Balancing the Activity and Selectivity of Propane Oxidative Dehydrogenation on NiOOH (001) and (010)

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Abstract

Propane oxidative dehydrogenation (ODH) is an energy-efficient approach to produce propylene. However, ODH suffers from low propylene selectivity due to a relatively higher activation barrier for propylene formation compared with that for further oxidation. In this work, calculations based on density functional theory were performed to map out the reaction pathways of propane ODH on the surfaces (001) and (010) of nickel oxide hydroxide (NiOOH). Results show that propane is physisorbed on both surfaces and produces propylene through a two-step radical dehydrogenation process. The relatively low activation barriers of propane dehydrogenation on the NiOOH surfaces make the NiOOH-based catalysts promising for propane ODH. By contrast, the weak interaction between the allylic radical and the surface leads to a high activation barrier for further propylene oxidation. These results suggest that the catalysts based on NiOOH can be active and selective for the ODH of propane toward propylene.

Keywords Density functional theory · Oxidative dehydrogenation · Propane · Nickel oxide hydroxide · Two-step radical mechanism · Selectivity

Introduction

The demand for propylene has remarkably increased over the past decade. Such increase is predicted to continue due to its importance as an industrial chemical in the production of polypropylene, propylene oxide, acrylic acid, ethanol, acrylonitrile, and other products [1–7]. Propylene can be produced from catalytic and steam cracking, as well as propane dehydrogenation (PDH) [8–10]. These processes suffer from high energy consumption because of the high endothermic reactions and fast deactivation of catalysts due to carbon deposits. In addition, catalytic and steam cracking use nonrenewable petroleum-based feedstock, making these processes unsustainable [11].

Over the past decade, the exploitation of shale gas has provided an abundant supply of light alkanes, including propane, making PDH and oxidative dehydrogenation (ODH) potentially cost-effective processes for propylene production [11–13]. ODH has the following advantages over PDH: (1) The ODH reaction is exothermic with a reaction enthalpy of -117 kJ/mol and is highly favorable over the PDH reaction ($\Delta H = 124$ kJ/mol); (2) The presence of oxidation reagents in ODH helps oxidize the residual carbon, thereby preventing coke deposition [14–16]. However, the presence of oxidation reagents in ODH may cause the further oxidation of propylene to either CO or CO₂, resulting in a low yield of propylene [7, 17]. Therefore, improving the selectivity to propylene while taking advantage of the thermodynamics of ODH is important in implementing the propane ODH technology in the industrial production of propylene.

Vanadium-based catalysts have been widely studied for ODH, including the ODH of propane [15, 18–22]. Several computational studies on the catalytic performance of vanadia for propane ODH were conducted on the basis of either slab models or supported clusters [23–25]. Fu et al. [26] investigated propane ODH over the V₂O₅(001) surface and found that the C–H bond may be activated at either the terminal or the bridging lattice O atoms. They concluded

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that the $\text{V}_2\text{O}_5(001)$ surface is not a highly selective catalyst for the ODH reaction due to facile further oxidation [26]. Marin et al. [27] analyzed the ODH reaction on a vanadium monolayer supported on the $\text{TiO}_2(001)$ surface; they concluded that TiO_2 not only improves the catalytic activity of the vanadium monolayer but also increases its selectivity toward propylene by limiting further oxidation reaction. Gong et al. [28] proposed that propane ODH over Al_2O_3 -supported vanadia can be divided into two steps: the initial $\text{V}=\text{O}$ -assisted ODH, followed by pure dehydrogenation after the surface loses its terminal O atom. Electronic structure analysis demonstrated that the Bader charge value and the p-band location of the active O atoms affected the reactivity by modulating the activation barrier for breaking the C–H bond [28, 29].

