

# Optimal Water Coverage on Alumina: A Key to Generate Lewis Acid–Base Pairs that are Reactive Towards the C–H Bond Activation of Methane\*\*

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Dedicated to K. Barry Sharpless on the occasion of his 70th birthday

The activation of methane is still a great challenge today,<sup>[1]</sup> because it constitutes one of the largest hydrocarbon resources on earth.<sup>[2]</sup> Many oxides catalyze processes involving the activation of C–H bonds.<sup>[3]</sup> Of these,  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is one of the most active: when treated beforehand at temperatures above 400 °C, it catalyses H/D exchange reactions of D<sub>2</sub>/CH<sub>4</sub> and CH<sub>4</sub>/CD<sub>4</sub> mixtures at room temperature with unexpectedly low activation energies (17–30 kJ mol<sup>−1</sup>).<sup>[4–6]</sup> These reactions involve a very small number of active sites (defects)<sup>[4]</sup> generated by the high-temperature pretreatment. Such a reactivity was attributed to the Lewis acidity of surface Al atoms,<sup>[7]</sup> yielding Al–CH<sub>3</sub> and O–H species,<sup>[4,6]</sup> and more recently specifically to surface three-coordinate Al<sub>III</sub> centers leading to the formation of four-coordinate Al<sub>IV</sub>–CH<sub>3</sub> moieties.<sup>[8]</sup>

However, it is not clear why Al<sub>III</sub>, the expected most Lewis acidic site, would exist in realistic conditions, that is, on a hydroxylated alumina surface. The predominant termination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles is the (110) facet (70–83 %);<sup>[9]</sup> complete dehydration would require temperatures (> 900 °C)<sup>[10]</sup> much higher than the window of stability of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.<sup>[11]</sup> Even after treatments at 400–500 °C, the OH density is 2–5 OH/nm<sup>2</sup> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,<sup>[7,12]</sup> therefore, the strongest Al<sub>III</sub> sites should be completely hydroxylated and thus their reactivity annihilated.

Therefore, several questions emerge: what is the real nature of the active site for C–H bond activation on alumina? Is it possible to have the two strong antagonists, highly Lewis acidic sites and a strong Lewis base (H<sub>2</sub>O), on the surface simultaneously without a direct annihilation between them? If these strong Lewis sites still exist, how would surface hydroxylation affect their reactivity towards CH<sub>4</sub>? Herein we provide answers to these questions and show the unexpected role of water by combining experiments and first-principle calculations. We underline that the reactive site is best described as an (Al,O) Lewis acid–base pair where oxygen basicity, apart from Al acidity, is also a key factor to reactivity.

We first investigated the influence of thermal treatment of alumina on the density of sites involved in the formation of Al–CH<sub>3</sub> species through reaction with CH<sub>4</sub> at 150 °C (Figure 1a). The density of sites gives a volcano-type curve as a function of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pretreatment temperature, reaching a maximum of 0.03 reactive Al sites per nm<sup>2</sup> at about 700 °C.<sup>[13]</sup> Below 400 °C, no site is generated, while at higher temperatures (> 800 °C) their density decreases. By comparison, both the hydroxy group coverage  $\theta_{\text{OH}}$  and the specific surface area  $S_{\text{BET}}$  decrease with increasing temperature (Figure 1b and Supporting Information, Figure S1):  $\theta_{\text{OH}}$  decreases exponentially while  $S_{\text{BET}}$  falls first slowly and then sharply above 800 °C. These phenomena are associated with a progressive change of the alumina bulk structure ( $\gamma \rightarrow \delta \rightarrow \theta$ ), as indicated by X-ray powder diffraction studies (Supporting Information, Figure S2).<sup>[14]</sup>

