Supporting Information

Tuning selectivity in nickel oxide-catalyzed oxidative dehydrogenation of ethane through control over non-stoichiometric oxygen density

Xiaohui Zhao, Mariano D. Susman, Jeffrey D. Rimer*, and Praveen Bollini*

Department of Chemical and Biomolecular Engineering
University of Houston, 4726 Calhoun Rd., Houston, TX 77204, USA

*Correspondence sent to: jrimer@central.uh.edu or ppbollini@uh.edu

Table of Contents

<table>
<thead>
<tr>
<th>Section No.</th>
<th>Title</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Materials Characterization</td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>As-synthesized NiO cubes, octahedra and trapezohedra</td>
<td>S2-S3</td>
</tr>
<tr>
<td>1.2</td>
<td>Thermally treated NiO cubes</td>
<td>S4-S8</td>
</tr>
<tr>
<td>2</td>
<td>Kinetic results of ethane ODH over NiO</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Approach-to-equilibrium</td>
<td>S9</td>
</tr>
<tr>
<td>2.2</td>
<td>Selectivity-conversion data</td>
<td>S10-S11</td>
</tr>
<tr>
<td>2.3</td>
<td>Ethene oxidation</td>
<td>S12</td>
</tr>
<tr>
<td>2.4</td>
<td>Water inhibition</td>
<td>S13-S14</td>
</tr>
<tr>
<td>3</td>
<td>NSO density derivation</td>
<td>S15</td>
</tr>
<tr>
<td>4</td>
<td>References</td>
<td>S16</td>
</tr>
</tbody>
</table>
1. Material Characterization

1.1 As-synthesized NiO cubes, octahedra and trapezohedra. All three samples synthesized via molten salt routes show a single phase that matches with the NiO reference pattern. Each faceted NiO presumably exposes a single type of surface facet; NiO \{100\} for cubes, \{311\} for trapezohedra, and \{111\} for octahedra. The proposed surface terminations and surface coordination numbers are shown in Scheme S1.

![Fig. S1 Powder X-ray diffraction patterns of NiO (a) cubes, (b) octahedra, and (c) trapezohedra prepared by molten salt synthesis. (d) NiO reference pattern: ICSD-9866, cubic, Fm-3m (225).](image_url)
Scheme S1 Proposed surface structures of NiO (a) cubes exposing Ni/O-terminated {100} facets, (b) trapezohedra exposing O-terminated {311} facets, and (c) octahedra exposing O-terminated {111} facets. Crystal planes are indicated in light grey. Oxygen anions and nickel cations are indicated in yellow and grey spheres, respectively.
1.2 Thermally treated NiO cubes. PXRD patterns and SEM images show that NiO cubes were morphologically stable upon thermal treatments up to 1000 °C. Nitrogen physisorption isotherms suggest a loss in BET surface areas from 1.33 to 0.7 m$^2$ g$^{-1}$ with increasing treatment temperature. The changing surface areas were taken into account when comparing areal rates.

Fig. S2 Powder X-ray diffraction patterns of NiO samples treated at 400–1000 °C for 5 h.
**Fig. S3** Scanning electron micrographs of NiO cubes after thermal treatments at 400–1000 °C for 5 h. Scale bars equal 1 µm.

**Fig. S4** SEM images of NiO catalysts after thermal treatment at a) 400 °C and b) 1000 °C for 5h. Histograms showing the particle size distribution of c) NiO$_{400}$ and d) NiO$_{1000}$. 
Fig. S5. Nitrogen physisorption isotherms of (a) NiO cubes after thermal treatment at 400–1000 °C for 5 h and (b) Repeat measurements on the NiO_{500} sample.

Table S1 Physical properties of as-synthesized NiO and samples after thermal treatment at 400–1000 °C

