Study of the Interaction of Ethanol with the Brønsted and Lewis Acid Sites on Metal Oxide Surfaces Using the DV-Xα Method

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The interactions of ethanol with a Brønsted acid site (a hydroxy group) and with a Lewis acid site (a metal ion) on surfaces of seven metal oxides (SiO2-Al2O3, SiO2, TiO2, ZnO, MgO, MnO and CdO) have been investigated using the DV-Xα method. The oxides were selected from a series of catalysts, whose selectivities for the dehydration and the dehydrogenation of ethanol had been experimentally determined by P. Sabatier and A. Mailhe.

By comparing the results of the DV-Xα calculations from several models of ethanol interacting with the Brønsted or Lewis acid sites with the experimental selectivities, it was concluded that a proton shift from the Brønsted site to the ethanol oxygen occurs when ethanol strongly interacts with the site and that this shift changed the electronic state of ethanol for the dehydration to be favorable. These results indicate that the dehydration of ethanol on oxide catalysts proceeds by the E1 mechanism.

Keywords: DV-Xα method, Ethanol, Dehydration, Dehydrogenation, Brønsted acid site, Lewis acid site

1. Introduction

Metal oxides have been used as inorganic materials in ceramics, glasses, pigments, etc. Especially, the oxides prepared by the thermal decomposition of hydrates, carbonates, sulfates, etc. are widely utilized for solid acid and base catalysts and catalyst supports. The reason for this is that the oxides thus prepared often have surface acid and/or base sites and large surface areas due to well-developed porous structures. The dehydration and the dehydrogenation of alcohols on the oxides have been two fundamental catalytic reactions studied since early times [1]. Some previous experimental studies have shown that the dehydration is promoted by surface Brønsted acid sites (hereafter abbreviated as B sites) or Lewis acid sites (hereafter abbreviated as L sites) on oxides [2], and that the dehydrogenation is promoted by surface basic sites on the oxides [3]. It has been clearly shown that ethoxide is involved in both reactions [4, 5, 6, 7]. However, details of the interaction of ethanol with the acid and base sites and the relationship of the dehydration and

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dehydrogenation selectivities with the interaction have not been sufficiently understood.

It is now popular to understand catalysis by using quantum chemistry. For example, some simple and complex oxides of light metals (Si, Al, Mg, etc.) have been calculated by the CNDO method, etc., to examine the relationship between the strength of the acidity or basicity of the oxides and partial electrical charges on the hydrogen and oxygen atoms of the oxides, or energies required for proton addition or abstraction from the sites [8, 9, 10]. Oxides of metals in the fourth and higher periodic groups, however, have not been studied by semi-empirical molecular orbital methods, because they cannot be dealt with by these methods. The effects of the kinds of metals and types of acid and base sites on reactivities of reactants have never been studied for such a complex system as that composed of ethanol interacting with acid and base sites on metal oxides.

Table 1 shows the selectivities of the dehydration and the dehydrogenation of ethanol on a series of oxides studied by P. Sabatier and A. Mailhe [1].

| Metal Oxide | Dehydration / % | Dehydrogenation / % |
|-------------|-----------------|---------------------|
| ThO₂        | 100             | trace               |
| Al₂O₃       | 98.5            | 1.5                 |
| W₂O₄        | 98.5            | 1.5                 |
| Cr₂O₃       | 91              | 9                   |
| SiO₂        | 84              | 16                  |
| TiO₂        | 63              | 37                  |
| BeO         | 45              | 55                  |
| ZrO₂        | 45              | 55                  |
| UO₂         | 24              | 76                  |

Table 1: Selectivities of various metal oxides for catalytic dehydration and dehydrogenation of ethanol. (P. Sabatier and A. Mailhe)

In the table, the dehydration selectivity is defined as the percentage of ethanol changed into water and ethylene, and the dehydrogenation selectivity as the percentage of ethanol changed into hydrogen and acetaldehyde.