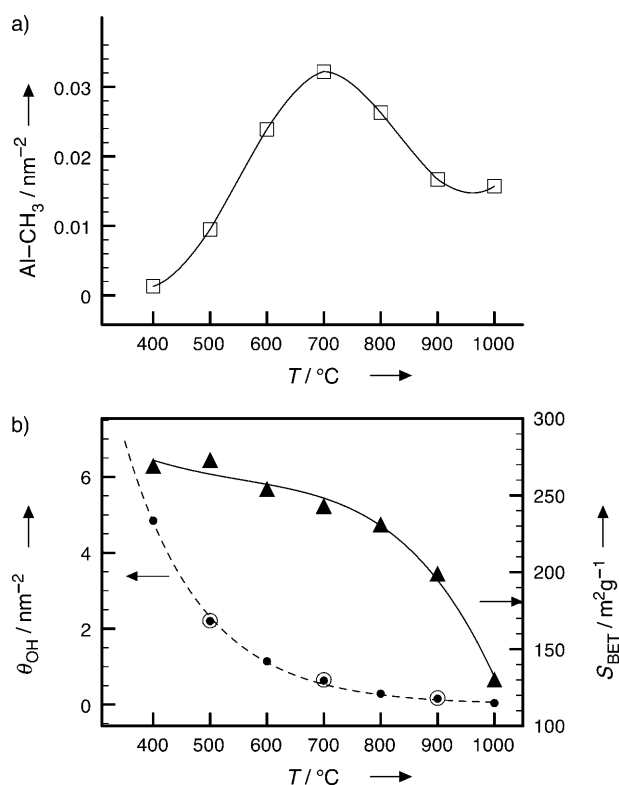
The nature of the active sites was studied by DFT calculations with a specific focus on low energy metastable terminations of partially hydrated alumina surfaces. The most abundant (110) surface was considered: its hypothetical fully dehydrated surface unit cell (**s0**) exposes three different aluminum Lewis acid centers: one three-coordinate (Al<sub>III</sub>) and two types of four-coordinate (Al<sub>IVa</sub> and Al<sub>IVb</sub>) sites, with decreasing intrinsic Lewis acidity according to Al<sub>III</sub> > Al<sub>IVb</sub> > Al<sub>IVa</sub>. It also exposes two- and threefold-coordinated O atoms with intrinsic Lewis basicity O<sub>2</sub> > O<sub>3</sub> (Supporting Information, Figure S3a).<sup>[15]</sup> This (110) termination has a rather high surface energy (1.5 J m<sup>−2</sup>) and strongly interacts with water.<sup>[15,16]</sup> At a simulated  $\theta_{\text{OH}}$  of about 3 OH nm<sup>−2</sup> (1 H<sub>2</sub>O per surface unit cell), close to the measured OH density at 500 °C, the OH group preferentially occupies the most Lewis acidic Al<sub>III</sub> site (Supporting Information, Figure S3b).<sup>[15]</sup> However, from the various structures explored, a configuration with OH bridging two Al<sub>IVa</sub> centers, keeping Al<sub>III</sub> free, is only 44 kJ mol<sup>−1</sup> less stable (**s1**, Figure 2a), making the

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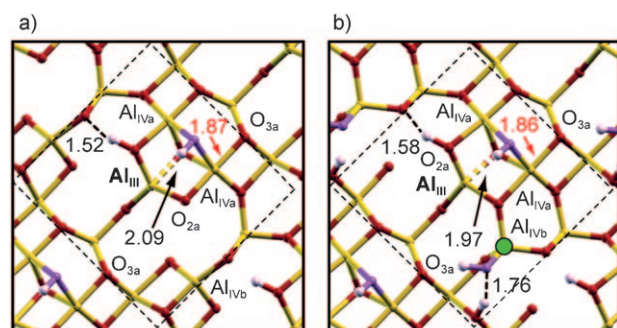
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**Figure 1.** The effect of the pretreatment temperature on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: a) surface density of Al-CH<sub>3</sub> as determined by reaction with CH<sub>4</sub>; b) left axis: hydroxy group coverage  $\theta_{\text{OH}}$  measured by titration with CH<sub>3</sub>MgBr (○) and integration of the OH bands in the IR spectrum (●; see also Supporting Information, Figure S1); right axis: specific surface area  $S_{\text{BET}}$  of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (▲).



