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C–H bond activation by nanosized scandium oxide clusters in gas-phase

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ABSTRACT

Scandium oxide cluster cations are prepared by laser ablation and reacted with *n*-butane in a fast flow reactor. A reflectron time-of-flight mass spectrometer is built to detect the cluster distribution before and after the reactions. Hydrogen atom abstraction (HAA) products $(Sc_2O_3)_NH^+$ ($N = 1–22$), $(Sc_2O_3)_NO_4H^+$ ($N = 4–22$) and their deuterated compounds are observed upon the cluster interactions with n-C_4H_{10} and n-C_4D_{10}, respectively. This indicates that C–H bond activation of *n*-butane over atomic clusters as large as $Sc_{44}O_{66}^+$ and $Sc_{44}O_{70}^+$ can take place in gas phase. The experimentally determined rate constants and values of kinetic isotopic effect for HAA vary significantly with the cluster sizes. Density functional theory (DFT) calculations are performed to study the structures and reactivity of small clusters $(Sc_2O_3)_{1-3}^+$. The DFT results suggest that the experimentally observed C–H bond activation by $(Sc_2O_3)_N^+$ is facilitated by oxygen-centred radicals bridgingly bonded in the clusters. The nature of unpaired spin density distributions within the clusters may be responsible for the experimentally observed size-dependent reactivity.

1. Introduction

Direct transformation of alkanes that are major constituents of natural gas and oil into more valuable products is a difficult problem. Activation of the strong and localized C–H bonds that are usually chemically inert at low temperature is an essential step in alkane transformation [1–4]. It is of interest and potentially useful to generate and study chemical entities that are able to activate C–H bonds efficiently at low temperatures, preferably room temperature, which may serve as a first step to solve serious problems involved with alkane transformation at high temperature that often results in low product selectivity, primary formation of thermodynamically stable by-products (such as carbon dioxide and water in the reaction with oxygen) and other related problems of economics and environments [1,5].

It has been reported that efficient C–H bond activation can take place over many atoms, ions, and atomic clusters, among which transition metal oxide (TMO) clusters [3,4,6–11] are an important type. By using mass spectrometry, the TMO cluster systems such as $(V_2O_5)_{1-5}^+$ [12,13], $V_{4-k}Y_kO_{10-k}^+$ ($k = 1–3$) [14], $V_{4-k}P_kO_{10}^+$ ($k = 1$ and 2) [15,16], $V_2O_5(SiO_2)_{1-4}^+$ and $V_2O_6(SiO_2)_{1-4}^-$ [17,18], $VAlO_4^+$ and $V_{4-k}Al_kO_{11-k}^-$ ($k = 1–3$) [19,20], and others [3–5] can activate C–H bonds of methane, ethane, or *n*-butane under near room-temperature conditions. Density functional theory (DFT) studies show that each of these clusters contains one or two oxygen atoms that have unpaired spin density (UPSD) values close to 1 μ_B (Bohr magnetron) and such oxygen atoms are oxygen-centred radicals ($O^{\bullet-}$). The $O^{\bullet-}$ radicals over the studied TMO clusters can effectively abstract hydrogen atoms from the reacting alkane molecules. It is noticeable that C–H bond activation of alkanes by $O^{\bullet-}$ radicals over several oxide clusters of main group elements including Mg [21], Al [22], P [23], S [24], and so on [4] have been also reported recently. So far, the largest oxide clusters that are able to activate C–H bonds of alkanes are $(Al_2O_3)_5^+$ [22] and $(V_2O_5)_5^+$ [13].

To identify further large TMO clusters that are able to activate C–H bonds, a reflectron time-of-flight mass spectrometer (Re-TOF-MS) is built and this paper reports the application of this instrument to the oxide cluster cations of the first transition metal, scandium. Scandium (Sc: [Ar]$3d^14s^2$) has only one 3d electron and scandium oxide clusters can server as a very simple system to understand transitional metal chemistry. In addition, bulk scandium oxides are used as catalytic promoters or supports in selective reduction of nitric oxide with methane [25] and in dehydration of 1,3-diols and 1-4-diols to produce unsaturated alcohols [26,27]. Study of scandium oxide clusters may also provide molecular level insights into the related heterogeneous catalytic systems.

Matrix isolation infrared spectroscopy, photoelectron spectroscopy, and mass spectrometry have been employed to study the electronic structure and reactivity of scandium oxide species

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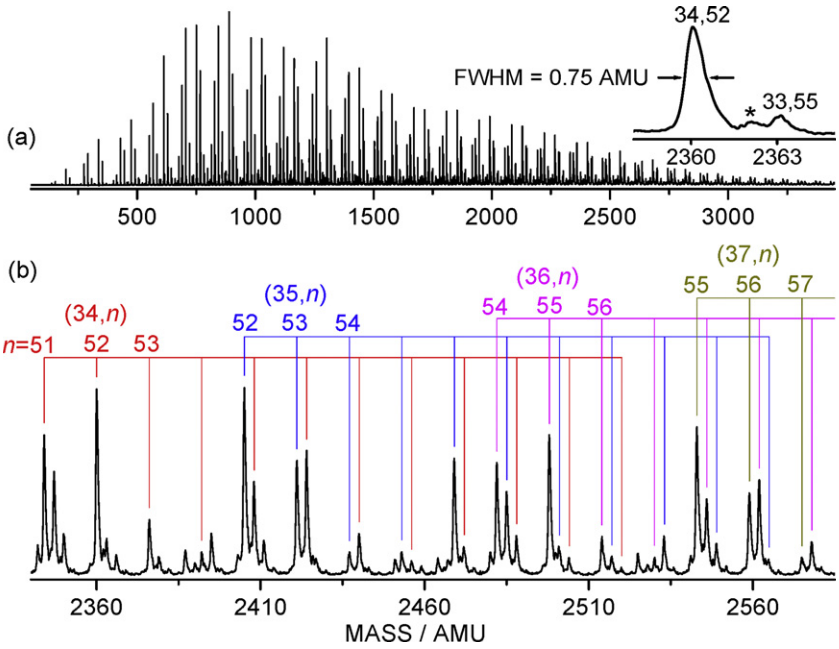

