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Density Functional Theory Simulations of Aluminium Alkoxide and Fluoride

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***Abstract*— A series of density functional theory (DFT) simulations was carried out to investigate the geometry and reaction pathways of aluminium alkoxides using three different exchange-correlation functionals, including the local-density approximation, generalized gradient approximation, and a hybrid functionals. The simulations of fluoride atoms (F) sticking to the Al alkoxide, varying their distances from 6.0 Å to their intermediate states along a straight line for the corresponding energy surfaces, were performed. It is found that the structural optimization obtained from different exchange-correlation functionals exhibits similar molecular configurations. The reaction pathways for the synthesis of Al fluoride was also simulated by utilizing the transition state searches method for investing the reaction pathways, including linear synchronous (LST) and quadratic synchronous (QST) maximization to investigate the reaction intermediate, and the converged results for all the distances were successfully obtained. It is found that the F atom replace one of bridging and terminal isopropoxide groups at the final state equivalently converted to the surrounded solvent molecules.**

***Index Terms*— Aluminium alkoxide; Aluminium fluoride; Density functional theory..**

I. INTRODUCTION

Metal fluorides have demonstrated many beneficial properties that characterize them from other materials, especially the extensive applied metal oxides. Due to their special collective characteristics like refraction index, dielectric functions, and permeability have certified their uses with numerous potential for utilizing in various areas such as optics technology [1], ceramic, catalysis [2,3], dental applications, and anti-corrosive coating with superior effectiveness than currently known alternate materials.

Sol-gel technology was formerly developed for metal oxides as a main target. However, it can also be applied for nanoscopic metal fluorides synthesis. The sol-gel route with anhydrous hydrogen fluoride (HF) has demonstrated the capability to synthesize certain metal fluorides in a steadfast and contented process. The typical synthesis uses metal alkoxides precursors by the reactions with HF in a suitable organic solvent, usually alcohols, such as methanol, ethanol, and isopropanol (1).

$$M(OR)_n + nHF \rightarrow MF_n + nROH \qquad (1)$$

Properly performed synthesis conventionally results into the formation of transparent metal fluoride sols with particle diameters up to 30 nm, depending on the particular metal such as magnesium fluoride (MgF_2), and aluminium fluoride (AlF_3). Nevertheless, previous work of sol-gel synthesis has allowed researchers to produce very small and formerly unavailable metal fluoride particles in stable forms. The original approach concerning a possible mechanism for the sol-gel fluorination was initially attempted by Rudiger *et al.* in 2005 [4].

For the past decades, the density functional theory (DFT) [5] has been the major role as a theoretical tool for computational research used to investigate, analyze, predict, and describe the characteristics of material properties and chemical processes, i.e., successful in explaining not only the finest details of many systems but also the very complex ones. In order to pursue further interests to simulate the possible structures of intermediate states and where they take place, the implementation of density functional theory (DFT) calculations is seemly appropriate in terms of low cost, time consuming, and reliable simulation results.

This work aims (i) to optimize geometries of Al alkoxide and its formation of product structure, (ii) to investigate their changes at fluorination, and finally (iii) to derive a possible reaction pathway for the sol-gel fluorination process by applying density functional theory (DFT) simulations to perform the calculations.

II. COMPUTATIONAL METHOD

In order to calculate the geometry optimization of the Al alkoxides, the Slater-Vosko-Wilk-Nusair (SVWN) exchange-correlation (XC) functional within the local-density approximation (LDA) and the double numerical (DN) basis set along with 4.4 basis file for all the simulations, where 3.5 basis is an original, and 4.4 one is from B. Delley in 2006 [6], were implemented. Next, the generalized gradient approximation (GGA) with Perdew- -Burke-Ernzerhof (PBE) functional [7], and a conventional hybrid, B3LYP, functional [8] were performed in the same manner. The convergence tolerance for the maximum force and maximum displacement for normal geometry optimization were set to 0.2 Ha $Å^{-1}$ and 0.5 Å, respectively. Panel (a) and (b) in Fig. 1 shows the optimized geometries of Al alkoxides. Next, we performed the LDA-SVWN simulations of fluoride (F) atom sticking to the Al alkoxide, varying their distances from 6.0 Å to their intermediate states along a straight line (not a reaction path). In Fig. 1 (b), the corresponding energy surfaces have been plotted. Although they do not simulate reaction pathways for

