Conversion of $n$-butane and product selectivity was calculated from mole fraction of products in outflow as below:

Conversion of $n$-butane ($\%$) = \( \frac{[C_4H_{10}]_{in} - [C_4H_{10}]_{out}}{[C_4H_{10}]_{in}} \times 100 \) .......................................................... (1)

Conversion of oxidant ($\%$) = \( \frac{[\text{oxidant}]_{in} - [\text{oxidant}]_{out}}{[\text{oxidant}]_{in}} \times 100 \) .......................................................... (2)

Selectivity ($\%$) = \( \frac{\text{moles of the product}}{\text{total moles of the product}} \times 100 \) .......................................................... (3)

1. Mass and Heat Transfer Calculations for $n$-butane oxidation over Ni-Mo/Al$_2$O$_3$ catalyst

*Mears Criterion for External Diffusion (Fogler, p841; Mears, 1971)*

$n$-butane activation over oxygen:

If \( \frac{-r_A \rho_b R n}{k C_{ab}} < 0.15 \), then external mass transfer effects can be neglected.

\(-r_A\) = reaction rate, kmol/kg-cat · s = 4.98 x 10$^{-5}$ kmol-C$_3$/kg-cat · s

n = reaction order = 2

R = catalyst particle radius, m=3 x 10$^{-5}$ m

\( \rho_b \) = bulk density of catalyst bed, kg/m$^3$

\( \phi = (1-\phi) \) (\( \phi \) = porosity or void fraction of packed bed) = 1024 kg/m$^3$

\( \rho_c \) = solid catalyst density, kg/m$^3$= 1.28 m/s

\( C_{Ab} \) = bulk gas concentration of A, kmol/m$^3$ = 0.0075 kmol/m$^3$
\( k_c \) = mass transfer coefficient, \( m/s = 1.28 \ m/s \)

\[
- \frac{r_A^{'} \rho_b R_n}{k_c C_{ab}} = 3.12 \times 10^{-4} < 0.15 \ \{\text{Mears for External Diffusion}\}
\]

Similarly, for \( \text{CO}_2 = 2.85 \times 10^{-4} \) and for \( \text{N}_2 \text{O} = 1.72 \times 10^{-4} \)

2. Weisz-Prater Criterion for Internal Diffusion (Fogler, p839)

If \( C_{wp} = -\frac{r_A^{'}(\text{obs}) \rho_c R^2}{D_e C_{As}} < 1 \), then internal mass transfer effects can be neglected.

\[-r_A^{'}(\text{obs}) = \text{observed reaction rate, kmol/kg-cat} \cdot s = 5.05 \times 10^{-5} \ \text{kmol-C}_3/\text{kg-cat} \cdot s\]

\( R = \) catalyst particle radius, \( m = 3 \times 10^{-5} \ m \)

\( \rho_c = \) solid catalyst density, \( \text{kg/m}^3 = 3600 \ \text{kg/m}^3 \)

\( D_e = \) effective gas-phase diffusivity, \( m^2/s \) [Fogler, p815]

\[
= \frac{D_{AB} \phi_p \sigma_c}{\tau} \quad \text{where}
\]

\( D_{AB} = \) gas-phase diffusivity \( m^2/s; \ \phi_p = \) pellet porosity; \( \sigma_c = \) constriction factor; \( \tau = \) tortuosity.

\( C_{As} = \) gas concentration of \( A \) at the catalyst surface, \( \text{kmol-A/m}^3 = 0.0041 \ \text{kmol-C}_3/\text{m}^3 \)

\[
C_{wp} = -\frac{r_A^{'}(\text{obs}) \rho_c R^2}{D_e C_{As}} = 4.9 \times 10^{-4} < 1 \ \{\text{Weisz-Prater Criterion for Internal Diffusion}\}
\]

Similarly, for \( \text{CO}_2 = 4.07 \times 10^{-4} \) and for \( \text{N}_2 \text{O} = 2.28 \times 10^{-4} \)