Let us assume that there exists a series of catalysts arranged in a certain order of experimentally determined selectivity for a given reaction. The quantum chemical computations are then carried out on a postulated transition state of the reaction. If the postulated one is valid, computed physical quantities, such as strength of a bond being broken or formed at the transition state, should change according to the catalyst order. On the other hand, if the postulated transition state is invalid, change in the calculated physical quantity should be independent of the catalyst order. Therefore, in the case of the reaction for which a series of catalysts is experimentally known to have an ordered catalytic property, it is considered possible to inspect the validity of the reaction mechanism by quantum chemically computing the transition state expected from the mechanism.

In this study, models consisting of B or L sites on oxides of several metals in the 3rd - 5th periodic groups and ethanol were computed for the first time using an ab initio method. From these results, it was investigated whether the dehydration and the dehydrogenation selectivities were determined by the electronic state of ethanol interacting with acid sites. It was also determined whether a population, a measure of strength of a covalent bond, changes in agreement with the catalyst series of
the dehydration selectivity. From these inspections, the validity of the proposed mechanisms for the dehydration and the dehydrogenation was discussed.

The DV-Xα method employed here is one of the ab initio methods and it is possible to significantly reduce its cpu time compared to the other ab initio methods. It is also possible to deal with much larger clusters involving heavy atoms. It is well known that the method supplies reliable values for many physical quantities except for the total energy of the system[11].

2. Calculation method

In the DV-Xα cluster method (Discrete Variational Xα cluster method), a molecular orbital of a cluster is represented by using an LCAO approximation, as \( \phi_l = \sum C_{il} X_i \), where \( \phi_l \) is the \( l \)-th molecular orbital and \( X_i \) is the \( i \)-th atomic orbital. This method is one of the Xα methods [11] which compute the electronic states of a given system by the Hartree-Fock-Slater method proposed by Slater [12], where the exchange potential is expressed by the 1/3rd power of the electronic density as

\[
V_{XC}(i) = -\frac{3\alpha}{4}\left(\frac{3r^\uparrow}{4\pi}\right)^{1/3},
\]

where \( r^\uparrow \) is the upper spin density and \( \alpha \) is a parameter.

Parameter \( \alpha \) can be determined by setting the total energy obtained by the Xα method to be equal to that obtained by the Hartree-Fock method. It was reported that errors in the molecular orbital calculations are generally negligible when using \( \alpha = 0.7 \) [13]. Computing time required for the DV-Xα calculation is much shorter than that required for the Hartree-Fock ab initio calculation.

In this study, the value 0.7 was employed for \( \alpha \). Calculations were carried out using the general-purpose M-860 computer made by the Hitachi Corporation located at the General Information Processing Center of Shinshu University. For making the coordinate data and processing the calculated results a personal computer PC-9801 made by the NEC Corporation was used.

3. Reaction model of transition state

Mechanisms of the dehydration and the dehydrogenation of ethanol on metal oxides so far proposed are shown in Figure 1.

The dehydration of alcohols on metal oxides has been considered to proceed through carbenium ions by an E1 mechanism, because olefins generated on Al₂O₃ and other oxides are consistent with Saytzeff's law [14]. The dehydrogenation has been thought to proceed through the ethoxide generated by breaking the O-H bond of alcohols on basic metal oxides [6].

![Fig. 1 Reaction mechanisms of ethanol dehydration and dehydrogenation on metal oxides. M = Metal ion](http://cssjweb.chem.eng.himeji-tech.ac.jp/jcs/content.html)
In this study, interactions of ethanol with the B or L sites were studied. The B sites are the protons of surface hydroxyl groups and the L sites are the surface metal ions [8, 15]. The interactions are the first step of the reactions where an alcohol interacts with the acid sites and produces either a carbenium ion or an ethoxyl group.

3.1 Model of the transition state in the B site - ethanol system

The simplest model was adopted for the transition state model. The model for the B site - ethanol system is shown in Figure 2.

Fig. 2 A model of ethanol interacting with a Bronsted acid.

