Mechanistic study of glycerol dehydration on Brønsted acidic amorphous aluminosilicate

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ABSTRACT

Si-(OH)-Al groups of amorphous aluminosilicate have been known to play important roles in acid-catalyzed reactions. However, there is a lack of theoretical understanding on the catalytic function of the acid sites and reaction mechanisms on the amorphous aluminosilicate surface. In this study, the preferred glycerol dehydration mechanism on Si-(OH)-Al sites was investigated via density functional theory calculation, and compared to experimental results. An amorphous aluminosilicate surface was constructed based on the β-cristobalite crystal structure, and adsorption and activation energies were calculated for each elementary step in the glycerol dehydration at Si-(OH)-Al sites. It was found that when the primary OH group of glycerol is adsorbed on Brønsted proton (Si-(OH)-Al sites), the adsorption strength is too strong to convert to acetol. On the other hand, the secondary OH group of glycerol is adsorbed with a relatively moderate strength at the acid site, which then leads to favorable production of 3-hydroxypropionaldehyde (3-HPA). Consequently, the 3-HPA is readily dehydrated into acrolein and water due to its reactive properties. Therefore, glycerol seemed to be preferentially converted into acrolein on amorphous aluminosilicate during dehydration. In order to verify the preferential formation of acrolein, catalytic activity test was experimentally conducted. The amorphous aluminosilicate catalyst exhibited remarkable selectivity for acrolein (46.5%), which supported our theoretical approach. In addition, the adsorbed and polymerized glycerol on the used catalyst surface was identified via ^{13}C NMR. This suggests that when glycerol is too strongly adsorbed, it can be transformed into coke during dehydration. Combining our theoretical and experimental observations, it was concluded that strongly adsorbed glycerol gives rise to not only a lower level of conversion but also coke deposition on the amorphous aluminosilicate surface. Comparative investigation of aluminosilicate and H-ZSM-5 zeolite gave new light on that the adsorption structure, adsorption energy, and reaction mechanism are altered by silanol groups on the aluminosilicate surface, although the active site (Si-(OH)-Al) of aluminosilicate is similar to that of H-ZSM-5 zeolite.

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1. Introduction

Since amorphous aluminosilicate was recognized as a highly active acid catalyst, many efforts have been made to reveal the relationship between the chemical structure of acid sites and catalytic activity [1–4]. In particular, the chemical structure of acid sites on amorphous silica-alumina (ASA) has been debated for decades. Crépeau et al. [5] have proposed silanol groups near Lewis acid Al^{3+} sites as Brønsted acid sites of ASA. Williams et al. [6] have reported that the water molecules bonded to surface Al atoms are

responsible for the acidity of ASA. According to their models, acidity of ASA would be expected to show moderate acidity. However, Poduval et al. [7] revealed that ASA possesses acid sites with strong acid strength as well as moderate one. Except for Si-(OH)-Al group, others such as silanol groups near Lewis acid Al^{3+} sites or water molecules bonded to surface Al atoms could not be the strong acid sites in ASA. In addition, pseudo-bridging silanols have been pointed as major components to cause acidity of ASA, theoretically [3] and experimentally [8]. The chemical structure of acid sites on ASA cannot be clearly explained yet. However, Si-(OH)-Al groups have attracted attention in various acid catalytic reactions in that they are strong Brønsted acid sites [2] and enable the production of value-added chemicals from hydrocarbons [9–11].

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Despite the significant role of Si-(OH)-Al groups, there has been an insufficient amount of theoretical investigation into the catalytic function of Si-(OH)-Al groups in amorphous aluminosilicate. This is because realization of an amorphous structure by means of periodic density functional theory (DFT) calculation is somewhat challenging. However, recent progress in modeling a structure of amorphous silica using β-cristobalite crystals [12] has made it possible to obtain various amorphous metal oxide structures. For example, functionalized-silica [13], mixed oxide [14] and supported oxide [15,16] catalysts were developed using a β-cristobalite model, which allowed their catalytic properties in the reaction to be investigated via theoretical calculation.

Glycerol dehydration is an acid-catalyzed reaction and a desirable pathway for petroleum-based processes because of its replaceability. Glycerol is biomass-based renewable feedstock and can be converted into valuable chemicals such as acrolein [17,18], acrylic acid [19,20], and propanediol [21,22]. Among these various utilizations, glycerol dehydration has attracted considerable attention, both industrially and academically. One of the most interesting aspects of the catalytic process of glycerol dehydration is that selectivity is dependent on the acid types of the catalysts [17,23]. In order to selectively form acrolein, the secondary OH group of glycerol should be abstracted in the first dehydration [23–25]. If the primary OH group is reacted first, then acetol is favorably produced rather than acrolein. In this step, Brønsted acid sites are more effective to produce acrolein than Lewis acid sites [23–26]. Aluminosilicates show superior selectivity for acrolein in this reaction because they have abundant Brønsted acid sites on the surface [17]. According to a previous report [27], the Brønsted acidity of aluminosilicate is strongly affected by neighboring Al atoms. When the Al content of aluminosilicate is increased, the ratio of Brønsted to Lewis acid strength is increased. This means that the Si-(OH)-Al groups of aluminosilicate can play a crucial role in glycerol dehydration as a selectivity-determining factor. However, how glycerol is converted on Si-(OH)-Al sites of aluminosilicate has not been studied. To achieve this, theoretical study is mandatory because it is difficult to comprehensively understand complex catalytic mechanisms based solely on experimental results. Moreover, observation of unstable intermediates (3-HPA) during glycerol dehydration is generally not available via experimental methods.

