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Solid acidity of metal oxide monolayer and its role in catalytic reactions

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Abstract

Such metal oxide as SO_4^{2-}, MoO_3, WO_3, and V_2O_5 spread readily on supports like SnO_2, ZrO_2, and TiO_2 due to the different properties between acid and base oxides to generate the acid site on the monolayer. Number, strength, and structure of the acid site were characterized by temperature-programmed desorption (TPD) of ammonia principally, together with various physico-chemical techniques, and its role for catalytic reactions was studied. Approximately, one to two acid sites were stabilized on 1 nm^2 of the surface, which consisted of four to eight metal atoms. The limit in surface acid site density was estimated on the monolayer based on the concept of solid acidity on zeolites. Sequence of the metal oxide to show the strong acidity was, $SO_4^{2-} > WO_3 > MoO_3 > V_2O_5$, and for the support oxide to accommodate the monolayer, $SnO_2 > ZrO_2 > TiO_2 > Al_2O_3$. From these combinations, the metal oxide monolayer to show the adequate strength of acid site could be selected. Brønsted acidity was observed often, however, the Lewis acidity was prevailing on the reduced vanadium oxide. The structure of acid site, Brønsted or Lewis acid site, thus depended on the oxidation state. Relationship of the profile of solid acidity with various catalytic activities was explained. The solid acid site on the monolayer will possibly be applied to *environment friendly technologies*.

Keywords: Metal oxide monolayer; Solid acidity; Temperature-programmed desorption

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1. Introduction

When such acidic metal oxide as SO_4^{2-}, MoO_3, WO_3, and V_2O_5 are loaded on basic metal oxide supports like SnO_2, ZrO_2, and TiO_2, a highly spreading of metal oxide is observed, and so-called the metal oxide monolayer is formed [1–8]. Such a formation of the metal oxide monolayer is due to the strong interaction between acid and base metal oxides. Among these combinations of metal oxide monolayer, many kinds of important catalytic material with strong acidity can be indicated, for example, SO_4^{2-} on ZrO_2, MoO_3 on SnO_2, V_2O_5 on TiO_2, etc. These are used as industrial catalysts, or regarded as candidate materials available for the important catalytic reactions. The structure of monolayer metal oxide, i.e. mono-atomic layer of metal oxide consisting of one component covers the surface of another component metal oxide, is often formed spontaneously. Therefore, the metal oxide monolayer is encountered on the catalyst prepared from binary mixture of metal oxide. The solid acid site on the monolayer seems to be formed on a usual catalyst with the same component. Our strategy in this field of investigation is to understand the formation and acidity of metal oxide monolayer, because only the loaded metal oxide is exposed to the surface, and the structure is relatively easy to understand. In this paper, we will summarize the solid acidity and catalytic activity of metal oxide

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monolayer that have been undertaken recently in our group.

2. Experimental methods

2.1. Catalyst preparation

Catalysts are prepared by an impregnation method. The amount of loaded metal oxide is adjusted to less than ca. 15 nm^{-2} of the surface concentration. Usually, 4–8 metals nm^{-2} is found to be a concentration sufficiently to cover the surface of support almost completely, as shown below.

2.2. Characterization

A method of benzaldehyde ammonia titration (BAT) is used to estimate the extent of coverage by the loaded metal oxide [1]. Principle of the method is a selective adsorption of benzaldehyde as benzoate anion on support metal oxide. Such basic metal oxides as SnO_2, TiO_2, ZrO_2 and Al_2O_3 can accommodate the anion with such a high surface concentration as 2 nm^{-2}, which is limited by the steric hindrance. In order to keep the metal oxide highly oxidized, the catalyst was oxidized using oxygen before the adsorption. Then, the temperature of catalyst bed decreased to 423 K, at which it was confirmed that the metal oxide surface was not reduced, and the saturated adsorption of benzaldehyde occurred. Ammonia was finally injected to form benzonitrile from which the amount of adsorbed benzoate anion was counted. The details of the experiment have been described elsewhere [1].