Fig. 1. An overview of a time-of-flight mass spectrum for distribution of scandium oxide cluster cations (a) and a portion of the spectrum with assignments of the peaks (b). The $Sc_mO_n^+$ cluster is labeled as *m*,*n*. The inset in panel (a) shows the full width at half maximum (FWHM) for the peak of $Sc_{34}{}^{16}O_{52}{}^+$ cluster. The weak peak labeled with an asterisk is due to $Sc_{34}{}^{16}O_{51}{}^{18}O^+$.

($ScO_n{}^{0,\pm1}$) [28–33] while the investigations of larger ones $Sc_mO_n^q$ ($m > 1$) are very limited [34,35] and most of which are theoretical studies [36–38]. We have recently identified that $Sc_3O_6{}^-$ anion is a bi-radical with two $O^{\bullet-}$ centres and can activate two *n*-butane molecules consecutively with rate constants on the order of 10^{-10} cm^3 molecule^{-1} s^{-1} under thermal collision conditions [35]. This study provides evidence of C–H bond activation by nanosized scandium oxide cluster cations in gas-phase.

2. Experimental and theoretical methods

2.1. Experimental details

The laser ablation and supersonic expansion cluster source coupled with a fast flow reactor is a copy of the one used in our previous studies [39–42] while the Re-TOF-MS for cluster detection is recently constructed. A brief outline of the experiments is given below. The $Sc_mO_n{}^+$ clusters are generated by laser ablation of a rotating and translating scandium metal disk (99.9%) in the presence of 0.1–0.5% O_2 seeded in a He carrier gas with backing pressure of 6 atm. A 532 nm (second harmonic of Nd^{3+}: yttrium aluminum garnet – YAG) laser with energy of 5–8 mJ/pulse and repetition rate of 10 Hz is used. The gas is controlled by a pulsed valve (General Valve, Series 9). To prevent residual water in gas handling system to form undesirable hydroxo species [$Sc_mO_n(HO)_z^q$, $z > 0$], the prepared gas mixture (O_2/He) is passed through a 10 m long copper tube coil at low temperature ($T = 77$ K) before entering into the pulsed valve. Similar treatment ($T = 273$ K) is also applied in the use of the reactant gases (see below). The reactant gases are pulsed into the reactor 20 mm downstream from the exit of the narrow cluster formation channel by a second pulsed valve (General Valve, Series 9). By using the method in Ref. [43], the instantaneous total gas pressure in the fast flow reactor is estimated to be around 220 Pa at $T = 300$ K. The number of collisions that a cluster (radius = 1.0 nm) experiences with the bath gas (radius = 0.05 nm, $T = 300$ K, $P = 220$ Pa) in the reactor is about 180 per 1 mm of forward motion. This corresponds to a collision rate of 1.8×10^8 s^{-1} for an approaching velocity of 1 km/s. The intra-cluster vibrations are likely equilibrated (cooled or heated, depending on the vibrational temperature after exiting cluster formation channel with a supersonic expansion) to close to the bath gas temperature before reacting with the diluted *n*-C_4H_{10} or *n*-C_4D_{10} molecules. It may be safe to assume than the bath gas has the temperature of the wall of reactor (300 K). Our recent experiments indicate that the cluster vibrational temperature in the reactor can be close to 300 K [17,42].

After reacting in the fast flow reactor, the reactant and product ions are skimmed (3.5 mm diameter in this study for $Sc_mO_n{}^+$ clusters) into the vacuum system of a Re-TOF-MS for mass and abundance measurements. The Re-TOF-MS is home-made and the principle of design is well documented in literature [44]. A brief description of our design is given in the Supporting Information (Fig. S1). The signals from detector of the Re-TOF-MS are recorded (without pre-amplification) with a digital oscilloscope (LeCroy WaveSurfer 42Xs-A) by averaging 1000 traces of independent mass spectra (each corresponds to one laser shot). The uncertainties of the reported relative ion signals are about 10%. The mass resolution of the Re-TOF-MS is above 3000 ($M/\Delta M$) in the mass range of 2000–3000 amu (see Fig. 1 and text below). Better mass resolution (~4000) can be obtained if skimmers [42] with smaller diameters (2 mm) are used.

2.2. Computational details

The DFT calculations are carried out by using the Gaussian 03 program [45]. The hybrid B3LYP functional [46–48] in combination with the TZVP basis sets [49] are used to study the structures and reaction mechanisms for $Sc_2O_3{}^+$, $Sc_4O_6{}^+$, and $Sc_6O_9{}^+$ cluster systems. The justification of the adopted functional and basis sets for scandium oxide and hydrocarbon systems can be found in previous works [50–52]. The cage structures of $Sc_4O_6{}^+$ and $Sc_6O_9{}^+$ have been optimized previously [50] while this study further considers many other possible structures constructed based on chemical intuition and a systematic consideration of the topological conformations [17]. The reaction mechanism calculations involve geometry optimizations of reaction intermediates and transition states (TSs). The TS optimizations are performed by employing the Berny algorithm