Nickel-based catalysts have also been widely used in ODH reactions. In particular, NiO has been shown to activate the C–H bond of light alkanes [30–32]. Guo et al. [30] studied CH_4 activation over NiO-based catalysts by using NiO/ ZrO_2 and NiO/ MgAl_2O_4 as the model catalysts and found that ZrO_2 enhances the activity of NiO for C–H activation by weakening the Ni–O bonds. Liu et al. [32] studied the ODH of ethane on the NiO catalyst on the basis of the results of density functional theory (DFT) calculations and found that NiO(100) and NiO(110) exhibited different activities toward ethane ODH. Although the reactivities of these catalysts varied, the ability of the Ni–O pairs to activate the C–H bonds in the light alkanes was clearly demonstrated. Furthermore, reports have stated that the catalysts based on the Ni–Al mixed oxides derived from the double layered hydroxides can actively break the C–H bonds of light alkanes while exhibiting an improved selectivity of alkenes over the NiO/ Al_2O_3 catalysts [33, 34].

Nickel oxide hydroxide (NiOOH) is a precursor to the preparation of NiO and has been widely investigated for oxygen evolution reactions (OERs) in electro/photocatalytic water splitting systems [35–38]. NiOOH shows high activity for water oxidation, which is rate limiting for the electrocatalytic water splitting reaction. NiOOH-based materials are also promising electrocatalysts for rechargeable batteries. The ODH of propane on NiOOH may be performed under mild electrocatalysis condition owing to the electronic and structural properties of the double-layer hydroxide. The Ni–O pairs can be exposed in a controllable manner; thus, we hypothesize that NiOOH may be tuned to have an optimal oxidation power for the activation of the C–H bond of propane while preventing the further oxidation of propylene. Although NiOOH has not been reported as a catalyst for thermal catalysis, studies on the thermal stability of $\beta\text{-Ni}(\text{OH})_2\text{-}\beta\text{-NiOOH}$ systems indicate that the decomposition of $\beta\text{-Ni}(\text{OH})_2\text{-}\beta\text{-NiOOH}$ systems occurs in a fairly wide temperature range and is far from being complete even at 300 °C [39, 40]. In addition, the NiO-based

catalyst has been shown to be active for alkane oxidation at a relatively low temperature and with the ODH of ethane at 240 °C [41]. In oxidative reactions involving alkanes, the formation of surface hydroxyls on the catalyst is anticipated. Therefore, we choose $\beta\text{-NiOOH}$ as the model and believe that it has potential to be a catalyst for the ODH of propane under mild conditions.

In the present study, we map out the reaction pathways, including water formation and reoxidation of the ODH of propane on the $\beta\text{-NiOOH}$ (001) and (010) surfaces. Our results indicate that NiOOH can be an active and selective catalyst for propane ODH. Aiming to understand the role of O atoms in the ODH reaction, we analyze the electronic structure of lattice O atoms on the (001) and (010) surfaces.

Methodology and Computational Details

Spin-polarized DFT calculations were performed by using the Vienna Ab initio Simulation Package code [42]. Projector-augmented wave potentials [43] with a cutoff energy of 400 eV and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [44] were used in the calculations. The on-site self-interaction was corrected using the DFT + U approach with a U – J value of 5.5 eV [38]. The DFT-D3 method was used to account for the van der Waals dispersion interactions [45]. All the structures were relaxed until the maximum force on the movable atoms was less than 0.01 eV/Å.

The structural and electronic analyses of NiOOH showed two different phases, i.e., $\beta\text{-NiOOH}$ and $\gamma\text{-NiOOH}$ [37, 46–48]. In the present work, we selected the $\beta\text{-NiOOH}$ phase, which has a staggered configuration of intercalated protons [47, 48] and constructed the active surfaces for the study of propane ODH. The $\beta\text{-NiOOH}$ (001) surface was modeled with either a one-layer or two-layer slab in a (2×4) surface unit cell. The atoms in the bottom layer of the two-layer slab were fixed at their corresponding bulk positions during optimization. The propane adsorption energy on the two-layer slab was shown to be similar to that on the one-layer slab. Consequently, propane ODH reaction was simulated using the one-layer slab. The $\beta\text{-NiOOH}$ (010) surface was modeled with a two-layer slab in a (1×2) surface unit cell. A vacuum space of 15 Å was inserted to build the (001) and (010) slabs. A $3 \times 3 \times 1$ grid was used for k-space sampling [49]. The supercells of the (001) and (010) models were $10.38 \times 12.19 \times 19.03 \text{ Å}^3$ and $9.13 \times 10.38 \times 19.57 \text{ Å}^3$, respectively. The top and side views of the NiOOH (001) and (010) surfaces are illustrated in Fig. 1.

