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

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We present the first example of bond activation of small alkanes (*n*-/iso-butane) on a metal oxide surface—CaO(100)—at ultra-high vacuum (UHV) conditions and at low surface temperatures studied by molecular beam scattering and thermal desorption spectroscopy.

Surface science research was historically focused on studying readily available metal single crystal surfaces due to their simple cleaning and characterization. However, most large-scale heterogeneously catalyzed reactions take advantage of catalysts which include metal oxide components. Therefore, the surface science of metal oxides became a vital research area of general interest for a still growing community.[1–3] However, most projects focused on systems such as TiO_2, MgO, and ZnO, for example. Inexpensive CaO catalysts have not been studied in detail by surface science techniques. Most important for heterogeneous catalysis is an understanding of the adsorption kinetics/dynamics of gas-phase species since this process is the first elementary step in all surface reactions. Molecular beam scattering techniques have often provided valuable insights.[4–10] Regarding metal oxides, the scattering of neutral probe particles is not affected by the conductivity of the samples, and highly defected or corrugated surfaces can be studied without the requirement to grow thin films. In particular, the surface chemistry of hydrocarbons is pertinent since the cracking of alkanes is vital for the petroleum industry, providing transportation fuels and chemical feedstock for synthesizing chemicals of greater value.

In this study, we present the first example we are aware of for bond activation of small alkanes on a metal oxide surface at ultra-high vacuum (UHV) conditions and at low surface temperatures, T_s, studied by means of UHV kinetics experiments. In addition, the alkane-to-surface energy transfer processes (adsorption dynamics) are strongly affected by the population of internal degrees of freedom of the alkanes as characterized by molecular beam scattering.[11–13] Theoretical studies predict great reactivity of CaO.[14,15] A higher activity of CaO as compared with, for example, MgO, is related to a lower Madelung potential, which leads to a more delocalized electron distribution of surface oxygen and hence to an eventually more efficient overlap with the orbitals of adsorbing molecules. In addition, oxygen vacancy sites are highly catalytically active for processes such as H_2O, O_2, and formic acid decomposition.[16,17]

The experiments were performed in a home-made supersonic molecular beam scattering system. CO and CO_2 thermal desorption spectroscopy (TDS) data indicated a defect density of 20–30%, *i.e.*,[18] the CaO(100) surface is partially reduced, providing a reference system for powder catalysts. Most likely those defects are pertinent for the high catalytic activity. Bond activation takes place already at 100 K, the lowest adsorption temperature used, and all fragments desorb at rather low temperatures ($T_s < 450$ K).

Panels I and II of Fig. 1 depict the results of multi-mass TDS experiments. The peak intensities shown were obtained by integrating TDS curves detected at a given m/e setting of the mass spectrometer. Thus, each panel summarizes the data collected in several TDS experiments. Panel I depicts results obtained by backfilling the UHV chamber with *n*-butane, while Fig. 1-II shows TDS data where the alkane was dosed on the surface by means of an energetic molecular beam. The impact energies, E_i, are indicated. The fragmentation pattern of gaseous *n*-butane, collected with the same mass spectrometer, is given in panel III. In the case of molecular

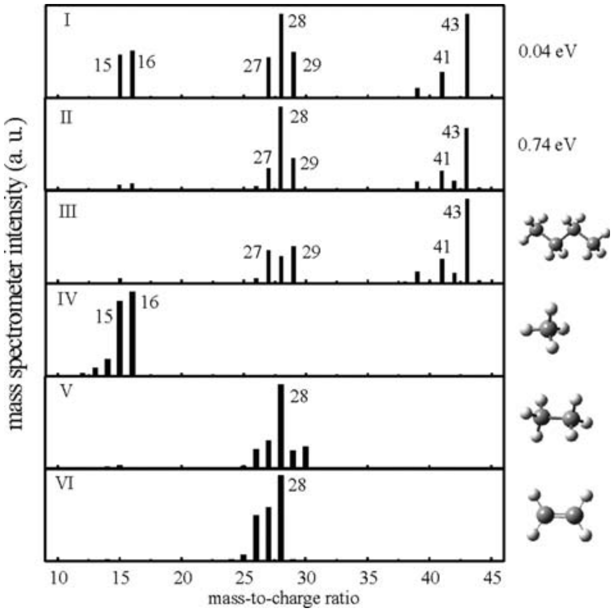

Fig. 1 (I & II) Adsorption of *n*-butane as studied by multi-mass thermal desorption spectroscopy (TDS); (III–VI) mass scans of *n*-butane, methane, ethane, and ethylene (gas phase).