3.2 Model of the transition state in the L site - ethanol system

The model on the L site is shown in Figure 3 for the case of SiO2. In this case, the acid site is a metal ion. The coordination number of a metal ion was reduced by one from that of the practical number realized in its oxide crystal. Experimental values from the literature [16, 17, 18] were adopted for bond distances of ethanol and the oxide. The distance between the B site and the oxygen of ethanol is set to 1.5 Å for the following reasons. The stable structure of the B site (SiO2-Al2O3, SiO2, ZnO, MgO, CdO) - ethanol system was calculated using the MOPAC-PM3 method in the range of 2.5 - 1.0 Å for the distance. For the case of SiO2-Al2O3 and SiO2, which exhibits the highest dehydration selectivity, the system had the highest stability at the distance of 1.8 Å. On the other hand, systems involving the other oxides had no stable structures. The systems were therefore compared to each other at the distance of 1.5 Å where the interaction must be stronger than that at 1.8 Å. Each terminal oxygen of the cluster was replaced by a hydroxyl group or water, and the system electrically was kept neutral. The coordination number of a metal ion or an oxide ion was set to the practical numbers realized in the oxide crystals. The central metal ion in the cluster was Si, Ti, Zn, Mg, Mn, or Cd. A similar model was made for the case of SiO2-Al2O3 and subjected to the computation. In the model, SiO2 was approximated by Si(OH)4. Similarly, TiO2, ZnO, MgO, MnO2, CdO, and SiO2-Al2O3 were approximated by Ti(OH)4(H2O)2, Zn(OH)2(H2O)2, Mg(OH)2(H2O)4, Mn(OH)2(H2O)4, Cd(OH)2(H2O)4, and Si(OH)3-OH-Al(OH)3, respectively.
4. Computed results and discussion based on the population of a bond

As mentioned above, the selectivities of oxide catalysts for the dehydration and the dehydrogenation of ethanol for the catalyst series shown in Table 1 have been reported [1]. Except for the two reactions, no other reaction took place under the experimental conditions. Therefore, the sum of the dehydration and the dehydrogenation selectivities is equal to one. Later, Tanaka reported a similar catalyst series together with a concept for ion electronegativity [16]. The series shows that the dehydration occurs on acidic catalysts such as Al₂O₃, SiO₂, TiO₂, etc. and that the dehydrogenation occurs on basic catalysts such as MgO. As explained above, the mechanisms shown in Figure 1 have been proposed for the dehydration and the dehydrogenation of ethanol.

Computation models were constructed on the basis of the mechanisms and were subjected to computation of the populations of the chemical bonds building ethanol which interacted with the B sites on six kinds of metal oxides and silica-alumina. The results of the computations are shown in Figure 4. The metal oxides were arranged on the abscissa in order of the dehydration selectivity experimentally determined by P. Sabatier and A. Mailhe, i.e., in the order where the selectivity decreases from left to right. The selectivity value is shown in the figure by using the right ordinate. The numbers on the left ordinate indicate the population of a bond of ethanol interacting with the B site, by setting that of the corresponding bond of free ethanol as a standard. The population used here is derived from Mulliken's population analysis and shows overlap of the orbitals of the two bonding atoms. Therefore, the value is a certain measure of the strength of the (covalent) bond. That is, when a value on the left ordinate is positive, the bond of the ethanol interacting with the B site is stronger than the corresponding bond of free ethanol. Inversely, when negative, the bond is weaker.
thought to be weaker. When ethanol interacts with the B site and is dehydrated to ethylene, it is favorable that the O-H and Cα-Cβ bonds in ethanol become stronger and that the Cα-O bond becomes weaker. As shown in the figure, the population of each bond significantly varies from one oxide to another. However, the variation has no relation to the order of the dehydration selectivity of the oxides. For example, the population of the Cβ-H bond, which breaks in the case of ethylene formation, has a similar value for every oxide, which exhibits very different dehydration selectivity. These results indicate that the ethylene formation by fission of the Cβ-H bond is not facilitated even if ethanol interacts with the B site.