In the present study, the surface structure of amorphous aluminosilicate was developed using a β-cristobalite model, and the catalytic mechanism of glycerol dehydration on Si-(OH)-Al sites was investigated via DFT calculation. The adsorption structures and activation energies for each step of glycerol dehydration at Si-(OH)-Al sites are presented. In addition, theoretical expectations are verified via experimental results, whereby the predicted selectivity for each product is compared with the outcome from catalytic activity test, and deposited carbon species of the used catalyst is confirmed to demonstrate the suggested reaction pathway. The calculated adsorption energy, proposed catalytic process and coking in the use of aluminosilicate were compared to those in the use of H-ZSM-5 based on the previously reported results.

2. Methods

2.1. Computational methods

All calculations were carried out using a Vienna *ab* initio simulation package (VASP, version 5.3.2) [28]. The generalized gradient approximation (GGA) parameterized by a Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [29] was employed and core electrons were represented by the projector-augmented wave (PAW) method [30]. Dispersion forces were taken into account with the DFT-D2 Grimme's empirical correction [31]. An energy cutoff for the plane waves of 400 eV was applied. The geometry optimizations were performed using a $3 \times 3 \times 1$ Monkhorst−Pack mesh for the k-point sampling. The total energies were converged until the forces on all atoms were less than 0.03 eV/Å. The electronic optimization steps were converged self-consistently to $<2 \times 10^{-4}$ eV.

An amorphous aluminosilicate surface was constructed using a β-cristobalite (111) surface [32]. The β-cristobalite structure was used to represent amorphous silica due to similar properties such as its refractive index and bulk density [12,33–35]. On the developed silica surface, the Si atom was replaced by an Al atom with a constant molar ratio (Si/Al = 15) in its bulk structure. In our calculations, all atomic positions were fully relaxed and the surface consisted of Si slabs of 4 layers with ∼20 Å of vacuum space. In order to determine the number of Si layers, we constructed amorphous aluminosilicate surface with 6 Si layers (Fig. S1), and the adsorption energies of glycerol via different OH groups were calculated (Fig. S2 and Table S1). As a result, adsorption configurations and energies were very similar in spite of the increase in the number of slab. This indicates that 4 Si layers are enough to establish the aluminosilicate surface. Bader charge analysis [36] was performed to evaluate the charge redistribution on silanol and Si-(OH)-Al groups.

Gas-phase glycerol was used based on previous study results, which showed it to be one of the stable conformers [37]. In their results, the molecular energies and structures of 126 possible conformers were presented. We selected the 5 most stable configurations based on their results, and then determined which was the most stable.

For the adsorption calculations, total 12 cases of glycerol adsorption configurations were investigated to determine the preferred adsorption structure. Details are presented in Supplementary material (Figs. S3–S5 and Table S2). The adsorption energies for single molecules were calculated as follows:

$$\Delta E_{ads} = E_{adsorbate/surface} - E_{adsorbate} - E_{surface}$$

The co-adsorption energies for the product with a water molecule were calculated as follows:

$$\Delta E_{co-ads} = E_{(adsorbate+H2O)/surface} - E_{adsorbate} - E_{H2O} - E_{surface}$$

Deprotonation energy was calculated based on a reaction with gaseous water molecule ($HA + H_2O(g) \leftrightarrow A^- + H_3O^+(g)$), and following equation for deprotonation energy was used:

$$E_{DPE} = E_{A^-} + E_{H3O+,gas} - E_{HA} - E_{H2O,gas}$$

where HA and A^- represent the acid site and deprotonated acid site, respectively. The charge density difference (Δq_i) was defined as follows:

$$\Delta q_i = q_{i,after\ adsorption} - q_i - q_{surface}$$

where $q_{i,after\ adsorption}$, q_i and $q_{surface}$ denote the charge density of the adsorbed system, molecule i and the surface, respectively.

Activation energy barriers and the transition images for all elementary steps were calculated using the climbing-image nudged elastic band (CI-NEB) method [38,39]. At least five intermediate images were interpolated between reactant and product states. In the CI-NEB calculations, the images were sampled using a $1 \times 1 \times 1$ Monkhorst-Pack k-point grid and obtained until the maximum atomic forces were converged within 0.05 eV/Å. When harmonic frequencies were calculated for NEB-optimized transition states, only a single imaginary frequency was obtained in all cases (Table S3). We calculated activation energies for the first dehydration step from various adsorption modes including less stable ones, and then we found the lowest activation energy for