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adsorption/desorption, the mass pattern obtained by TDS would match the one of the gaseous alkane. Clearly, the patterns differ distinctly, indicating bond breaking. Bond activation of alkanes is pertinent to utilize them in the chemical process industry.

More specifically, signals at $m/e = 15$ and 16 are present in the TDS data but not for the gaseous alkane. Interestingly, the impact energy of *n*-butane affects the mass pattern distinctly, indicating that bond activation takes place on the surface at 100 K and before the start of the temperature ramp. Second, the TDS intensity for $m/e = 28$ is significantly larger than in the gas phase mass spectra. The relative peak intensities at $m/e = 27$ and 29 are also greater than for gas phase *n*-butane. Furthermore, a large (background corrected) TDS signal for $m/e = 2$ corresponding to hydrogen abstraction was observed.

In order to identify the reaction products, fragmentation patterns of possible products are additionally depicted in Fig. 1, as indicated. The TDS peaks at $m/e = 15$ and 16 correspond to methane. The structure at $m/e = 28$ can result from fragmentation into ethane and ethylene. Since bond breaking is accompanied by hydrogen desorption and no signal was detected at $m/e = 30$ (characteristic for ethane), ethylene is most likely formed *via* hydrogen abstraction involving lattice oxygen, as suggested in prior catalysis studies.[19] Note that the formation of carbonates by CO_2 and lattice oxygen, likely affected by oxygen vacancy sites, is an established mechanism for CaO powders[16] and single crystals.[17] In addition, low-coordinated sites promote bond scission in alkanes.[20] The small intensity of the signal detected for $m/e = 26$, which is characteristic of ethylene fragmentation, can result from two mechanisms. First, C_2H_4 can desorb from the surface as an ion, which significantly lowers its electron-impact ionization cross section. Second, $C_2H_2^+$ readily reacts with hydrogen, even at low temperatures (see ESI for details†). Other reaction products—propane, propylene, 1-butene, 2-butene, and 1,3-butadiene—might be possible, which would lead to TDS features at $m/e = 29$, 39, and 41. However, the relative intensities of $m/e = 39$ and 41 peaks in TDS do not differ from those of the gaseous *n*-butane. Therefore, the formation of hydrocarbons with more than three C-atoms can be ruled out. In addition, Auger electron spectroscopy did not indicate carbon residuals on the surface,[21] and catalyst deactivation was absent.

Interestingly, the selectivity of *n*-butane cracking is related to the impact energy of the alkane and has been estimated from the TDS data. At low E_i, methane (55 ± 3%) and ethylene (45%) are formed approximately in equal amounts. However, at large E_i, ethylene (88%) is the main product (Fig. 2). The total alkane conversion efficiency amounts to approximately 25 ± 3% which appears to agree with the estimated defect density. For isobutane (see ESI†), larger amounts of methane are formed, which appears plausible considering the molecular structure of these alkanes. The TDS results already indicate the importance of internal degrees of freedom of the alkanes facilitating the bond activation as studied additionally by molecular beam scattering.

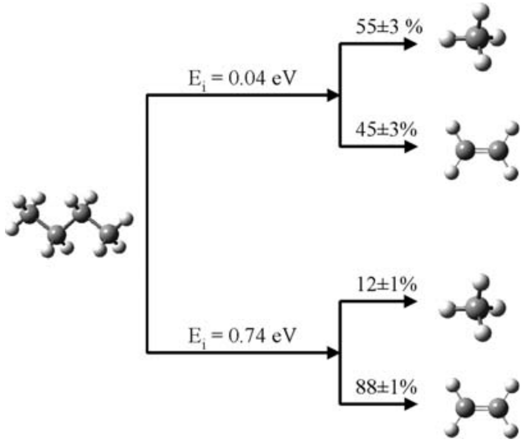

Fig. 2 Branching ratios of *n*-butane bond activation.