<table>
<thead>
<tr>
<th>sample</th>
<th>S_{BET} (m^2 g^{-1})</th>
<th>TPD onset temperature (°C)</th>
<th>H_2-TPD onset temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO as synthesized</td>
<td>1.40</td>
<td>380</td>
<td>-</td>
</tr>
<tr>
<td>NiO_{400}</td>
<td>1.33</td>
<td>400</td>
<td>312</td>
</tr>
<tr>
<td>NiO_{500}</td>
<td>1.18</td>
<td>428</td>
<td>312</td>
</tr>
<tr>
<td>NiO_{600}</td>
<td>0.99</td>
<td>510</td>
<td>325</td>
</tr>
<tr>
<td>NiO_{700}</td>
<td>0.77</td>
<td>515</td>
<td>331</td>
</tr>
<tr>
<td>NiO_{1000}</td>
<td>0.70</td>
<td>-</td>
<td>351</td>
</tr>
</tbody>
</table>
Table S2 XPS-derived surface atomic compositions of NiO samples thermally treated at 400, 700, and 1000 °C.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>NiO&lt;sub&gt;400&lt;/sub&gt;</th>
<th>NiO&lt;sub&gt;700&lt;/sub&gt;</th>
<th>NiO&lt;sub&gt;1000&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.2</td>
<td>48.2</td>
<td>48.8</td>
</tr>
<tr>
<td>Ni</td>
<td>27.6</td>
<td>33.7</td>
<td>37.1</td>
</tr>
<tr>
<td>C</td>
<td>27.1</td>
<td>16.4</td>
<td>14.2</td>
</tr>
<tr>
<td>Na</td>
<td>1.1</td>
<td>1.4</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>K</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Fig. S6 TPD profiles of as-synthesized Ni<sub>1-x</sub>O cubes thermally treated under various conditions prior to O<sub>2</sub> desorption analyses as follows: (a) heated up inside the reactor to 600 °C and maintained for 5 h following by natural cooling to room temperature under 100 mL min<sup>-1</sup> He flow (TPD analysis immediately followed without exposure to air), (b‒c) similarly treated in a muffle furnace under static lab air at 600 °C for (b) 0, (c), 5 and (d) 15 h (i.e., exposed to ambient conditions and then transferred to the reactor for TPD measurements). In all cases, heating rates were 2.5 °C min<sup>-1</sup>.
In Fig. S7, the UV–Vis absorption spectra after TPD (traced green) are shown in comparison with those measured before TPD (traced black). For NiO_{400}–NiO_{700} samples, subjection to TPD protocols increased their degree of stoichiometry, and therefore they showed lower absorption backgrounds. For NiO_{1000}, the absorption spectrum was not altered after TPD, suggesting that the highest degree of stoichiometry has been reached at 1000 °C, and did not increase further upon TPD.

**Fig. S7** (a) UV–Vis absorption spectra of NiO cubes thermally treated at different temperatures after synthesis (indicated in the legend), and (b) corresponding absorption spectra of the same samples after TPD measurements.
2. Kinetic results of ethane ODH over NiO

2.1 Approach-to-equilibrium. The approach-to-equilibrium \( \eta \) \( (0 \leq \eta \leq 1) \) measures the distance of the reaction from equilibrium. Under typical operating conditions for ODHE: 700 K, \( P_{C_2H_6} = 10 \) kPa, \( P_{O_2} = 10 \) kPa and 10% conversion, the values of \( \eta \) for all three reactions are much smaller than unity (eq. S3, S6, S9), suggesting that the reactions are far from equilibrium with negligible extent of reverse reaction. Therefore, the overall reaction rate \( v = v^+ - v^- = v^+ \).

\[
C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \quad \Delta G_{700K}^0 (ODH) = -180 \text{ kJ/mol} \tag{S1}
\]

\[
K_{eq,ODH} = \exp \left( - \frac{\Delta G_{700K}^0}{RT} \right) = 2.7 \times 10^{13} \tag{S2}
\]

\[
\eta_{ODH} = \frac{1}{K_{eq}} \times \frac{[P_{C_2H_4}] [P_{H_2O}]}{[P_{C_2H_6}] [P_{O_2}]^{0.5}} = 1 \times 10^{-16} \tag{S3}
\]

\[
C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O \quad \Delta G_{700K}^0 (ethane total oxidation) = -1601 \text{ kJ/mol} \tag{S4}
\]

\[
K_{eq, ethane total oxidation} = \exp \left( - \frac{\Delta G_{700K}^0}{RT} \right) = 3 \times 10^{119} \tag{S5}
\]

\[
\eta_{ethane total oxidation} = \frac{1}{K_{eq}} \times \frac{[P_{H_2O}]^3 [P_{CO_2}]^2}{[P_{C_2H_6}] [P_{O_2}]^{3.5}} = 5 \times 10^{-123} \tag{S6}
\]

\[
C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta G_{700K}^0 (ethane total oxidation) = -1388 \text{ kJ/mol} \tag{S7}
\]

