in their most favorable configurations, which helps explain why propane exhibited a higher low-temperature reducibility if compared to methane. However, neither NO nor NO2 could be directly activated on the propane adsorbed catalyst or its oxidated product. In addition, propane-SCR for NO and NO2 has two entirely different transition states and routes, yet NO2 was still the more important molecule in the SCR process as it was in methane-SCR. Lastly, methane-SCR was very likely to have a lower energy of optimized final products. Overall, together with our previous work, the results in this work successfully explain the experimental fact that methane and propane had different reaction windows: propane had a lower adsorption energy than methane, yet methane’s final product was more stable. Hopefully, this work could provide more detailed evidence and insight for future studies in hydrocarbon SCR. Future researchers could propose a mechanism of how NO and NO2 were activated on the catalyst and then verify it with experiments.

4. COMPUTATIONAL METHODS

All DFT computations in this work were performed on a periodic BEA zeolite model as shown in Gao et al.19 based on DMol3 implemented in Material Studio 2017R226 in which the Perdew–Burke–Ernzerhof (PBE)27 functional in the generalized gradient approximation (GGA)28 was used to calculate the exchange-correlation potential. And the following convergence tolerance criteria were used in the geometry optimization and energy calculation: SCF tolerance (1.0 × 10−5), atomic force (0.004 hartree/Å), max displacement (0.005 Å), and total energy variation (2.0 × 10−8 hartree). The molecular orbitals were expanded using a doubled numerical basis set with d-polarization functions (DND). The range of integration for charge density and functional was confined within a global orbital cutoff value of 4.4 Å. The core electrons were treated using the all electron method. A (2 × 2 × 1 or 1 × 1 × 1) Monkhorst-Pack k-point grid, based on different fine or medium settings for the target optimization structure, was used for In/BEA unit cell optimization. All the atoms in the model were allowed to be relaxed during the calculation.

Also note that the [InO]2+ and [InOH]2+ moieties introduced one and two positive charges, respectively. Thus, a similar substitution method of Si4+ to Al3+ as it was in Gao et al.19 was used to keep the charge balance. For the sake of simplicity, the formed [InO]2+/BEA model was denoted as the L-model (L for Lewis), and the [InOH]2+/BEA model was denoted as the B-model (B for Bronsted). Further calculations were performed after geometry optimization of these two models.

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

$$E_{\text{ad}} = E_{\text{total}} - E_{\text{sub}} - E_x$$  (1)

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

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Notes

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