3. Mears Criterion for Combined Interphase and Intraparticle Heat and Mass

Transport (Mears, 1971)

\[
- \frac{r_A^{'} R^2}{C_{ab} D_e} < \frac{1 + 0.33 \gamma \chi}{n - \gamma \beta_h |1 + 0.33 n \omega|}
\]

\[
\gamma = \frac{E}{R g T_s^3}; \ \gamma_b = \frac{E}{R g T_b^3}; \ \beta_b = \left( -\Delta H_f \right) \frac{D_e C_{ab}}{\lambda T_b}; \ \chi = \left( -\Delta H_f \right) \frac{-r_A^{'} R}{h_i T_b}; \ \omega = -\frac{r_A^{'} R}{k_c C_{ab}}
\]

\( \gamma = \) Arrhenius number; \( \beta_b = \) heat generation function;
\( \lambda \) = catalyst thermal conductivity, W/m.K;

\( \chi \) = Damköhler number for interphase heat transport

\( \omega \) = Damköhler number for interphase mass transport

\[-r_A' R^2 \over C_{AB} D_e \] = 3.11 x10^{-5} < 3 \{Mears Criterion for Interphase and Intraparticle Heat and

Mass Transport \}

Similarly, for CO\(_2\) = 2.15 x 10^{-5} and for N\(_2\)O = 1.72 x 10^{-5}

**Table S1:** The effect of metal oxide, support and promoter on the \( n \)-butane oxidative activation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( n )-butane conversion (mol %)</th>
<th>Oxidant</th>
<th>Temperature</th>
<th>TOF (s(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 % V(_2)O(_5)/SiO(_2)</td>
<td>1.2</td>
<td>Air</td>
<td>230</td>
<td>0.4 x 10^{-5}</td>
<td>[1, 2]</td>
</tr>
<tr>
<td>17.5 % V(_2)O(_5)/Al(_2)O(_3)</td>
<td>7.2</td>
<td>Air</td>
<td>230</td>
<td>0.9 x 10^{-5}</td>
<td>[1, 2]</td>
</tr>
<tr>
<td>6 % V(_2)O(_5)/Nb(_2)O(_5)</td>
<td>17.3</td>
<td>Air</td>
<td>230</td>
<td>3.6 x 10^{-5}</td>
<td>[1, 2]</td>
</tr>
<tr>
<td>4 % V(_2)O(_5)/ZrO(_2)</td>
<td>16.0</td>
<td>Air</td>
<td>230</td>
<td>4.5 x 10^{-5}</td>
<td>[1]</td>
</tr>
<tr>
<td>3 % V(_2)O(_5)/CeO(_2)</td>
<td>10.6</td>
<td>Air</td>
<td>230</td>
<td>6.3 x 10^{-5}</td>
<td>[1]</td>
</tr>
<tr>
<td>5 % V(_2)O(_5)/TiO(_2)</td>
<td>27.8</td>
<td>Air</td>
<td>230</td>
<td>19.6 x 10^{-5}</td>
<td>[1]</td>
</tr>
<tr>
<td>1 % V(_2)O(_5)/5 % P(_2)O(_5)/TiO(_2)</td>
<td>12.1</td>
<td>Air</td>
<td>230</td>
<td>27.0 x 10^{-5}</td>
<td>[1]</td>
</tr>
<tr>
<td>6 % WO(_3)/1 % V(_2)O(_5)/TiO(_2)</td>
<td>23.6</td>
<td>Air</td>
<td>230</td>
<td>34.1 x 10^{-5}</td>
<td>[1]</td>
</tr>
<tr>
<td>( \gamma )-Bi(_2)MoO(_6)</td>
<td>30.2</td>
<td>Air+steam</td>
<td>420</td>
<td>43.6 x 10^{-4}</td>
<td>[3]</td>
</tr>
<tr>
<td>( \beta )-Bi(_2)Mo(_2)O(_9)</td>
<td>39.8</td>
<td>Air+steam</td>
<td>320</td>
<td>57.8 x 10^{-4}</td>
<td>[3]</td>
</tr>
<tr>
<td>BiMoZr(_x) oxide</td>
<td>42.3</td>
<td>Air</td>
<td>440</td>
<td>6.11 x 10^{-4}</td>
<td>[4]</td>