Number and strength of acid site is measured by temperature-programmed desorption (TPD) of ammonia. Water vapor treatment is carried out before elevation of the bed temperature, because ammonia adsorbed on the support is selectively removed by admitting water vapor, and the profile of ammonia only on the supported metal oxide is revealed [5]. Strength of the acid site, i.e. ΔH for ammonia adsorption, is calculated from the theoretical equation, previously derived based on the equilibrium-controlled conditions [6]. Not only the temperature of desorption peak but also the desorbed amount of ammonia therefore affects the parameter ΔH.

3. Results and discussion

3.1. Formation of monolayer and number of the acid site

Formation of the metal oxide monolayer was revealed by the measurements of coverage on supports and the cation site density expected on the monolayer. An example of the monolayer formation is shown for WO_3 on ZrO_2 in Fig. 1. The extent of coverage by WO_3 loaded, measured by BAT, was plotted against the surface concentration of W. As shown in this figure, the coverage increased linearly with increasing the concentration of W on the support. By extrapolating the linear plot to 100% of coverage, it is expected that the support surface is completely covered by WO_3 at about 4 W nm^{-2}. On the other hand, the surface cation site density on the crystal of WO_3 was 4–7 nm^{-2} depending on the exposed crystal face. The averaged value of the cation site density on the WO_3 crystal is therefore in good agreement with the surface cation site density expected on the monolayer with 100% of the coverage. This means that the monolayer of WO_3 is loaded on the support of ZrO_2 in less than 4 W nm^{-2}, and multiple layer of WO_3 is formed on further loading. WO_3 is loaded selectively on the surface of ZrO_2 support until the surface cation density is 4 W nm^{-2}. This behavior of loading is explained

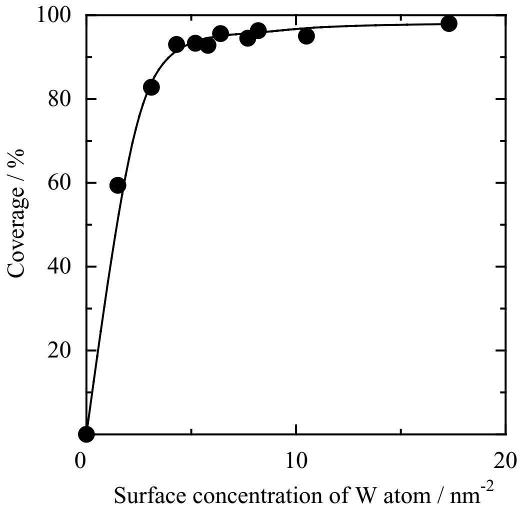

Fig. 1. Measurements of extent of coverage by WO_3 on ZrO_2 by a method of BAT.

simply by the different properties of WO_3 and ZrO_2 as to acidic and basic character of metal oxide, respectively. Such a confirmation of the monolayer formation has been done on MoO_3 on various supports such as SnO_2, ZrO_2, TiO_2, Al_2O_3, and Fe_2O_3 [3].

From the BAT experiment, we have a rough estimation of loaded metal oxide on the supports. In order to obtain a more precise structure of the loaded oxide, physical techniques such as IR, laser Raman, EXAFS, etc. are to be measured. In fact, the species of metal oxide on the support has different structures, completely isolated or polymerized cluster, of which formation depends on the surface concentration. Therefore, we know only the extent of coverage with a surface cation density from the BAT experiment.

Amount of acid site on the metal oxide monolayer on various supports was determined from the desorbed amount of ammonia. Table 1 shows the surface density of acid site, determined from the TPD of ammonia after the water vapor treatment. The loaded metal cation density was controlled 4–8 metals nm^{-2} to form the monolayer with the high coverage except for MoO_3/Al_2O_3. Surface density of acid site was usually less than 2 nm^{-2}, and typically 1–2 nm^{-2}. Fe_2O_3 based catalysts have shown unusual low and high values of acid site density, which indicates that the simple monolayer was not formed, and a mixing of cations of Fe and loaded metal is estimated.