**Figure 2.** Metastable terminations with free Al<sub>III</sub> sites for the (110)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. a) **s1** with 1 H<sub>2</sub>O dissociated on Al<sub>IVa</sub> ( $\theta_{\text{OH}} \approx 3 \text{ OH nm}^{-2}$ ), b) **s2** with 2 H<sub>2</sub>O dissociated on Al<sub>IV</sub> ( $\theta_{\text{OH}} \approx 6 \text{ OH nm}^{-2}$ ). Only the top two layers of the 8-layer periodical slab are represented. A dashed line indicates the unit cell. Al yellow, H white, O from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> red, O from H<sub>2</sub>O dissociation purple, Al<sub>IVb</sub> after surface reconstruction green. All distances in Å.

presence of Al<sub>III</sub> defects probable upon high-temperature treatment. For a simulated  $\theta_{\text{OH}}$  value of about 6 OH nm<sup>-2</sup> (2 H<sub>2</sub>O per surface unit cell), the second hydroxy group is expected to simply occupy the second strongest Lewis acidic center (Al<sub>IVb</sub>) along with Al<sub>III</sub>. However, several low-energy structures are found (Supporting Information, Figure S3c and d), and a configuration with hydroxy groups on Al<sub>IVa</sub> and Al<sub>IVb</sub> (**s2**, Figure 2b) with the Al<sub>III</sub> site free is only 4 kJ mol<sup>-1</sup> less

stable than the most stable configuration (with OH on Al<sub>III</sub> and Al<sub>IVb</sub>). At higher  $\theta_{\text{OH}}$  (9 OH nm<sup>-2</sup>), surfaces with a free Al<sub>III</sub> site become less stable (+64 kJ mol<sup>-1</sup>) and much less probable.

The following questions then arise: why are these **s1** and **s2** structures energetically competitive, keeping free the potentially more reactive Al<sub>III</sub> site? Do these sites still possess a high reactivity? The stability of the **s1** surface mainly arises from the occupation of two Al<sub>IVa</sub> centers by a bridging OH group, a situation not possible for the other sites, Al<sub>III</sub> or Al<sub>IVb</sub>. The high stability of **s2** is due, in addition, to a reconstruction of the surface: Al<sub>IVb</sub> changes its geometry from a truncated octahedron into a tetrahedron upon hydration. Furthermore, the Al<sub>III</sub> site, which is planar on **s0**, is weakly coordinated to a second layer O atom in **s1** and **s2**, leading to a slight inward pyramidalization (Al<sub>III</sub>...O(2nd layer) distances of 2.09 and 1.97 Å respectively, versus 2.76 Å on **s0** and about 1.8 Å for a tetrahedral Al in the bulk). This effect further stabilizes **s1** and **s2** but could mitigate the Lewis acidity and reactivity of Al<sub>III</sub>.

The Lewis acidity of the Al<sub>III</sub> centers was therefore probed by adsorption of CO. The adsorption energy, which is -71, -69, and -37 kJ mol<sup>-1</sup> on **s0**, **s1**, and **s2** surfaces, respectively, indicates a comparable Lewis acidity of Al<sub>III</sub> on **s0** and **s1**, but a strong reduction on **s2**. An energy decomposition analysis reveals that the deformation of Al<sub>III</sub>, required for coordination of CO, is much more difficult on **s2** because it involves a more rigid surface and the de-coordination of a more strongly bound second-layer oxygen atom.

The reactivity of the Al<sub>III</sub> sites on **s0**–**s2** surfaces towards C–H bond activation of CH<sub>4</sub> was then investigated. Two pathways were found, depending on where the proton generated by the dissociation ends: either on twofold coordinated O<sub>2a</sub> atoms directly bonded to Al<sub>III</sub> (adjacent (Al<sub>III</sub>,O<sub>2a</sub>) site) or on one of the threefold-coordinated O<sub>3a</sub> atoms facing Al<sub>III</sub> (non-adjacent (Al<sub>III</sub>,O<sub>3a</sub>) site).