When ethanol interacts with the B site, the population of the O-Cα bond is positive for any oxide. This result means that the bond becomes stronger with the interaction. On the other hand, the population of the Cβ-H bond is negative, so the bond becomes weaker during the interaction. It may be impossible, however, to discuss the reaction mechanisms from these results for the two bonds, because absolute values of the populations and their variations with the kind of metal oxides are too small.

Figure 5 shows the computed populations of the bond between ethanol oxygen and the B site formed during the early stage of the dehydration. Except for the case of CdO and MnO, there is a close relationship between the population and the dehydration selectivity. This relationship means that the dehydration becomes favorable when the bond between the B site and the ethanol oxygen becomes stronger. This result agrees with the E1 mechanism, i.e., the proton moves from the B site to the ethanol oxygen in the first stage of the dehydration, and then the protonated species is dehydrated to an ethyl cation, which converts into ethoxide by reacting with surface oxygen. The generation of the ethoxide is rate-determining. For the case of CdO and MnO, there is no correlation between the population and the dehydration selectivity. This is likely caused by using 1.5 Å, which could be unsuitable for the two oxides as the distance between the B site and the ethanol oxygen, and that oxide surfaces could not be sufficiently represented by such small clusters as our computation models.

In the field of theoretical organic reactions, the electronic density in the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) is widely used as an important index of reactivity. Therefore, the electronic density and orbital composition of HOMO of the transition state of the dehydration were examined. As a result, it was found that the main component of HOMO was the orbitals of the oxygens of ethanol and the surface hydroxyl group. In Figure 6, the electronic density of the ethanol oxygen in HOMO was plotted against the kind of oxides. The obtained curve corresponded well to the variation in dehydration selectivity. This result means that the higher the electronic density of the ethanol oxygen in HOMO becomes, the higher the dehydration selectivity.

The population of each bond of ethanol which interacts with the Lewis acid site is shown in Figure 7. In this system, the absolute value of the population of the bond building ethanol was bigger than that computed for the B site - ethanol system, because the metal ion interacts directly with the ethanol oxygen. Furthermore, the population varied greatly with the kind of oxides. The variations in the populations of the O-H and the Cα-Cβ bonds were especially large. However, the trend in the variation was independent of the dehydration selectivity of the oxides. On the other hand, the strength of the O-Cα bond had a trend to become stronger by the interacting of ethanol with the acid site on the oxides. However, this trend is likely within the error range of the computation, as is the trend in the case of ethanol interacting with the B site.
The population of the bond between the metal ion and the ethanol oxygen is plotted in Figure 8 against the kind of oxides, together with the dehydration selectivity. In contrast to the case of the B site, the population has no correlation to the dehydration selectivity of the oxide. For example, although the dehydration selectivity of titanium dioxide is high, the bond of the titanium ion with the ethanol oxygen is weak. Incidentally, in contrast to the case of the B site, the main component of the orbital near the HOMO of the L site system was not the orbital of the ethanol oxygen and of the
surface hydroxyl group. Therefore, the electronic density of ethanol oxygen in HOMO could not be computed.

5. Discussion on the basis of the band theory

In order to further understand the relationship between the kinds of oxides, the types of acid sites and the reaction selectivity, band structures of the oxide - ethanol systems were studied for the B site and the L site - ethanol systems, respectively. The band structures obtained are schematically shown in Figure 9.

