Supplementary information

Unexpected bond activation of small organic molecules on a metal oxide – butane/CaO (100)

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1. Experimental setup

The measurements have been conducted by a home-built, triply-differentially pumped molecular beam system. The supersonic beam is attached to a scattering chamber, which contains a shielded mass spectrometer for thermal desorption spectroscopy (TDS) and adsorption probability measurements as well as an AES (Auger electron spectroscopy) system. The impact energy, Ei, of the molecules has been varied by seeding 3% of iso/n-butane in He combined with a variation of the nozzle temperature within 300–700 K. The measuring error in the initial adsorption probabilities, S0, amounts to ±0.02. Measurements have been taken for normal impact angles. In some of the TDS experiments, the gases also have been dosed on the sample with the molecular beam system, which keeps the background pressure while dosing the gas below 2x10⁻⁸ mbar and eliminates entirely contributions from the sample holder. The sample temperature could be reduced down to 100 K for the less conducting metal oxide by bubbling He gas through a LN₂ dewar. (For details of the TDS setup, see ref.²) The reading of the thermocouple has been
calibrated *in situ* (±5 K) by measuring the condensation temperature of alkanes; a nonlinear correction was required.

2. Sample cleaning

![Figure 1](image)

**Figure 1.** Sample characterization by Auger electron spectroscopy (1000 eV, $V_{pp} = 10$ V). Curve **a** as-received sample, **b** after 120-min annealing at 1000 K.

The CaO(100) surface (from Goodfellow) has been prepared by cleaving in air and polishing, as described in prior studies. The sample (10×10×2 mm) was immersed in petroleum for storage (CaO is hygroscopic) and has been rinsed in acetone and ethanol before being mounted in the vacuum chamber. Figure 1 (curve a) shows AES data of the as-received sample. Carbon contaminations are evident (see the AES line at 265 eV). After annealing cycles (see Figure 1, curve b: 120 min at 1000 K) in a vacuum, the carbon AES line intensity dropped below the
detection limit, and only Ca and oxygen AES peaks remained. A shift of the AES peaks (by ~20 eV) due to charging of the sample as compared with reference data was present.

The defect density of the sample has been estimated by CO and CO$_2$ TDS experiments as detailed in ref.\textsuperscript{4}, a procedure used before for metal oxide surfaces (see e.g. refs.\textsuperscript{5-7}).

3. Iso-butane TDS data

![Figure 2. TDS relative intensities of selected masses for I) 2 L iso-butane II) 60 sec beam exposure of iso-butane (E$_i$ = 0.74 eV, T$_g$ = 300 K). The mass spec. cracking patterns of III) iso-butane, IV) methane, V) ethane, and VI) ethylene are provided for comparison.](image)
4. Proposed mechanism of alkanes cracking on the oxide surface (see e.g. ref. 8, 9)

The initial step of the bond activation could follow this schematic:

\[
\text{Surface - O} + \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \rightarrow \text{Surface - OH} + \cdot \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \quad (1)
\]

\[
\cdot \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \rightarrow \text{CH}_2 = \text{CH}_2 + \cdot \text{CH}_2 - \text{CH}_3 \quad (2)
\]

Where Eq.(1) is the hydrogen abstraction step and Eq. (2) the C-C bond activation as discussed in the letter. The bond activation involved lattice oxygen. The branching ratios (included in the draft) are illustrated in the following:

**Figure 3.** Relative yields of methane and ethylene as a function of impact energy for *n*-butane and *iso*-butane.

The error of relative yields was computed using the general procedure for the relative standard deviation. It can be derived that for methane:
Here $Y$ – the relative yield of methane; $I_{\text{methane}}$ and $I_{\text{ethylene}}$ – TDS intensities of peaks at masses 16 and 28, respectively. $\Delta I_{\text{methane}}$ and $\Delta I_{\text{ethylene}}$ are the accuracies of the second significant digit for TDS intensities.

5. Low intensity of m/e = 26 signal in product fragmentation: possible reasons.

If ethylene is formed as a result of n/iso-butane cracking on the CaO (100) surface, the intensity of the signal detected at m/e = 26 may be expected to be strong. However, in Fig. 1 it is rather small. There are two plausible explanations:

a) Ethylene can desorb from the surface in form of a neutral particle as well as an ion. The electron-impact ionization cross section for $\text{C}_2\text{H}_4$ molecule is 5.115 Å$^2$, while for $\text{C}_2\text{H}_4^+$ it is equal to 2.455 Å$^2$ (see Ref.10). The decrease in the cross section value by a factor of two results in a significantly lower degree of ethylene fragmentation.

b) The fragment ion $\text{C}_2\text{H}_2^+$, corresponding to m/e = 26 in the fragmentation pattern of ethylene is highly reactive with molecular hydrogen.$^{11}$ Since $\text{H}_2$ is present in the background of the UHV chamber, it can mask the corresponding mass spectrometer signal. This reaction is exothermic and can occur at temperatures as low as 2 K at collision energies less than 0.5 meV.$^{11,12}$

\[ \text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H} \]

The heat of formation of $\text{C}_2\text{H}_3^+$ ion lies in the range $\Delta H^0 = 267-269$ kcal/mol.
6. Estimate of vibrational excitations

The fraction of n-butane molecules in the first excited state of the $i^{th}$ vibrational mode was estimated according to the following equation:\textsuperscript{13}

$$\frac{n_i}{N} = \frac{g_i e^{-\frac{\nu_i}{kT}}}{\sum q_j}; \quad q_j = (1 - e^{-\frac{\nu_j}{kT}})^{-g_j}$$

Here $q_i$ is the partition function, $T$ is the nozzle temperature, $g_i$ is the degeneracy, and $\nu_i$ is the frequency of the vibrational mode $i$. The vibrational frequencies of n-butane were calculated \textit{ab initio} using Gaussian 03 package (B3LYP/6-31G* level).

Table 1. Vibrational frequencies of $n$-butane and their degeneracy.

<table>
<thead>
<tr>
<th>$\nu_i$, cm$^{-1}$</th>
<th>$g_i$</th>
<th>$\nu_i$, cm$^{-1}$</th>
<th>$g_i$</th>
<th>$\nu_i$, cm$^{-1}$</th>
<th>$g_i$</th>
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<td>1537</td>
<td>1</td>
<td>3106**</td>
<td>4</td>
</tr>
</tbody>
</table>

*C-C stretching modes

**C-H stretching modes

For example, for $E_i$ kept constant at 1.3 eV (see arrow in Fig. 3), changing the gas temperature from 500 to 700 K, increases the fraction of n-butane in the first excited state for all vibrational modes from 0.089 to 0.12. The fraction of n-butane in specific excited states (C-C and C-H stretching modes) increases even more dramatically (from 0.0028 to 0.0069). Correspondingly, the value of $S_0$ rises by 0.14 ± 0.04.
Table 2. Relative population of the first vibrationally excited state for n-butane at different temperatures.

<table>
<thead>
<tr>
<th>Gas temperature, K</th>
<th>First excited state (all modes)-to-ground state ratio</th>
<th>C-C and C-H of the 1st excited state-to-ground state ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.051</td>
<td>0.00040</td>
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<td>400</td>
<td>0.071</td>
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<tr>
<td>500</td>
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<tr>
<td>700</td>
<td>0.122</td>
<td>0.0069</td>
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References