Optimized adsorption minima were used to construct the elementary reaction steps along the reaction pathway. Transition states (TSs) were determined using the climbing image nudged elastic band (CI-NEB) algorithm and

Fig. 1 Configurations of the NiOOH (001) and (010) surfaces: **a** side view of NiOOH (001), **b** top view of NiOOH (001), **c** side view of NiOOH (010), **d** top view of NiOOH (010). Red, blue, and white balls denote the O, Ni, and H atoms, respectively

the dimer method [50, 51]. A total of five images generated from the linear interpolation between the initial state (IS) and the final state (FS) were used as the initial prediction for the reaction coordinates and were optimized using the nudged elastic band algorithm. The dimer method was then used on the images close to the TS to locate the exact saddle point. The activation barrier (E_a) was determined as the energy difference between the TS and IS, and the reaction energy was calculated as the energy difference between the FS and IS. Frequency analysis was applied to all stationary points. The TSs were confirmed to have one imaginary

mode corresponding to the mode for C–H bond breaking. Zero-point energy corrections were applied to all reported energy values.

Adsorption energy (E_{ads}) is defined as

$$E_{\text{ads}} = E_{\text{adsorbate/surface}} - E_{\text{surface}} - E_{\text{adsorbate}} \quad (1)$$

where $E_{\text{adsorbate/surface}}$, E_{surface} , and $E_{\text{adsorbate}}$ represent the total energies of the slab with the adsorbate, the clean slab, and the isolated adsorbate, respectively.

Results and Discussion

Thermal Stability of NiOOH

To test whether NiOOH has sufficient thermal stability during propane ODH reaction, we first calculated the dehydration of surface hydroxyl groups from the NiOOH (001) and (010) surfaces to form water. The results are shown in Fig. 2. On the NiOOH (001) surface, a proton transfers from one hydroxyl group to another to form adsorbed H_2O (Fig. 2a), which has a high activation barrier of 2.25 eV and is endothermic by 1.05 eV. Subsequently, the H_2O desorbs from the surface, leaving an oxygen vacancy and consuming 0.82 eV energy. On the NiOOH (010) surface, the H_2O formation process (Fig. 2b) is similar to that on the (001) surface. However, it has a slightly higher activation barrier (2.51 eV) and is more endothermic (1.58 eV) than that on NiOOH (001). In addition, the desorption of H_2O is endothermic by 0.62 eV. Clearly, the dehydration from both NiOOH surfaces has high activation barriers (2.25–2.51 eV), which are remarkably higher than those for dehydrogenation of propane

Fig. 2 Geometries, activation energies, and reaction energies of water formation and desorption on NiOOH (001) and (010) surfaces: **a** gas-phase water formation on the (001) surface, **b** gas-phase water forma-

tion on the (010) surface. Solid lines: O–H distance (Å) in TS configurations

(0.66–1.27 eV, see below). Therefore, we expect the NiOOH to have sufficient thermal stability during propane ODH.

Adsorption of Propane

To study the mechanism of propane ODH, the IS of a possible reaction pathway must be established. Figure 3 displays two possible adsorption configurations of propane on each surface: (a) and (b) on NiOOH(001), and (c) and (d) on NiOOH(010). The corresponding adsorption energies, selected interatomic distances, and Bader charges are summarized in Table 1. As shown in Table 1, E_{ads} of propane on both surfaces are low, and the values on surface (001) are generally more negative than the corresponding configurations on surface (010), indicating a slightly stronger dispersive interaction on NiOOH (001). However, the low E_{ads} values on both surfaces also indicate the physisorptive nature of propane on these surfaces; these values are consistent with the small Bader charges on the O and H atoms.