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the synthesis of metal fluorides, the converged results for all the distances have been successfully obtained, unlike when

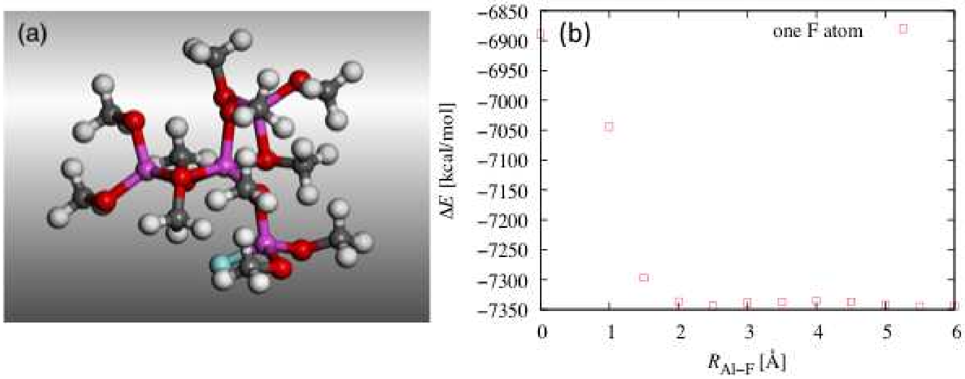

Fig. 1. (a) optimized geometries of Al alkoxide, (b) Energy sufaces of F atom sticking to the Al alkoxides.

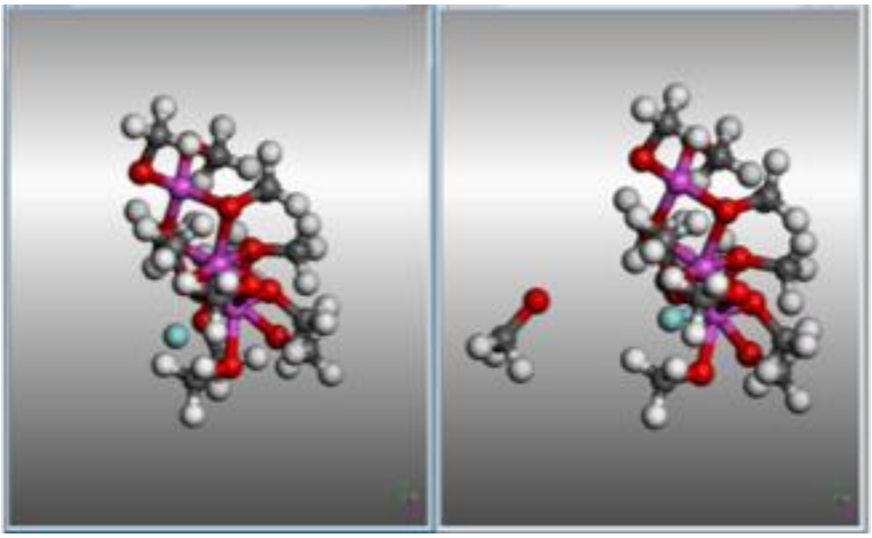

Fig. 2. Snapshot for possible reaction pathway for the sol-gel fluorination obtained with DFT calculations (light blue sphere is F atom).