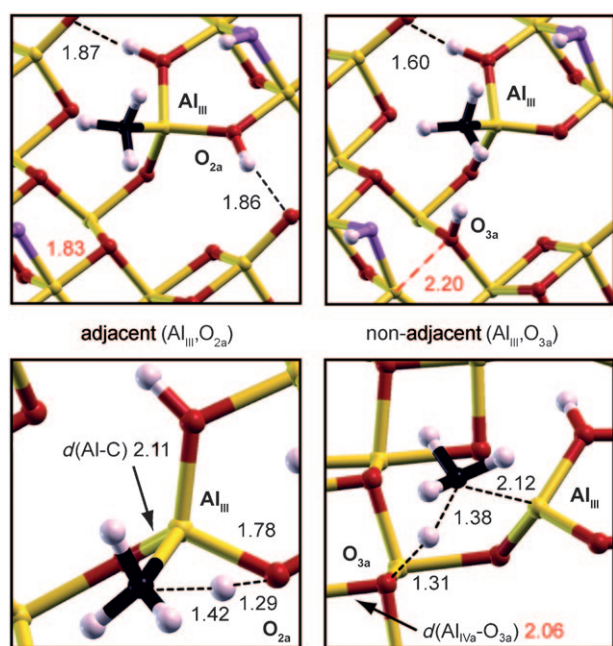
As previously reported,<sup>[8]</sup> the dissociation of CH<sub>4</sub> on the adjacent (Al<sub>III</sub>,O<sub>2a</sub>) site of the hypothetical fully dehydrated **s0** surface is highly exoenergetic (Supporting Information, Figure S4a;  $\Delta E = -84 \text{ kJ mol}^{-1}$ ). A precursor state (PS) with CH<sub>4</sub> molecularly adsorbed on Al<sub>III</sub> and a low-energy (64 kJ mol<sup>-1</sup>) transition state (TS; Supporting Information, Figure S5a) were found along the reaction pathway (Table 1).

For the more realistic metastable termination **s1** at moderate  $\theta_{\text{OH}}$  (3 OH nm<sup>-2</sup>) the reactivity is similar, with a

**Table 1:** Energies for the reaction of CH<sub>4</sub> on (Al<sub>III</sub>,O) sites of the (110) termination (**s0**: fully-dehydrated, **s1** and **s2**: partially hydrated) and on (Al<sub>IV</sub>,O) sites of the (100) termination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Sites	Adjacent (Al <sub>III</sub> ,O <sub>2a</sub> )			Non-adjacent (Al <sub>III</sub> ,O <sub>3a</sub> )			Al <sub>V</sub>
surfaces	<b>s0</b>	<b>s1</b>	<b>s2</b>	<b>s0</b>	<b>s1</b>	<b>s2</b>	(100)
OH [nm <sup>-2</sup> ]	0	3	6	0	3	6	0
$\Delta E^{\text{[a]}}$	-84	-65	-10	+18	-26	-22	+76
$\Delta E_{\text{PS}}^{\text{[b]}}$	-24	-12	-6	-24	-12	-6	
$\Delta E_{\text{TS}}^{\text{[c]}}$	+64	+74	+116	+86	+45	+103	

[a] Reaction energy. [b] Energy of the precursor state. [c] Energy of the transition state. All energies [kJ mol<sup>-1</sup>] are given with respect to separated reactants (surface + gas-phase CH<sub>4</sub>).