Propane ODH on NiOOH (001) and (010) Surfaces

Reaction Mechanism

Primary and secondary hydrogen atoms may be abstracted; thus, four propane ODH reaction pathways are possible on the NiOOH (001) and (010) surfaces. The activation of the C–H bonds in alkanes may follow two mechanisms: concerted [52] and radical-mediated [23] mechanisms. The adsorption of alkane on the surface is the first step shared

Table 1 Adsorption energies, interatomic distances, and net charges on O and H atoms in different adsorption configurations

	E_{ads} (eV)	$d_{\text{C-H}}$ (Å)	$d_{\text{O-H}}$ (Å)	O charge	H charge
(a)	−0.40	C_1^-	$\text{H}_2\text{-O}=2.07$	−0.04	0.05(H_2)
		$\text{H}_1=1.10$			
		C_2^-			
		$\text{H}_2=1.11$			
(b)	−0.43	C_3^-	$\text{H}_1\text{-O}=2.12$	−0.05	0.05(H_1)
		$\text{H}_3=1.10$			
		C_1^-			
		$\text{H}_1=1.10$			
(c)	−0.13	C_2^-	$\text{H}_2\text{-O}=2.40$	−0.10	0.04(H_2)
		$\text{H}_2=1.10$			
		C_3^-			
		$\text{H}_3=1.10$			
(d)	−0.19	C_1^-	$\text{H}_1\text{-O}=2.46$	−0.08	0.04(H_1)
		$\text{H}_1=1.10$			
		C_2^-			
		$\text{H}_2=1.11$			
		C_3^-			
		$\text{H}_3=1.10$			

Negative charge values indicate gaining electronic charge, whereas positive values indicate losing electron

Fig. 3 Stable adsorption configurations of propane on NiOOH (001) and (010) surfaces. **a** IS of reaction pathway A of propane ODH on NiOOH (001); **b** IS of reaction pathway B of propane ODH on NiOOH (001); **c** IS of reaction pathway C of propane ODH on NiOOH (010); **d** IS of reaction pathway D of propane ODH on NiOOH (010). The arrows pointing to the bonds where the first step C–H bonds activation occurs in pathways. Dash lines: O–H distance (Å) in adsorption configuration

by both mechanisms. In the concerted mechanism, the alkane molecule first dehydrogenates to form an alkyl group adsorbed on the catalyst. The concerted pathway features a four-center TS in which the Lewis base site abstracts the hydrogen atom and the nearby Lewis acid center binds the carbon atom of the alkyl. In the radical mechanism, the hydrogen atom of a C–H bond is transferred to a surface O atom, forming a surface hydroxyl species. The alkyl radical may rapidly bind another surface O atom, resulting in a surface alkoxy species.

For propane ODH on NiOOH, we could not isolate a TS for the C–H activation following the concerted mechanism on either NiOOH (001) or (010). Based on the weak physisorptive nature and the steric hindrance of the propane molecule at the surface, we predicted that the reaction would likely follow the radical mechanism.

Following the radical mechanism, the formation of propylene from propane involves two consecutive dehydrogenation steps. The first dehydrogenation step converts propane (C_3H_8) to a propyl radical species (C_3H_7^*), and propyl radical species bind to the surface (C_3H_7^*). The second dehydrogenation step transforms the surface propyl species (C_3H_7^*) to propylene (C_3H_6). Two propyl species, i.e., n-propyl ($\text{CH}_3\text{CH}_2\text{CH}_2^*$) and i-propyl ($(\text{CH}_3)_2\text{CH}^*$), may form,

depending on the order of the H atom being abstracted first. In the present study, gas-phase radical coupling reactions were not considered.

Reaction Pathways on NiOOH (001) and (010) Surfaces

Four possible pathways, depending on the ISs on the two surfaces, have been identified and are shown in Fig. 3. The pathway that starts by first abstracting a secondary hydrogen atom of the propane on the (001) surface is denoted as pathway A, whereas the one that starts by first abstracting a primary hydrogen atom is labeled as pathway B. The corresponding pathways on the (010) surface are designated as pathways C and D, respectively. The TSs along each pathway have been isolated and are shown in Figs. 4 and 5. The interatomic distances in the TSs are summarized in Table 2.