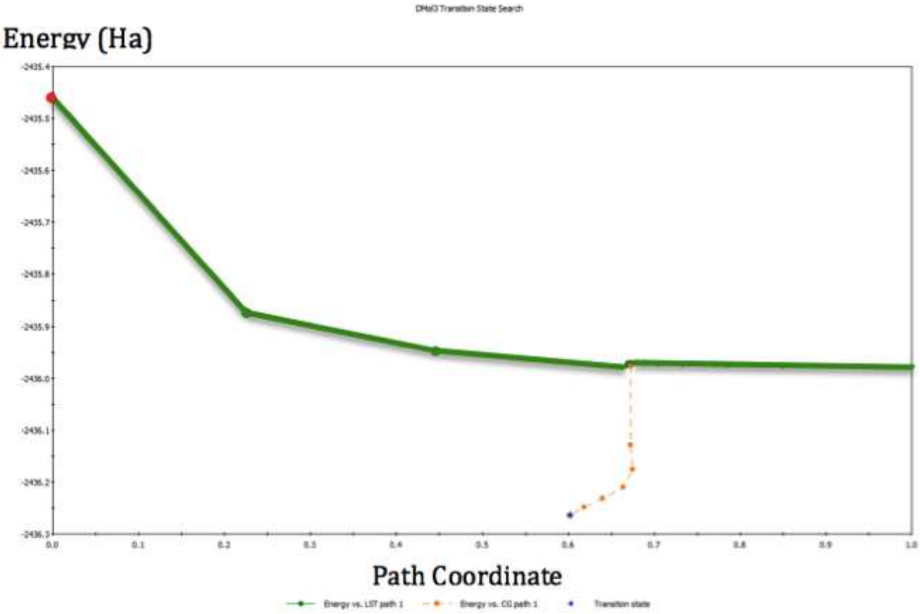

Fig. 3. DMol3 transition state search of Al alkoxide.

using the GGA-PBE functional. This may imply that the choice of DFT functional is promising for the next step, i.e., transition state (TS) searches which included linear synchronous transit (LST) and quadratic synchronous transit (QST) maximization methods for the reaction pathways.

Limited techniques have been well validated for finding a transition-state structure and among the better known of these are linear synchronous transit (LST) and quadratic synchronous transit (QST). In order to prepare the structures for the TS calculation, the reactants and products in two different 3D atomistic configurations were separately constructed. The aluminium alkoxide obtained from previous geometry-optimized structure was used as the reactant source. Afterward, for the develop structure, it can be modified from the same reactant in the previous step and then place it into the new 3D structure. The bonding was changed and rearranged the atoms so as to finally obtain the product structure.

To perform a transition-state search, all the atoms in the reactant and product structures need to be manually paired and individually matched for DMol^3 calculation. Subsequently, in order to execute a transition-state search with the LST/QST functionality, we then need to create a pathway between the reactant and product, as it is required as input to the DMol^3 calculation. Within a few seconds, a new 3D atomistic trajectory document is generated that the DMol^3 calculation is obliged to run on this new file. The self-consistent field (SCF) tolerance and maximum SCF cycles were set to 1.0e^{-4} and 100, respectively, and SCF convergence can also be improved by setting smearing to 0.005 Ha.

I. RESULTS AND DISCUSSION

For consideration of the structural transformations during sol-gel fluorination, the first step is correspondingly supported by the DFT based calculations recently accomplished. The consequent steps of the fluorination feasibly involve an attack of fluorine ions or HF, which can coordinate to single Al atom and substitute the protonated isoproxide (O*i*Pr) group dissolved in isopropanol (*i*PrOH) as illustrated in Fig 2. Starting from this point, the observation of formation of structures in aluminum alkoxide fluoride and sol-gel as well as concentrating the changes during the fluorination process should be potentially possible. During this process, central AlO$_6$ are farther distorted and disoriented. Besides, species with an indistinctly downfield mainly shifted for sixfold coordinated aluminum atom as indicated by the feasible intermediate arisen.

Following by the next consequence is the combined incidence of fivefold Al species, which results from the former fourfold AlO$_4$ species. These following steps are additionally close to possible structures of intermediates as simulated with DFT calculations independently. The simulation results shown the process that ended with a cleavage of the initial tetrameric structure and the previously bridging isopropoxide (OiPr). The bridging and terminal isopropoxide groups at the final state were equivalently converted to the surrounded solvent molecules. The molecular structure in this state has been optimized and checked its stability by applying the SVWN exchange-correlation (XC) functional within the LDA, PBE, and B3LYP. The DN basis set along with 4.4 basis file for all the structures. The convergence tolerance for the maximum force and maximum displacement for normal geometry optimization were set to 0.2 Ha Å-1 and 0.5 Å, respectively. Conclusively, this should result in a better understanding of other metal alkoxide structures.

II. CONCLUSION

It is found in the simulation that as a result of the fluorolysis of Al alkoxide, not only nanoscopic sols can be formed from our simulations, but also crystalline intermediate states having stable structures with extraordinary fluorine linkages can be obtained. Therefore, once structural information for Al alkoxide and fluoride are included, it will assist to gain insights into the mechanism of anhydrous sol-gel synthesis of other metal fluorides, especially in our next research on calcium fluoride (CaF2) in the near future.

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