Fig. 3 summarizes the dependence of the initial reactivity, S_0, of the surface toward adsorption of the alkanes on impact energy for T_s just above the condensation temperature. A few technical comments need to be provided in order to discuss the results; however, for details see the ESI.† The average excitation of vibrational modes of the alkanes can be varied by changing the gas temperature, T_g, prior to expansion of the alkanes through the nozzle of the beam system as well as by using pure and mixed (alkane seed in He) gases while keeping E_i constant. The translational energy, E_i, and T_g, are indicated. S_0 decreases with E_i for the vibrationally cold alkanes and is systematically larger for the less spherical alkane, in agreement with a simple hard sphere model.[22] Interestingly, vibrationally hot alkanes (T_g large) have systematically larger S_0 than vibrationally cold alkanes at a given E_i (see arrow). Furthermore, S_0 increases with E_i for a hot beam while it decreases for the vibrational cold beam of alkanes. Thus, interestingly the alkane bond breaking and adsorption probability depends on the excitation of internal degrees of freedom. In addition, S_0 increases with T_s over the E_i range studied (not shown). The observed T_s dependence indicates that a precursor-mediated mechanism is active since a collisional activation occurs on a very short time scale with little effect of the surface temperature. Furthermore, the decrease in S_0 with E_i at low T_g is consistent with molecular adsorption.

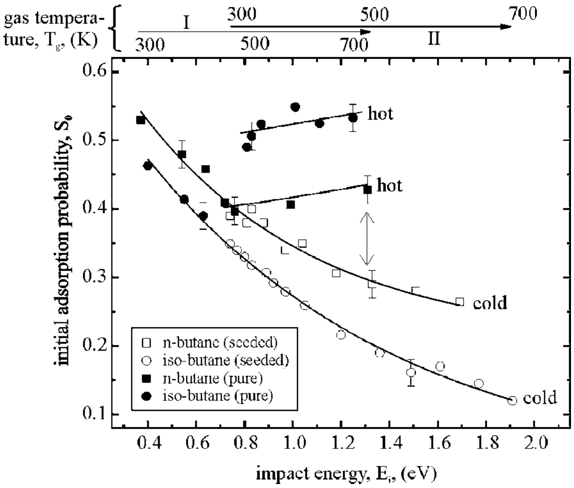

Fig. 3 Adsorption dynamics. (Section I) pure beams (solid symbols); (section II) 3% alkanes in He (open symbols).

Thus, the molecularly trapped alkanes diffuse along the surface and sample different adsorption sites and molecular configurations, some of which lead to bond activation and adsorbed fragments, as identified in subsequent TDS runs. In addition to this precursor-mediated adsorption pathway, a direct channel also exists since for vibrational hot alkanes S_0 increases slightly with E_i. Steric effects, leading to an enhancement in S_0 for spherical over linear alkanes, respectively, have also been seen for metal surfaces. Isobutane has a greater number of primary C–H bonds than *n*-butane, and these break more easily than secondary C–H bonds in direct dissociative adsorption.[23]

Some effects seen here—trapping mediated dissociation competing with direct dissociative adsorption and the importance of vibrational excitation—are quite similar to results obtained before for metal surfaces.[24] However, we are not aware of an example of bond activation in small alkanes on technologically important metal oxide surfaces. Alkanes adsorbed at UHV conditions molecularly on all other metal oxides studied heretofore with surface science techniques, including, for example, reduced ZnO and TiO_2.[26,27] However, indications for the unique catalytic activity of CaO come from studies of powders.[25] Furthermore, Ca-containing zeolites have been considered for industrial alkane cracking,[28] and other metal oxides have been tested for high-temperature/pressure alkane conversion.[19] Certainly, more work is required to elucidate details of the mechanism, including the effect of oxygen vacancy sites; CaO materials promise unexpected results also for other catalytic processes.

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