\[
K_{eq, ethene total oxidation} = \exp \left( - \frac{\Delta G_{700K}^0}{RT} \right) = 4 \times 10^{103} \tag{S8}
\]

\[
\eta_{ethene total oxidation} = \frac{1}{K_{eq}} \times \frac{[P_{H_2O}]^2 [P_{CO_2}]^2}{[P_{C_2H_4}] [P_{O_2}]^3} = 1.4 \times 10^{-107} \tag{S9}
\]
where $\Delta G_{700K}^0 (i)$ is the standard Gibbs free energy at 700 K, $K_{eq,i}$ is the equilibrium constant, and $\eta$ is the approach-to-equilibrium of reaction $i$. 
2.2 *Selectivity-conversion data.* Decreasing ethene selectivity with increasing ethane conversion (Fig. S8) is consistent with the conversion of ethene to CO\(_2\) through secondary reactions \((r_3)\). The existence of \(r_3\) from ethene to CO\(_2\) is also consistent with decreasing ethene formation rates with increasing residence time (Fig. S9). However, CO\(_2\) formation rates were also found to decrease, not increase, with residence time, which is inconsistent with CO\(_2\) formation through secondary reactions; therefore, we suspect that CO\(_2\) formation is inhibited by product concentrations.

Scheme S2. Proposed reaction network for ethane oxidation reactions

Fig. S8 Ethene selectivity plotted as a function of ethane conversion. Increasing ethane conversion was achieved by increasing residence times from 0.1 to 1.6 g s cm\(^{-3}\). Reaction conditions: 375 °C, 10 kPa C\(_2\)H\(_6\), 10 kPa O\(_2\), balance He.
**Fig. S9** Formation rates of ethene (▲) and CO₂ (■) as a function of residence time. Reaction conditions: 375 °C, 10 kPa C₂H₆, 10 kPa O₂, balance He.
2.3  *Ethene oxidation.* Rates of ethene oxidation—the secondary reaction of ethane ODH—were tested. CO₂ and H₂O are the only observed products. Ethene showed rates comparable to the total oxidation of ethane (Fig. S10a). Meanwhile, ethene oxidation rates increased with C₂H₄ pressure (Fig. S10b). Based on these results, we expect that with 0.04 kPa C₂H₄ at typical ethane conversions, \( r_3 \) was approximately \( 2.1 \times 10^{-7} \) mol min⁻¹, which was insignificant compared with \( r_2 \).

Table S3. Bond dissociation energy (BDE) of ethane (C₂H₆) and ethene (C₂H₄) at 298 K

<table>
<thead>
<tr>
<th>molecule</th>
<th>bond type</th>
<th>BDE (kJ/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃CH₃</td>
<td>C-C</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>410</td>
</tr>
<tr>
<td>H₂C=CH₂</td>
<td>C=C</td>
<td>682</td>
</tr>
<tr>
<td></td>
<td>C-H</td>
<td>452</td>
</tr>
</tbody>
</table>

**Fig. S10** (a) Total oxidation rate of ethane (▲) and ethene (■). Reaction conditions: 375 °C, 10 kPa C₂H₆/C₂H₄, 10 kPa O₂, balance He. (b) CO₂ formation rate at increasing ethene pressure. Reaction conditions: 375 °C, 10 kPa O₂, 2-20 kPa C₂H₄, balance He.
2.4 *Water inhibition.* Decreasing ethene and CO$_2$ formation rates with residence time are consistent with the presence of product inhibition. To test this hypothesis, 1–10 kPa H$_2$O was cofed during reaction. We observed decreasing rates with increasing H$_2$O pressure; besides, these rates are invariant in residence time, consistent with H$_2$O inhibition. We envision that in the absence of water cofeeds, the average water pressure increases with conversion (Scheme S2a), thereby exerting a stronger inhibiting effect at higher residence times, which would explain the decreasing ethene and CO$_2$ formation rates with increasing residence time. Cofeeding excess water during ODHE creates constant water pressures along the bed, resulted in non-integral beds whose rates can directly be calculated from product molar flow rates (Scheme S2b).

![Fig. S11 Water inhibition effect on (a) ethene and (b) CO$_2$ formation rates. Reaction conditions: 400°C, 10 kPa C$_2$H$_6$, 10 kPa O$_2$, and 1–10 kPa H$_2$O.](image-url)
Scheme S2 Diagrams representing reaction rate (a) before and (b) after water cofeeds as a function of residence time.

