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# Theoretical Investigation of Water Exchange on the Nanometer-Sized Polyoxyocation $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (Keggin- $\text{Al}_{13}$ ) in Aqueous Solution

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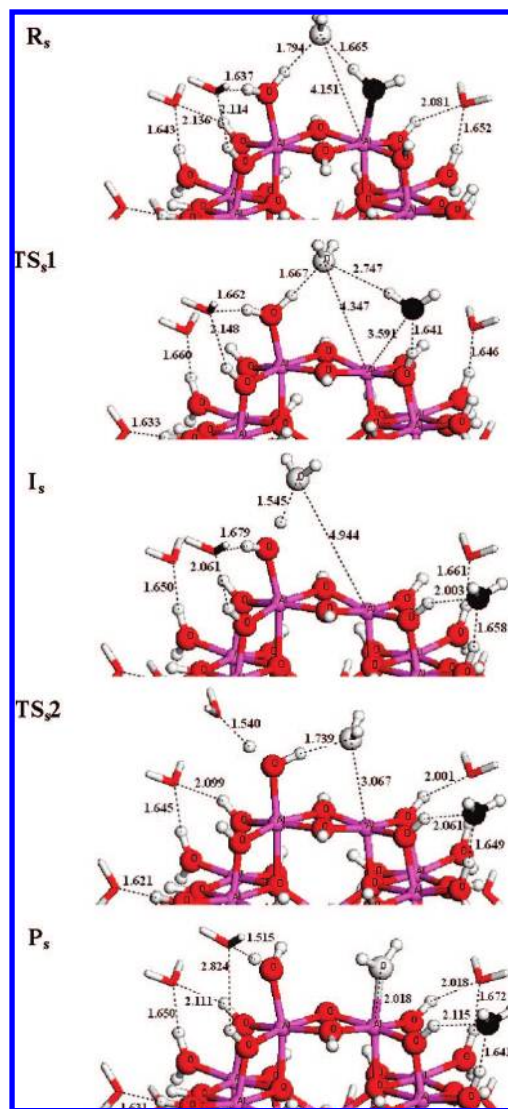
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Water-exchange reactions are important for understanding broad aqueous reactions involving minerals and environmental processes.<sup>1</sup> Water-exchange reactions in nanometer-sized clusters are particular interesting because they can be studied using simple experimental methods and simulated with different theoretical methods.<sup>1</sup> Recently, the nanometer-sized clusters such as Keggin- $\text{Al}_{13}$  ( $\text{K-Al}_{13}$ ) have been used as experimental models to determine reaction rates and pathways of oxygen exchange reactions at the fundamental level because they expose functional groups that resemble those found on the minerals.<sup>2,3</sup> The nanometer-sized clusters such as  $\text{K-Al}_{13}$  are also widely used as catalysts, clay-pillaring, and water-treat agents, and extensive studies of various aspects were carried out.<sup>4</sup>

Although the experimental methods can determine the water exchange rate, they do not provide the detailed microscopic nature of the underlying reaction mechanism.<sup>5</sup> The structure and stability of  $\text{K-Al}_{13}$  in aqueous solution were investigated by molecular dynamics simulations,<sup>6</sup> and oxygen-exchange reactions of  $\text{K-Al}_{13}$  were also explored by the MD method.<sup>7</sup> The structure and NMR properties of  $\text{K-Al}_{13}$  were also investigated by *ab initio* calculations with the gas-phase cluster model.<sup>8</sup> The water exchange on  $\text{Al(III)}$  and  $\text{GaO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  have been simulated using the gas-phase cluster model, but the calculations did not reproduce accurately since their models neglected the solvent effect.<sup>9,10</sup> Recently Hanauer et al.<sup>11</sup> and Evans et al.<sup>12</sup> employed the cluster models with additional water molecules for water exchange on aquated  $\text{Al(III)}$  species. Evans et al.<sup>12</sup> pointed out that the pathways could not be identified priorly for complicated reactions, and the symmetry-distinct pathways had barriers that differed largely. In our previous work,<sup>13</sup> we simulated the water exchange on aquated  $\text{Al(III)}$  species using a supermolecule model<sup>13,14</sup> successfully. However, water-exchange processes of  $\text{Al(III)}$  and aluminum polyoxocations such as  $\text{K-Al}_{13}$  are very different.<sup>10</sup>

In this work, we simulated the water exchange on  $\text{K-Al}_{13}$  successfully by performing supermolecule density functional theory calculations. In the supermolecule model, fifteen solvent water molecules were explicitly included for consideration of the explicit solvent effect, and the remainder bulk solvent effect was considered by PCM<sup>14</sup> calculations. For comparison, the gas-phase model calculations were also performed at the same level. For confirmation of the sufficiency of the adopted methods and explicit structures, we compared our calculated data with those by the other methods and the experimental data, and modeled the supermolecules for the first step with consideration of 13 and 14 explicit water molecules. The calculated results indicate that our calculated data were consistent with those by the other methods and close to the experimental data, and the convergence with respect to the number of water molecules is satisfactory for  $n > 14$ . Therefore, we expect that our adopted method and supermolecular model will simulate the water exchange on  $\text{K-Al}_{13}$  species accurately.



**Figure 1.** Structures of the species in water exchange on  $\text{K-Al}_{13}$  for the supermolecular reaction system. The oxygen atoms of the incoming water and leaving water are colored with white and dark, respectively.