Along pathway A, the physisorbed propane (marked as IS-A) overcomes a barrier of 0.79 eV to break the secondary C–H bond and form an i-propyl radical, which is denoted as Int-A1. At TS-A1, the C–H bond of methylene is stretched from 1.10 to 1.39 Å, and the distance between the abstracted H atom and the lattice O atom is reduced to 1.27 Å. This dehydrogenation step is slightly exothermic by -0.03 eV. Subsequently, the i-propyl radical binds to another lattice O atom, forming intermediate state Int-A2 and releasing an energy of 2.59 eV. For the second dehydrogenation step, Int-A2 can be activated to form propylene (denoted as Int-A3) via TS-A2 with C–H and O–H distances at 1.41 Å and 1.29 Å, respectively. The activation barrier of the second dehydrogenation step is 0.74 eV. The second dehydrogenation step is slightly endothermic by 0.26 eV. Subsequently, the resulting propylene desorbs from the surface with an energy cost of 0.70 eV.

Fig. 4 Optimized geometries of TSs and reaction pathways of propane ODH on the NiOOH (001) surface. Pathway A: The first C–H bond activation step occurs at the methylene group. Pathway B: The C–H bond activation step occurs at the methyl group. Black dash line: catalyst cycle. The figures show the distances of O–H and C–H (Å)

Fig. 5 Reaction pathways of propane ODH on the NiOOH (010) surface and optimized geometries of TSs. Pathway C: The first C–H bond activation step occurs at the methylene group. Pathway D: The C–H bond activation step occurs at the methyl group. The bond distances of O–H and C–H are in Å

Table 2 Activation barriers (eV) and bond distances (Å) of the C–H and O–H in the TSs for the dehydrogenation steps

Surface	Elementary step	Activation barrier (eV)	$d_{\text{C-H}}$ (Å)	$d_{\text{O-H}}$ (Å)
(001)	$(\text{CH}_3)_2\text{CH}_2 \rightarrow (\text{CH}_3)_2\text{CH}^* + \text{H}^*$	0.79	1.39	1.27
	$(\text{CH}_3)_2\text{CH}^* \rightarrow \text{CH}_3\text{CHCH}_2^* + \text{H}^*$	0.74	1.41	1.29
	$(\text{CH}_3)_2\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^* + \text{H}^*$	1.00	1.51	1.28
	$\text{CH}_3\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHCH}_2^* + \text{H}^*$	0.66	1.31	1.37
(010)	$(\text{CH}_3)_2\text{CH}_2 \rightarrow (\text{CH}_3)_2\text{CH}^* + \text{H}^*$	0.89	1.61	1.55
	$(\text{CH}_3)_2\text{CH}^* \rightarrow \text{CH}_3\text{CHCH}_2^* + \text{H}^*$	0.85	1.59	1.53
	$(\text{CH}_3)_2\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2^* + \text{H}^*$	1.16	1.46	1.63
	$\text{CH}_3\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_3\text{CHCH}_2^* + \text{H}^*$	0.97	1.34	1.51

Following pathway B, the activation barrier of the first dehydrogenation step of activating the C–H bond of the methyl group is 1.00 eV, which is significantly higher than that of pathway A. The breaking of the second C–H bond has an activation barrier of 0.66 eV, which is lower than that in pathway A. The desorption of propylene is endothermic by 0.77 eV.

For propylene production on the (001) surface, the activation barriers of the first dehydrogenation step are higher than those of the other steps along pathways A and B; moreover, the difference is more evident in pathway B. To complete the catalytic cycle, two hydroxyl groups formed through propane dehydrogenation may disproportionate to form H_2O that has an activation barrier of 2.21 eV and is endothermic by 1.03 eV. Then, the formed H_2O desorbs from the catalyst surface, consuming an energy of 0.79 eV and leaving an oxygen vacancy behind. The overall H_2O formation and desorption process are highly endothermic, consuming an energy of 1.82 eV on the (001) surface. The reoxidation of the surface by gas-phase O_2 is exothermic, releasing an energy of 1.29 eV. The reoxidation of the vacancy O sites is facile in the presence of O and not likely relevant with kinetics in reaction [53, 54]. The activation barrier of H_2O formation from the ODH-formed –OH is similar to that from the original –OH on the clean NiOOH (001) surface and is much higher than that of dehydrogenation of propane. This comparison indicates that the dehydration step is likely the rate-determining step of the overall reaction, and the surface is stable during the reaction of propane ODH.