</tr>
<tr>
<td>BiMoFe(_x) oxide</td>
<td>68.6</td>
<td>Air</td>
<td>420</td>
<td>9.23 x 10^{-4}</td>
<td>[5]</td>
</tr>
<tr>
<td>ZrFe(_{2-x})Al(_x)O(_4)</td>
<td>55.1</td>
<td>Air</td>
<td>420</td>
<td>7.96 x 10^{-4}</td>
<td>[6]</td>
</tr>
<tr>
<td>ZnFe(_2)O(_4)</td>
<td>41.3</td>
<td>Air</td>
<td>420</td>
<td>5.97 x 10^{-4}</td>
<td>[3, 7]</td>
</tr>
<tr>
<td>TiP(_2)O(_7)-M1</td>
<td>24.0</td>
<td>CO(_2)</td>
<td>530</td>
<td>3.47 x 10^{-4}</td>
<td>[8]</td>
</tr>
<tr>
<td>TiP(_2)O(_7)-M2</td>
<td>22.3</td>
<td>CO(_2)</td>
<td>530</td>
<td>3.22 x 10^{-4}</td>
<td>[8]</td>
</tr>
<tr>
<td>1.2 % Cr 2.8 %</td>
<td>10.2</td>
<td>CO(_2)</td>
<td>550</td>
<td>1.47 x 10^{-4}</td>
<td>[9]</td>
</tr>
<tr>
<td>Catalyst Type</td>
<td>Cr, V Composition</td>
<td>CO$_2$ Formation</td>
<td>Reaction Temperature (°C)</td>
<td>Carbon Dioxide Yield</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------</td>
<td>------------------</td>
<td>---------------------------</td>
<td>----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>V/MCM-41</td>
<td>1.2% Cr, 2.8% V</td>
<td>8.3</td>
<td>550</td>
<td>1.20 x 10$^{-4}$</td>
<td>[9]</td>
</tr>
<tr>
<td>V/ZSM-5</td>
<td>1.2% Cr, 2.8% V</td>
<td>7.2</td>
<td>550</td>
<td>1.04 x 10$^{-4}$</td>
<td>[9]</td>
</tr>
<tr>
<td>V/MCM-22</td>
<td>1.2% Cr, 2.8% V</td>
<td>6.1</td>
<td>550</td>
<td>8.81 x 10$^{-5}$</td>
<td>[9]</td>
</tr>
</tbody>
</table>

**XPS analysis of fresh reduced and reoxidised catalyst:**

**Figure S1**: X-ray photoelectron spectra (Mo 3d - S 2s region) of NiMo/Al$_2$O$_3$ catalysts. Reduced and reoxidised samples are included for comparison.
4. Kinetics of reduction and oxidation:

The kinetics of reduction and oxidation was calculated using Autochem 2920 Chemisorption analyser. A series of reduction (TPR) and oxidation (TPO) experiments (as explained in Experimental section) were done at different heating rates namely 2 °C/min, 5 °C/min, 7 °C/min, 10 °C/min, 14 °C/min and 20 °C/min. The data are plotted and the slope determined to calculate the rate, activation energy for reduction and oxidation [10].

![First order kinetics of reduction experiments of Ni-Mo/Al₂O₃ catalyst](image)

**Figure S2:** First order kinetics of reduction experiments of Ni-Mo/Al₂O₃ catalyst
**Figure S3:** Arrhenius relationship profile of reduction (with H$_2$) of Ni-Mo/Al$_2$O$_3$ catalyst

**Figure S4:** Arrhenius relationship profile of oxidation (with O$_2$) of Ni-Mo/Al$_2$O$_3$ catalyst
Figure S5: Arrhenius relationship profile of \( n \)-butane activation over different oxidants

References