As shown in Figure 1, for  $\text{R}_s$ , the incoming water molecule is located in the second coordination sphere at a distance of 4.151 Å to the reacted aluminum, and bound through two hydrogen bonds to the leaving water molecule and one neighboring water ligand. Detaching the leaving water molecule leads to the transition state  $\text{TS}_s1$ . In  $\text{TS}_s1$ , the leaving water molecule forms one hydrogen bond,  $r(\text{H}-\text{O}_L) = 1.641$  Å, with one of the hydroxo-bridges and is located between the first and second coordination spheres at a

**Table 1.** Calculated and Experimental Reaction Parameters for Water Exchange on K-Al<sub>13</sub>

	log $k_{\text{TST}}$ (s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ·mol <sup>-1</sup> )	$\Delta S^\ddagger$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
calcd data <sup>a</sup>	3.35	62.2	28
calcd data <sup>b</sup>	3.2	64.3 ± 1.4	13 ± 4
exptl data <sup>c</sup>		53 ± 12	-7 ± 25

<sup>a</sup> From this paper. <sup>b</sup> From ref 17. <sup>c</sup> From ref 2.

distance of 3.591 Å. On lengthening the distance between the reacted aluminum and the leaving water molecule, the leaving water molecule becomes part of second coordination sphere, and intermediate **I<sub>s</sub>** with a five-coordinate aluminum forms. As depicted in Figure 1, the leaving water molecule in **I<sub>s</sub>** forms two hydrogen bonds and is located in the second coordination sphere at a distance of 4.639 Å. The intermediate with five-coordinate aluminum was also found in the Car–Parrinello molecular dynamics simulations.<sup>6</sup> As the reaction proceeds, the incoming water molecule approaches the five-coordinate aluminum to a distance of 3.067 Å and the transition state **TS<sub>s</sub>2** forms. In **TS<sub>s</sub>2**, the incoming water molecule is located between the first and second coordination spheres, and the hydrogen bond length between the incoming water molecule and the neighboring water ligand is lengthened to 1.739 Å from 1.545 Å in **I<sub>s</sub>**. The distance between the incoming water molecule and the reacted aluminum is continuously shortened till the formation of the stable Al–O bond, and then the reacted product **P<sub>s</sub>** is reached.

The calculated mean Al–OH<sub>2</sub> bond length (1.959 Å) for **R<sub>s</sub>** is shorter than that (2.014 Å) for the gas-phase species **R** and closer to the experimental data (1.961 Å)<sup>16</sup>, demonstrating that the consideration of a second coordination sphere can describe the geometrical parameters more accurately. The changes of the sum of Al–O bond length between transition state **TS<sub>s</sub>1** and reactant **R<sub>s</sub>** for the supermolecular reaction system are positive, which suggests the D mechanism<sup>5</sup> for the water exchange on K-Al<sub>13</sub>.

The energy barriers for the first and second step of water exchange on K-Al<sub>13</sub> in the gas-phase reaction system are 45.2 and 35.8 kJ·mol<sup>-1</sup>, respectively. However, after accounting for the bulk solvent effect the energy barriers for the first step of water exchange on Al<sub>13</sub> are increased to 92.0 kJ·mol<sup>-1</sup>. With the experimental conclusion in mind, one can see that the energy barriers for the gas-phase reaction system deviate largely from the corresponding experimental data, indicating that the gas-phase model calculations cannot describe the energies of the water exchange on K-Al<sub>13</sub> correctly.<sup>13</sup> For the supermolecular reaction system, the energy barrier and reaction energy for the first step are increased to 49.4 and 12.1 kJ·mol<sup>-1</sup>, respectively, whereas the energy barrier and reaction energy the second step are decreased to 12.4 and -0.9 kJ·mol<sup>-1</sup>, respectively, relative to the gas-phase reaction system, indicating that the involvement of a second hydration sphere has obvious influence on the water exchange on K-Al<sub>13</sub>. After accounting for the bulk solvent effects, the energy barrier for the first step is increased to 62.2 kJ·mol<sup>-1</sup>, whereas the energy barrier for the second step is decreased to 3.7 kJ·mol<sup>-1</sup>, which underscores long-range electrostatic interactions.

According to the transition state theory, our calculated transition-state rate constant  $k_{\text{TST}}$  and enthalpy of activation are consistent with those obtained by the MD method<sup>17</sup> and are close to the corresponding experimental data.<sup>2</sup> In agreement with that obtained by the MD method,<sup>17</sup> our calculated entropy of activation is large and positive, consistent with considerable dissociative<sup>5</sup> character to water exchange on K-Al<sub>13</sub>. In principle the rate constant  $k_{\text{ex}}$  must include a transmission coefficient  $\kappa$ , that is,  $k_{\text{ex}} = \kappa k_{\text{TST}}$ . The transition state theory assumes  $\kappa = 1$ ; however, according to the

paper<sup>17</sup> and the reviews<sup>18,19</sup> on transmission coefficient, one can note that  $\kappa$  is not going to be 1. Because  $\kappa$  does depend upon dynamics, it was not considered in this work.

In summary, we have investigated the water exchange on K-Al<sub>13</sub> in aqueous solution by supermolecule density functional theory calculations. Our results suggest a dissociative mechanism (D) for the water exchange on K-Al<sub>13</sub>. This framework reveals the detailed mechanism of water exchange on K-Al<sub>13</sub>, and provides a means for exploring the chemical behavior of mineral-water interfaces and dissolution and transformation processes of the minerals.<sup>20</sup>

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**Supporting Information Available:** Complete ref 1e; confirmation of adopted methods and model, computation details, structures and energy profiles, and Cartesian coordinates. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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