On the NiOOH (010) surface, the first dehydrogenation (IS-C) step following pathway C breaks the C–H bond of the methylene group to produce an i-propyl radical, whereas the hydrogen atom adsorbs on the lattice O atom. The resulting structure is denoted as Int-C1. This step overcomes an activation barrier of 0.89 eV and is exothermic by –1.15 eV. At the TS (denoted as TS-C1), the C–H bond is elongated from 1.10 to 1.61 Å, and the O–H distance decreases to 1.55 Å. Similar to pathway A, the resulting i-propyl radical binds to another lattice O atom to form intermediate Int-C2, releasing an energy of 2.56 eV as a result of strong adsorption. The

dehydrogenation of Int-C2 proceeds by elongating the C–H bond of the methyl group from 1.14 to 1.59 Å at TS-C2. This step has an activation barrier of 0.85 eV and is slightly exothermic by –0.20 eV. Meanwhile, the activation barriers of the two consecutive dehydrogenation steps are 1.16 and 0.97 eV along pathway D. Both steps must overcome higher activation barriers than the corresponding steps of pathway C.

Along pathways C and D, the desorption of propylene is endothermic by 0.79 and 0.64 eV, respectively. The dehydration from two ODH-formed hydroxyl groups that form H_2O has an activation barrier of 2.43 eV and is endothermic by 1.53 eV. Then, the desorption of H_2O with the formation of an oxygen vacancy consumes an energy of 0.66 eV. The overall H_2O formation and desorption on the (010) surface consumes an energy of 2.19 eV. The filling of the oxygen vacancy O on the (010) surface is strongly exothermic by –1.78 eV. On the (010) surface, propane dehydrogenation process is also more feasible than water formation.

The comparison of the pathways on the (001) surface (A and B) with those on the (010) surface (C and D) reveals that the (001) surface has lower activation barriers of dehydrogenation compared with (010) surface. Moreover, the water formation and desorption process on (001) surface are less endothermic than that on (010) surface. These results indicate that (001) surface is more kinetically feasible for propane ODH and thermodynamically favorable for H_2O formation process compared with the (010) surface. This result can be intuitively rationalized by examining the structures of the two surfaces: the (010) surface exposes more unsaturated O atoms, making it more oxidative than the (001) surface. Furthermore, the C–H bond of β -C, i.e., the C atom of the methylene group, is more facile to break compared with the C–H bonds of α -C. This observation is consistent with previous reports showing that the dissociation energy of the C–H bonds of the methyl group (420 kJ/mol) is higher than that of the methylene group (401 kJ/mol) [25, 55].

On the vanadia-based ODH catalysts, the activation barriers of dehydrogenation depend on the nature and oxidation state of vanadium [28, 56, 57]. For example, the activation

barriers of the first hydrogen abstraction on the monomeric and dimeric vanadium oxide supported on TiO_2 are 1.73 and 1.91 eV, respectively [57]. The activation barrier for breaking the first C–H bond of propane on an isolated silica-supported vanadium oxide site is 1.48 eV, whereas that for breaking the next C–H bond to form propylene increases to 1.92 eV [56]. The activation barriers we calculated are lower than those reported in the studies above, suggesting that lattice O atoms on NiOOH exhibit promising catalytic activity toward propane ODH. By contrast, the disproportion of hydroxyl groups to form H_2O is energetically more favorable on VO_x than on NiOOH because the most common active site on vanadium oxide-based catalysts is the vanadyl oxygen site. For example, the energy cost to produce gas-phase H_2O is only 1.27 eV on a monomer VO_x/TiO_2 [24].

To the best of our knowledge, a detailed DFT study of propane ODH on the NiO surface has not been reported. Lemonidou et al. [58] experimentally investigated the reaction mechanisms of ODH of ethane on Ni oxide-based catalysts and reported an activation energy of 0.95 eV at 330 °C. Based on the DFT results, the activation barriers for breaking the C–H bonds of ethane on the Co_3O_4 (111) surface are 1.02 and 0.87 eV [59]. Water formation from the two hydroxyls has the largest activation barrier (2.02 eV) and is the overall rate-determining step. Meanwhile, the activation barrier of propane ODH on Co_3O_4 (111) is 0.95 eV [60]. Compared with the literature results, the activation barriers of 0.66–1.16 eV for propane dehydrogenation on the NiOOH (001) and (010) surfaces are moderate, making NiOOH a good potential catalyst for propane ODH.