For the case of the B site - ethanol system, the band structures could be classified into three types according to the reaction selectivity of the oxide. The first is the system involving oxides (SiO$_2$-Al$_2$O$_3$, SiO$_2$, etc.) with the highest dehydration selectivity. For this type of system, the energy level of the 2p orbital (HOMO of the system) of the ethanol oxygen was higher than that of the 2p band of the oxygen of the metal oxide. The second is the system involving oxides (TiO$_2$, ZnO, etc.) with moderate dehydration selectivity. The energy level of the 2p orbital of the ethanol oxygen was as high as that of the 2p band of the oxygen of metal oxide. There was to some extent, hybridization between the orbital and the band, and therefore, the HOMO is a hybrid orbital of the 2p orbitals of the oxygens of ethanol and of the metal oxides. The third and the last is the system involving oxides
(MgO, MnO, etc.) with no dehydration selectivity. The energy level of the 2p orbital of the ethanol oxygen was lower than that of the oxygen 2p band (HOMO of the system) of the metal oxide. With regard to CdO, although the dehydration selectivity was low, the band structure was similar to that of the oxides with the highest selectivity. This is likely caused by the fact that the computation model used was too small and too simple. Anyway, it was impossible to determine the right mechanism based on the discussion of the band structures, because the interaction of ethanol with the B site was thought to take place via the following two routes: the first is the route where a proton moves from an oxygen of the oxide to the ethanol oxygen, and the second is the route where some electrophile attacks the ethanol oxygen and then the dehydration occurs.

The band structure of the L site - ethanol system is schematically shown in Figure 9(b). The kind of oxide had no substantial influence on the band structure. The 2p orbital of the ethanol oxygen made an energy band, which agreed with that of the 2p band of the oxygen of the oxides. From these results, it was suggested that the electronic state of the oxygen of ethanol interacting with the L site was more similar to that of oxygen of the oxide than to that of the hydroxyl oxygen of ethanol.

It was also suggested that the electronic state of the ethanol oxygen was essentially the same for any oxide. Therefore, from the point of view of computational chemistry, the adsorption state of ethanol is nearly identical on any oxide. The dehydration selectivity of each oxide is, however, quite different from that of another oxide. Therefore, it is reasonable to conclude that the dehydration of ethanol does not occur on the L site.

6. Conclusion

When ethanol interacted with the B site on the oxides, there was little change in the population of the bond building ethanol. Therefore, the population has little relationship to the dehydration selectivity of the oxide. On the other hand, the population of the bond between the B site and the ethanol oxygen had a clear tendency in accordance with the dehydration selectivity of the oxide. Therefore, for the oxide having the highest dehydration selectivity, its B site makes a strong interaction with the ethanol oxygen. In such a case, the reaction is thought to proceed as follows: ethanol receives a proton from the B site, and then, the protonated ethanol releases a water molecule to form the ethyl cation, which transfers its H⁺ to the oxide and simultaneously converts into ethylene. This process agrees with the E1 mechanism. Based on band theory, it became clear that the electron density of the HOMO of the ethanol oxygen corresponds well to the dehydration selectivity of the oxides.

However, with regard to ethanol interacting with the L site, the population of any bond of the system, including those of the bonds between the L site and the ethanol oxygen, had no regular relationship with the dehydration selectivity of the oxides. Moreover, the band structure of the system did not correspond to the dehydration selectivity. These results indicate that the dehydration of ethanol does not occur on the L site.

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金属酸化物表面上の Brønsted 酸点および Lewis 酸点とエタノールとの相互作用の DV-Xα 法による検討

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7種の金属酸化物（SiO₂-Al₂O₃、SiO₂、TiO₂、ZnO、MgO、MnO およびCdO）表面上のBrønsted 酸点（表面ヒドロキシル基）およびLewis 酸点（表面金属イオン）とエタノールとの相互作用を、DV-Xα法により検討した。これらの酸化物は、P. Sabatier / A. Mailhe（1910年）により報告されているエタノール脱水・脱水素反応選択性についての触媒序列の中から選択された。

表面Brønsted 酸点とエタノールおよび表面Lewis 酸点とエタノールからなるモデルについて、それぞれ DV-Xα 法により計算した結果と実験的に決定された脱水反応選択性を比較することにより、エタノールが Brønsted 酸点と強く相互作用する場合にはエタノールの酸素にプロトン付加が起こること、また、この付加によりエタノールの電子状態が脱水反応に好ましい状態に変化することを結論した。これらの結果は、酸化物触媒上でのエタノールの脱水反応が E1 機構で起こることを支持している。