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Interactions of methane, ethane and pentane with the (110C) surface of γ-alumina

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Abstract

Adsorptions of methane, ethane and pentane on the γ-alumina (110C) surface are investigated with semi-empirical (PM3) cluster calculations. It is found that the abstraction of an H atom accompanied by the formation of a C–O bond is the most favorable reaction for methane on the alumina surface. For ethane– and pentane–alumina interactions, the abstraction of two H atoms accompanied by the formation of an alkene is the most favorable reaction. The surface Al atoms help to promote the reactions, but are not directly involved in the bond formation.

Keywords: Chemisorption; Methane; Ethane; Pentane; Semi-empirical calculations; γ-Alumina

1. Introduction

The interpretation of H/D exchange between surface OH-groups of a metal oxide and CD_4 as an indication of strong Brönsted acidity [1–4] was questioned by Engelhardt et al. [5,6], who proposed an alternative explanation that H/D exchange could be initiated by dissociative methane chemisorption over Lewis acid–Lewis base pair sites. Such chemisorption would produce the surface species $CD_3^{\delta-}$ and $D^{\delta+}$, with the $CD_3^{\delta-}$ moiety bound to a valence unsaturated Al atom of Lewis acid character.

The Lewis acidity of surface Al sites on γ-alumina has been the subject of several previous investigations [7–9], as has the reactivity of these sites with water [10–12], hydrogen sulfide [10], carbon monoxide [10], ammonia [11], pyridine [11], and methanol [13]. Previously we applied theoretical calculations to gain insight into the interaction of 1-hexene with γ-alumina, and found the interaction to be purely repulsive at valence unsaturated surface Al sites [14]. By contrast, investigations of the interactions of simple alcohols with γ-alumina showed participation of the surface Lewis acid sites [15].

Herein we report the results of calculations designed to investigate the adsorption of methane, ethane and pentane on the γ-alumina (110C) surface. Two cluster models, $H_8Al_{40}O_{64}$ (which exposes an Al–O terminated face on the hydrogen-spinel form of γ-alumina) and $Al_{48}O_{72}$ (which exposes an oxygen terminated face on the hydrogen-free defect-spinel form of γ-alumina), were used to model the γ-alumina surface. By employing models with different degrees of hydrogenation we can explore the temperature dependence of the reactivity of γ-alumina as a heterogeneous catalyst. We found that on both models, the most energetically favorable first reaction step for methane is H abstraction from the carbon (C1) position, with C1 bonding to a surface oxygen. (*Note*: atomic labels are C1–C2–C3–C4–C5 for pentane, C1–C2 for ethane and C1 for methane. H*n* refers to the H atoms bonding to C*n*.) For ethane and pentane, the most energetically favorable first reaction step is the dehydrogenation of two H atoms from different carbon atoms. In pentane–alumina interactions, the two H atoms are abstracted from C2 and C3, respectively, producing 2-pentene. Under certain conditions these reactions can be exothermic. The lowest energy barriers to these reactions are around 60–70 kcal/mol on $H_8Al_{40}O_{64}$ model and around 26–37 kcal/mol on $Al_{48}O_{72}$ model.

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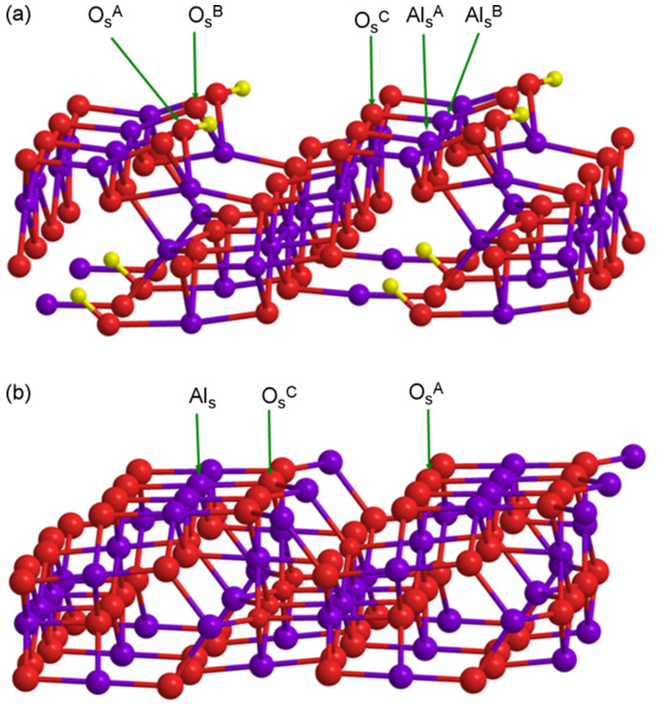

Fig. 1. Cluster models used in this study. (a) Model I: an Al–O terminated surface; (b) Model II: an oxygen terminated surface. The purple, red and yellow spheres represent Al, O, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