Selectivity of Propylene

The further oxidation of the dehydrogenation intermediates is the main reason for low propylene yield in propane ODH.

We have demonstrated that the NiOOH surfaces exhibit a reasonable activity for the first two steps of propane dehydrogenation. We also studied the further oxidation of propylene on the (001) and (010) surfaces (Fig. 6). Based on the adsorption structures of propylene from propane dehydrogenation, we mapped out the pathways for its further oxidation. Given that the surface oxygen sites next to the adsorbed propylene are now occupied by the H atoms, the further oxidation of propylene at these sites is not expected to occur. Consequently, the further oxidation of propylene is likely to happen at different sites of the surface through readsorption. Propylene oxidation is commonly considered to follow two pathways: (1) activation of the double bond by the lattice O atoms, resulting in the formation of propylene-oxy intermediate, which is believed to be a precursor of forming propylene epoxide; and (2) activation of the C–H bond of the terminal CH_3 group, resulting in an allyl radical and the hydroxyl group on the surface, with the radical considered to be a precursor for complete combustion. Similar to propane adsorption, propylene is physisorbed on the (001) and (010) surfaces. The physisorptive nature of propylene on the surfaces allows for further oxidation to follow the second mechanism, i.e., oxidation is initiated at the methyl group. The activation barriers for breaking the C–H bond of the methyl group on the (001) and (010) surfaces were calculated to be 1.14 and 1.27 eV and are exothermic by -0.12 and -0.51 eV, respectively. Interestingly, these activation barriers are higher than those of breaking the C–H bonds in the initial propane. Consequently, propylene formation is anticipated to be favorable over further oxidation.

On the basis of the Brønsted–Evans–Polanyi (BEP) relationship [61, 62], the activation barriers for the breaking of the C–H bond are linearly correlated with the bond dissociation energy (BDE) in the parent organic molecule and the association energy of H atom (HAE) to lattice O. By

Fig. 6 Reaction pathways of propylene oxidation on the NiOOH **a** (001) and **b** (010) surfaces. The overall reaction energy and activation barrier are shown for each pathway. The red lines denote the distances (Å) of O–H and C–H

contrast, the BEP relationship constructed on the basis of BDE and HAE neglects the contribution of the interaction between the catalyst and the organic moiety to the activation barrier in the TS [63]. This BEP relationship predicts a lower activation barrier for the activation of weaker allylic C–H bond in propylene compared with the activation of strong C–H bonds in propane; this prediction is not consistent with the present results. Thus, the interaction between organic radical and hydroxylated surface oxygen at the TS must be considered [63]. The *i*-propyl and *n*-propyl radicals exhibit a highly localized electron density at the C atom on which the C–H bond activation occurs. By contrast, as a result of propylene dehydrogenation, the allylic organic radical has an unpaired electron, which becomes delocalized. The delocalization of the unpaired electron weakens the interaction of the allylic radical, consequently destabilizing the TS. Thus, the activation barrier for the activation of the weak allylic C–H bond in propylene is higher than the BEP relationship prediction that only considered BDE and HAE [63]. In addition, the distances of O–H and C–H in TSs (Fig. 6) show that the TS for breaking the allylic C–H bond (C–H bond in CH₃ group) of propylene occurs earlier along the reaction coordinate compared with those for the formation of propylene by dehydrogenation (Figs. 4, 5) and therefore has weaker radical-surface interactions at TS [64, 65]. Based on these analyses, we predict that the NiOOH-based propane ODH catalysts will result in high selectivity and high propylene yield.

