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.[1] 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, E_i, 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, S_0, 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 2×10^{-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 lN_2 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
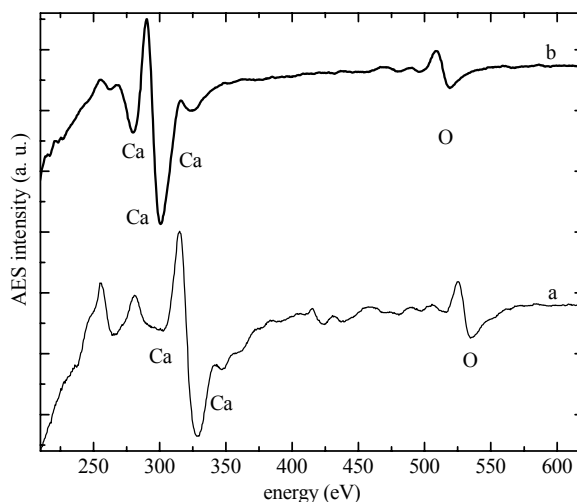
correction was required.

2. Sample cleaning

Figure 1. 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.[3] 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.[4], a procedure used before for metal oxide surfaces (see e.g. refs.[5-7]).
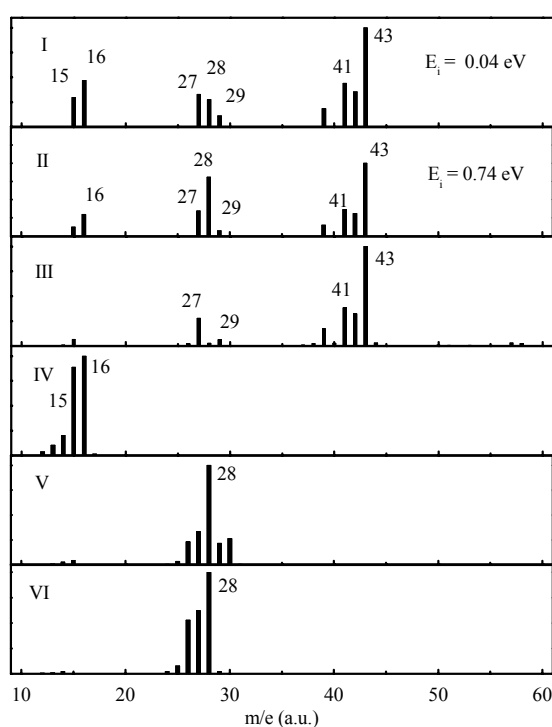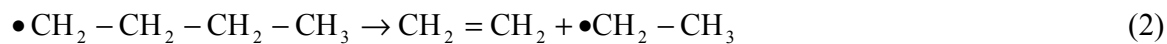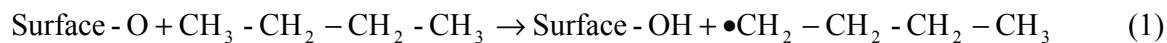
3. Iso-butane TDS data

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.

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:

$$Surface\text{-}O + CH_3\text{-}CH_2 - CH_2\text{-}CH_3 \rightarrow Surface\text{-}OH + \bullet CH_2 - CH_2\text{-}CH_2 - CH_3 \qquad (1)$$

$$\bullet CH_2 - CH_2 - CH_2 - CH_3 \rightarrow CH_2 = CH_2 + \bullet CH_2 - CH_3 \qquad (2)$$

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:
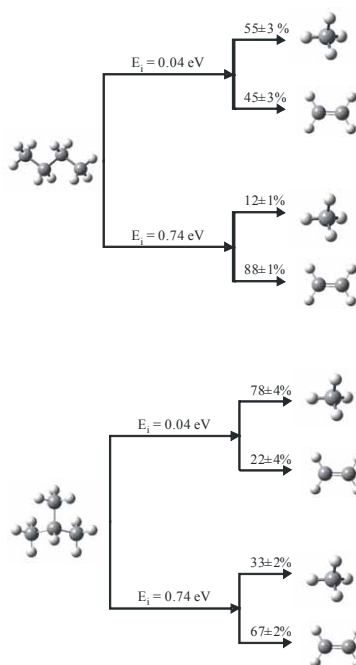

Figure 3. Relative yields of methane and ethylene as a function of impact energy for *n*-butane and *iso*-butane.

The error of relative yields was computed using the general procedure for the relative standard deviation. It can be derived that for methane:

$$\frac{\Delta Y_{methane}}{Y_{methane}} = \sqrt{\left(\frac{\Delta I_{methane}}{I_{methane}}\right)^2 + \frac{\Delta I^2_{methane} + \Delta I^2_{ethylene}}{(I_{ethylene} + I_{methane})^2}}$$

Here Y – the relative yield of methane; $I_{methane}$ and $I_{ethylene}$ – TDS intensities of peaks at masses 16 and 28, respectively. $\Delta I_{methane}$ and $\Delta I_{ethylene}$ 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 C_2H_4 molecule is 5.115 $Å^2$, while for $C_2H_4^+$ 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 $C_2H_2^+$, corresponding to m/e = 26 in the fragmentation pattern of ethylene is highly reactive with molecular hydrogen.[11] Since 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]

$$C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$$
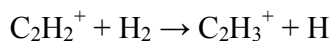
The heat of formation of $C_2H_3^+$ ion lies in the range $\Delta H° = 267\text{-}269$ kcal/mol.

6. Estimate of vibrational excitations

The fraction of n-butane molecules in the first excited state of the ith vibrational mode was estimated according to the following equation:[13]

$$\frac{n_i}{N} = \frac{g_i e^{-hv_i/kT}}{\sum_i q_i}; \quad q_i = (1 - e^{-hv_i/kT})^{-g_i}$$

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

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

v_i, cm^{-1}	g_i	v_i, cm^{-1}	g_i	v_i, cm^{-1}	g_i	v_i, cm^{-1}	g_i	v_i, cm^{-1}	g_i
122	1	820	1	1182	1	1440	1	1542	1
236	1	849	1	1225	1	1443	1	3018**	1
261	1	972	1	1307	1	1515	1	3025**	1
270	1	990	1	1340	1	1521	1	3040**	3
426	1	1027*	1	1348	1	1531	2	3062**	1
742	1	1073*	1	1418	1	1537	1	3106**	4

*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.

Gas temperature, K	First excited state (all modes)-to-ground state ratio	C-C and C-H of the 1st excited state-to-ground state ratio
300	0.051	0.00040
400	0.071	0.0013
500	0.089	0.0028
600	0.106	0.0046
700	0.122	0.0069

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