2. Computational method and models

The adsorptions of methane, ethane and pentane on the γ-alumina (110C) surface were investigated with electronic structure calculations based on the semi-empirical PM3 Hamiltonian [16,17] and $H_8Al_{40}O_{64}$ and $Al_{48}O_{72}$ cluster models of γ-alumina (see Fig. 1). We chose the PM3 model Hamiltonian because it is parameterized for Al and because the much lower computational cost of semi-empirical calculations allows for modeling a cluster that includes all atoms up to and including second-nearest-neighbors of the adsorption site, much larger than is currently practical with first-principles methods. The large cluster size is important because second-nearest-neighbor effects have been shown to heavily influence surface chemistry in cubic aluminas [18]. Semi-empirical models have been used effectively in theoretical investigations of similar systems [8,15,19,20] and have been shown to lead to qualitative conclusions and energetic behavior consistent with first-principles calculations.

γ-Alumina has been described as a defect-spinel structure closely related to that of Mg-spinel (space group $Fd\bar{3}m$) [21] but with the Al cations distributed over both the octahedral (O_h, Al sites) and tetrahedral (T_d, Mg sites) interstitial sites within the oxygen anion sublattice. γ-Alumina has a range of valid stoichiometries $H_{3m}Al_{2-m}O_3$ $(0 \leq m \leq (1/3))$, but the lowest energy form has the stoichiometry of a hydrogen–aluminum spinel [22]. The primitive unit cell of the lowest energy form is HAl_5O_8, where the H atom and one Al atom occupy (nominally) the Mg sites in the spinel structure, and the remaining four Al atoms occupy the Al sites in the spinel structure. Surface studies show that the (110C) layer of γ-alumina is preferentially exposed [23–26]. The $H_8Al_{40}O_{64}$ cluster model [14] (Model I, Fig. 1(a)) was constructed based on structural relaxation studies of a 56-atom slab of γ-alumina (HAl_5O_8 stoichiometry) four atomic layers thick [18]. This is representative of γ-alumina at low to moderate temperatures. The $Al_{48}O_{72}$ cluster model (Model II, Fig. 1(b)) is constructed based on the $Al_{48}O_{64}$ supercell of hydrogen-free γ-alumina. The cation vacancies required for valence balance were assigned to tetrahedral sites parallel to the (110C) surface [15]. This model is representative of the γ-alumina surface at high temperatures. These two models ensure that the coordination environment of the surface atoms interacting with the adsorbate, and their nearest-neighbors, are representative of those on the surface of the periodic crystal.

For Model I, two different surface aluminum sites for alkane adsorption were studied as indicated in Fig. 1(a). Only surface Al atoms at O_h sites were considered since three-coordinated Al practically does not exit on the surface [26–28]. At site A, the surface Al atom interacting with the alkane has a neighboring OH. (Denoted as Al_s^A. The subscript "s" indicates an atom on the alumina surface.) At site B, there is no neighboring OH around the Al atom that interacts with alkane (denoted as Al_s^B). Interactions of an alkane with three different surface O sites were considered as indicated in Fig. 1(a). At site A, the surface O atom is coordinated by one H atom and two Al atoms (denoted as O_s^A). At site B, the surface O atom is coordinated by two Al atoms (denoted as O_s^B). At site C, the surface O atom is coordinated by three Al atoms (denoted as O_s^C). As previous density-functional calculations have shown no appreciable relaxation effects or consequence for surface atoms, with the exception of the three-coordinated Al atoms that are not considered here [26], the alumina substrate was frozen in all calculations with the exception of the H atom bound to the O_s^A atom.

For Model II, the slab is free of H atoms so Al_s^A and Al_s^B atoms are equivalent, as are O_s^A and O_s^B (see Fig. 1(b)). Therefore, we only consider Al_s, O_s^A and O_s^C sites. The alumina substrate was frozen in all calculations.

In structural optimizations, the adsorbed molecules were fully relaxed, including their positions relative to the surface, except in the case of energy barrier calculations where one of the H1–O_s distances was fixed at different values from about 0.1 to 0.5 nm in steps of approximately 0.02 nm. For all chemisorbed states, vibrational frequencies were calculated to ensure that each state is a true local minimum.

To study molecule/surface interactions the free molecule was placed in close proximity to the surface in various orientations and for each orientation a geometry optimization was carried out. We specify the interaction as A–X_s. This notation denotes atom A of the free molecule in close proximity to atom X_s of the surface slab. In some cases the initial orientation of the free molecule involved two close contacts, denoted as A–X_s & B–Y_s, where atom A of the free molecule is in close proximity to atom X_s of the surface slab and atom B of the free molecule is simultaneously in close proximity to atom Y_s of the surface slab. The following possible interaction modes were investigated: (1)