Fig. S12 Ratios of ODHE ($r_1$) to total oxidation rates ($r_2$) as a function of TPR-derived NSO density for samples NiO$_{400}$ to NiO$_{1000}$. Error bars were obtained from rate measurements at three distinct residence times. Reaction conditions: 375 °C, 10 kPa C$_2$H$_6$, 10 kPa O$_2$, 1 kPa H$_2$O; C$_2$H$_6$ conversion less than 1%.
3. Derivation of the formula for TPD and TPR-derived NSO densities

Ni_{1-x}O samples with \( x \) being unknown have a molar mass \( M_{Ni_{1-x}O} = (1-x) \times 58.7 + 16 \) g mol\(^{-1}\). The total moles of sample, and the moles of Ni and O can then be expressed based on the mass of sample loaded during the TPD experiment (0.25 g). The difference between \( N_{Ni} \) and \( N_{O} \) is equal to the total moles of O desorbed during the TPD experiment, hence \( x \) can be solved for by integrating molar flow rates of \( O_2 \) over time. Once \( x \) is calculated, the NSO density can be further obtained.

\[
M_O = 16 \left( \frac{g}{mol} \right), \quad M_{Ni} = 58.7 \left( \frac{g}{mol} \right) \quad \text{(S10)}
\]

\[
M_{Ni_{1-x}O} = (1-x) \times 58.7 + 16 \left( \frac{g}{mol} \right) \quad \text{(S11)}
\]

\[
N_{Ni_{1-x}O} = N_O = \frac{0.25}{M_{Ni_{1-x}O}} \quad \text{(mol)} \quad \text{(S12)}
\]

\[
N_{Ni} = \frac{(1-x) \times 0.25}{M_{Ni_{1-x}O}} \quad \text{(mol)} \quad \text{(S13)}
\]

\[
N_O - N_{Ni} = \frac{0.25x}{M_{Ni_{1-x}O}} = \frac{0.25x}{(1-x) \times 58.7 + 16} = \frac{N_{O2,desorb}}{2} \quad \text{(mol)} \quad \text{(S14)}
\]

\[
\text{NSO density} = \frac{x_{TPD}}{1-x_{TPD}} = \frac{74.7 \times N_{O2,desorb}}{0.5 - 16N_{O2,desorb}} \left( \frac{\text{mol excess } O}{\text{mol Ni}} \right) \quad \text{(S15)}
\]

where \( M_O \) and \( M_{Ni} \) are the atomic mass of oxygen and nickel

\( x \) is the degree of non-stoichiometry in Ni_{1-x}O

\( M_{Ni_{1-x}O} \) is the molar mass of Ni_{1-x}O

\( N_{Ni_{1-x}O}, N_O, N_{Ni} \) are the mole of Ni_{1-x}O, O and Ni

\( N_{O2,desorb} \) is the total mole of \( O_2 \) that desorb during TPD

\( x_{TPD} \) is the degree of non-stoichiometry of Ni_{1-x}O as determined by TPD

In TPR experiments, the moles of Ni and O can be expressed in the same way based on the mass of sample loaded (0.02 g). The term \( N_O \) is equal to the total moles of H\(_2\) consumed during the H\(_2\)-
TPR experiment, following $\text{Ni}_{1-x} \text{O} + \text{H}_2 \rightarrow (1-x_{\text{TPR}}) \text{Ni} + \text{H}_2\text{O}$. Therefore, $x$ can be solved by calculating the total moles of H$_2$ consumed over time.

$$N_{\text{Ni}_{1-x} \text{O}} = N_O = \frac{0.02}{M_{\text{Ni}_{1-x} \text{O}}} = \frac{0.02}{(1-x) \times 58.7 + 16} = N_{\text{H}_2, \text{consumed}} \text{ (mol)}$$

(S16)

$$\text{NSO density} = \frac{x_{\text{TPR}}}{1 - x_{\text{TPR}}} = \frac{74.7 \times N_{\text{H}_2,\text{consumed}} - 0.02}{0.02 - 16N_{\text{H}_2,\text{consumed}}} \left(\frac{\text{mol excess } O}{\text{mol Ni}}\right)$$

(S17)

where $N_{\text{H}_2, \text{consumed}}$ is the total moles of H$_2$ that consumed during H$_2$-TPR

$x_{\text{TPR}}$ is the degree of non-stoichiometry of Ni$_{1-x}$O as determined by H$_2$-TPR

References