**Figure 3.** Reaction of CH<sub>4</sub> with the metastable **s1** alumina surface (3 OH nm<sup>-2</sup>): top panel: products, bottom panel: transition states. Left column: adjacent pathway (Al<sub>III</sub>, O<sub>2a</sub>). Right column: non-adjacent pathway (Al<sub>III</sub>, O<sub>3a</sub>). Same color codes as in Figure 2, with C black.

slight reduction of the reaction energy ( $\Delta E = -65$  versus  $-84$  kJ mol<sup>-1</sup>) and an increase of the activation energy by 10 kJ mol<sup>-1</sup>. The TS (Figure 3) is similar to that on **s0**; that is, planar ( $\angle(\text{H-O-Al-C}) = 3.1^\circ$ ), with an acute Al-C-H angle ( $55^\circ$ ) and a wide C-H-O angle ( $152^\circ$ ). The differential electron density indicates a heterolytic splitting of CH<sub>4</sub> (methyl anion and proton transferred to Al<sub>III</sub> and O<sub>2a</sub>, respectively). However, at higher  $\theta_{\text{OH}}$  (**s2**, 6 OH nm<sup>-2</sup>), the reactivity of Al<sub>III</sub> is strongly decreased, as evidenced by the much less favorable reaction and the sharp increase in activation energy (almost twice as high as on **s0**). The destabilization of the TS results from the higher rigidity of the surface and the interaction of Al<sub>III</sub> with a second-layer O atom, which hinders its necessary pyramidalization and reduce its Lewis acidity (as shown for CO).

On the non-adjacent (Al<sub>III</sub>, O<sub>3a</sub>) site, CH<sub>4</sub> is dissociated on Al and O atoms distant by 4.1 Å. The reaction on the dehydrated **s0** surface is much less favorable than on the adjacent site ( $\Delta E = +18$  versus  $-84$  kJ mol<sup>-1</sup>) because a less-basic O<sub>3a</sub> site is protonated. However, the TS is only slightly destabilized ( $+86$  versus  $+64$  kJ mol<sup>-1</sup>). The TS geometry (Supporting Information, Figure S5c) is again planar with a similar C...H elongation, but now with a wider Al-C-H angle ( $92^\circ$ ), an almost linear O-H-C angle ( $171^\circ$ ), and longer Al-C and Al-O distances because of the more distant (Al,O) pair. The difference of charge density at the TS is also consistent with heterolytic splitting of the C-H bond (Supporting Information, Figure S5d). However, the effect of partial hydroxylation (**s1** and **s2**) on the reactivity towards CH<sub>4</sub> is completely unexpected: 1) the dissociation of CH<sub>4</sub> on non-adjacent sites is favored (reaction energy) by the presence of one or two H<sub>2</sub>O molecules, and 2) the dissociation barrier is

dramatically decreased by the presence of the first H<sub>2</sub>O molecule and then increased by the second molecule. The presence of H<sub>2</sub>O dissociated on Al<sub>IVa</sub> (**s1**, **s2**) leads to a weaker Al<sub>IVa</sub>-O<sub>3a</sub> bond, as seen by its elongation ( $d(\text{Al-O}) \approx 1.87$  Å on **s1** and **s2** versus 1.83 Å on **s0**), and thus to an increased basicity of O<sub>3a</sub>. This is further apparent from the density of states with an up-shift of the highest-occupied levels on O<sub>3a</sub> (Supporting Information, Figure S6). The increased basicity of O<sub>3a</sub> favors the dissociation of CH<sub>4</sub> on non-adjacent sites of hydrated surfaces. The TS on **s1** (Figure 3), similar on **s2** is earlier than on **s0**, with a shorter C-H bond (1.38 versus 1.47 Å) and a longer O-H distance (1.31 versus 1.25 Å). The low barrier on **s1** stems from the reduced deformation of CH<sub>4</sub> in the TS. On **s2** however, although the reaction energy is almost unchanged, the TS energy is increased to 103 kJ mol<sup>-1</sup>, again because of the higher rigidity of this surface. Thus, for the realistic hydrated surfaces with free Al<sub>III</sub> sites, the non-adjacent pathway is kinetically preferred with a low barrier at an optimal OH coverage of 3 OH nm<sup>-2</sup> (**s1**). This preference arises from the remaining high Lewis acidity of Al<sub>III</sub> combined with the increased Lewis basicity of the non-adjacent O<sub>3a</sub> atom upon hydration of Al<sub>IVa</sub>. Overall, a more frustrated Lewis acid-base pair<sup>[17]</sup> is created which is optimally reactive for the heterolytic splitting of the C-H bond of methane at low hydration level, associated with pretreatment at high temperatures. For comparison, the reactivity of surface Al centers with higher coordination was studied: the Al<sub>IVa</sub> and Al<sub>IVb</sub> sites on the fully dehydrated (110) termination and the Al<sub>V</sub> sites on the less abundant (100) facet of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are much less reactive ( $\Delta E = +18$ ,  $-15$ , and  $+76$  kJ mol<sup>-1</sup>, respectively).