NiOOH has been shown as a catalyst for OERs [36, 37, 66], and the exposed surface O sites play a vital role for its OER activity [49]. In the present work, we showed that the O sites on the NiOOH surface can activate the C–H bonds of propane. Compared with the other ODH catalysts, the NiOOH-based catalysts exhibit comparatively low activation barriers for propane dehydrogenation. Moreover, intermediate configurations indicate that the further oxidation of adsorbed propylene is effectively inhibited on NiOOH due to the formation of the surface hydroxyl groups, making NiOOH a selective propane ODH catalyst with balanced activity and selectivity.

Electronic Origin of the Activity for ODH

Bader Charge Analysis

The breaking of the C–H bonds involves electron transfer from the H atom to the lattice O atom; thus, the electronic property of the lattice O atom is expected to have a significant effect on ODH activity. To understand the electronic origin of the activity of the NiOOH (001) and (010) surfaces for activating the C–H bond, we analyzed the electronic structures of the surface. Following the activation of the C–H bond, the *s* electron of the H atom is partially

transferred to the *p* orbitals of the lattice O atom. The Bader charge analysis shows that the lattice O atom becomes more negative after binding the H atom. In addition, the electronic affinity of the lattice O atom is positively correlated with dehydrogenation activity.

As shown in Table 3, the activation barrier of the first dehydrogenation step from the secondary C–H bond of propane is directly proportional to the net charge on the lattice O atom, i.e., the higher the charge on the O atom, the higher the activation barrier. The difference of Bader charges of the lattice O atoms is also closely related to the Ni–O bond lengths on the NiOOH (001) and (010) surfaces. The Ni–O bonds on the (001) and (010) surfaces are 1.96 and 1.90 Å, respectively. A short Ni–O bond distance on the (010) surface corresponds to the lattice O atoms gaining additional electrons from the Ni atom while reducing its ability of abstracting H. Consequently, the NiOOH (010) surface exhibits a lower dehydrogenation activity compared with the (001) surface.

Density of States Analysis

To understand the different activities of the (001) and (010) surfaces further, we analyzed the density of states (DOSs). Figure 7 shows the projected *p* DOSs of the O atom involved in the C–H bond activation and *d* DOSs of Ni atoms next to the O atom. As shown in the projected DOSs, the *p*-derived features dominate in the energy range close to the Fermi level. As an indicator of Pauli repulsion, the relative position of the *p* states of the O atom to the Fermi level was used to predict the activity for C–H bond activation. The closer the edge of the *p* states to the Fermi level, the more active the O atom becomes to break the C–H bond [28, 29]. As shown in Fig. 7a, the *p* states of the O atom on the NiOOH (001) surface (blue line) is closer to the Fermi level compared with the O atom on the NiOOH (010) surface. This order of the *p* states is consistent with the activity order of these surfaces to break the C–H bonds.

Table 3 Net Bader charge of the lattice O atom and the activation barrier of the first dehydrogenation step from the secondary C–H bond on different surfaces from propane

Surface	Net Bader charge of O	Activation barrier (eV)
NiOOH (001)	−0.79	0.79
NiOOH (010)	−0.89	0.89

Fig. 7 **a** pDOSs of lattice O atoms; **b** dDOSs of Ni atoms

Conclusions

In this work, we report a DFT computational study of selective propane ODH to propylene on the NiOOH (001) and (010) surfaces. Our results show that propane and propylene are physisorbed on the NiOOH (001) and (010) surfaces. Four possible reaction pathways for propane ODH on the NiOOH (001) and (010) surfaces (i.e., two on each surface) are identified and examined. The reaction follows a radical mechanism in which the activation barriers for breaking the C–H bonds are moderate. The hydroxyl groups formed in the dehydrogenation steps of forming propylene on the NiOOH (001) and (010) surfaces limit the accessibility to active O atoms and become disproportionate in the form of H₂O. The relatively weak interaction between the allylic radical and catalyst surface destabilizes the TSs due to the delocalization of unpaired electrons, resulting in a higher activation barrier for propylene dehydrogenation compared with that for propane dehydrogenation. These results demonstrate that NiOOH is a promising catalyst for propane ODH with improved activity and selectivity over the vanadia-based ODH catalyst. The C–H bond activation barriers correlate with the net charge on the active lattice O atoms. These

understandings are beneficial for the design of highly active and selective catalysts for the ODH of propane and other alkanes.

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