Overall, the high reactivity of alumina towards C-H bond activation and the experimentally observed volcano-type behavior for active site density (Figure 1a) can be rationalized as follows: at low pretreatment temperatures (for example 400 °C), corresponding to a relatively high  $\theta_{\text{OH}}$  (ca. 5 OH nm<sup>-2</sup>) and best represented by the **s2** surface (6 OH nm<sup>-2</sup>), low-energy metastable Al<sub>III</sub> sites can exist. However, they are unreactive owing to their difficult pyramidalization. With increasing pretreatment temperatures, more extended dehydration takes place (decrease of  $\theta_{\text{OH}}$ ), which can be modeled by the gradual formation of **s1** (3 OH nm<sup>-2</sup>). Here, Al<sub>III</sub> sites can still exist as defects and water adsorbed on Al<sub>IVa</sub> sites increases the basicity of neighboring oxygen atoms, O<sub>3a</sub>, without significantly modifying the Lewis acidity of Al<sub>III</sub>. Thus highly reactive acid-base (Al<sub>III</sub>, O<sub>3a</sub>) pairs are created, enabling low-energy pathways for the heterolytic splitting of the C-H bond of CH<sub>4</sub>. The number of reactive defect sites further increases up to pretreatment temperatures of about 700 °C, corresponding to a hydroxy group coverage of about 1 OH nm<sup>-2</sup>, before decreasing sharply for higher pretreatment temperatures. Indeed, water has another critical role, namely the stabilization of the (110) surface that is otherwise unstable, the energy of the fully dehydrated (110) facet (**s0**) being 50 % higher than that of the (100) facet.<sup>[15]</sup> Combined with the high mobility of oxygen atoms at high temperatures ( $> 500^\circ\text{C}$ ),<sup>[18]</sup> a too strong dehydration induces a reconstruction of the surface, as evidenced by the marked loss of surface area and the phase transformation from  $\gamma$ - into mixtures of  $\gamma$ -,

$\delta$ -, and  $\theta$ - $\text{Al}_2\text{O}_3$ . The formation of  $\theta$ - $\text{Al}_2\text{O}_3$ , the most abundant facets of which expose unreactive  $\text{Al}_{\text{IV}}$  and  $\text{Al}_{\text{V}}$ <sup>[19]</sup> explains the decrease of reactive site density for thermal treatments performed at temperatures above 700 °C. A minimum and optimal hydroxylation of alumina is therefore required for stabilizing the metastable (110) termination presenting the highly reactive  $\text{Al}_{\text{III}}$  defect sites.

In conclusion, combined experimental and DFT studies reveal that the reactivity of  $\gamma$ - $\text{Al}_2\text{O}_3$  and probably of many other oxides towards  $\text{CH}_4$  and other molecules with polarizable  $\text{X}^+-\text{Y}^-$  bonds results from a combined action of (metal,O) Lewis acid–base pairs. The reactive sites are located on the most abundant but metastable (110) termination. Water stabilizes this termination, increases the basicity of specific O atoms and, counter to intuition, allows the presence of metastable  $\text{Al}_{\text{III}}$  centers at low OH coverage. Therefore, at an optimal pretreatment temperature of 700 °C, adsorbed water increases the reactivity of non-adjacent (Al,O) pairs towards C–H bond activation. Such findings clearly illustrate the importance to control and to understand molecular phenomena associated with the thermal pretreatment step for the preparation of supports and catalysts.

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