From the surface densities of metal cation and acid, the generation probability of the acid site is approximately 1/5 to 1/4 of the loaded metal atom. From this ratio, it is expected that four to five metal atoms create one acid site. Therefore, formation of cluster compound or hetero-poly anion consisting of four to five metal cations is expected for the surface compound to show the acidity. In fact, a recent study on V_2O_5 on TiO_2 using density functional theory indicates a cluster compound consisting of four metal cations has one proton [9].

Table 1
Amount and density of acid site on the monolayer

Catalyst	Loaded metal (metals nm^{-2})	Acid site	
		Amount ($mol\,kg^{-1}$)	Density (nm^{-2})
V_2O_5/ZrO_2	8.5	0.26	2.2
V_2O_5/TiO_2 (a + r)	4.4	0.08	1.1
MoO_3/SnO_2	6.0	0.04	1.0
MoO_3/ZrO_2	6.7	0.07	0.7
MoO_3/Al_2O_3	11.9	0.39	1.4
MoO_3/Fe_2O_3	8.0	0.13	4.3
MoO_3/TiO_2	8.0	0.04	0.5
WO_3/SnO_2	6.8	0.03	0.6
WO_3/ZrO_2	6.4	0.21	1.3
WO_3/Fe_2O_3	4.2	0.04	0.5
WO_3/TiO_2	6.3	0.23	1.7
SO_4^{2-}/ZrO_2	7.0	0.20	1.8

Acid site density at the monolayer may be explained by an idea, i.e. limit of acid site surface density [8]. We learn the conditions of acid site stabilization from the zeolite investigation, because a more correct understanding of the acidity is possible in zeolites. Amount of acid site in zeolite mordenite and Y has the volcano-type dependence on the amount of framework Al. Our recent study shows that the acid sites are not stabilized in the topologically excess Al concentration [10], and collapse of acid sites occurred due to the mutual interaction in the presence of adsorbed water. Highest acid site concentration of zeolites 1.5 $mol\,kg^{-1}$ is observed on the H-mordenite with Si/Al_2 ratio of 15. From the surface area, this value, i.e. an optimum high concentration of acid site on zeolite, corresponds to about 2 nm^{-2}. Therefore, similar conditions would be plausible in the metal oxide monolayer, and too high concentration of acid site is not allowed. This idea, limit in surface density, could explain the surface concentration of acid site on the monolayer; approximately, one to two acid sites are stabilized on 1 nm^2 of the surface, which consists of four to eight metal atoms.

3.2. *Strength and structure of acid site on the monolayer*

Strength of the acid site on the monolayer is summarized in Fig. 2. The strength is influenced not only by loaded metal oxide but also support. Usually, ΔH is high in the low concentration of metal oxide, and decreases gradually with increasing the loaded amount. An isolated species of metal oxide may be stabilized in the low concentration, and a surface cluster compound becomes abundant as the concentration increases. Change of ΔH with the concentration may be explained by the formation of surface species with different structures, and the isolated species has the higher strength than the corresponding cluster compound.

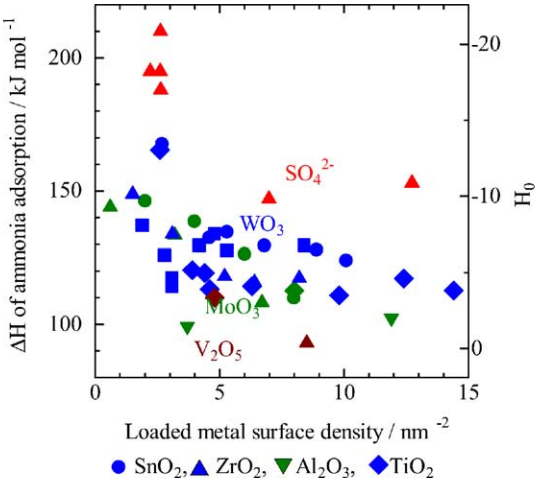

Fig. 2. ΔH and H_0 of the metal oxide monolayer on various supports with increasing the loaded metal surface density.

Fig. 3 shows the ΔH of the metal oxide monolayer on supports at the concentration of 4–8 metals nm^{-2}. Sequence of the metal oxide to show the strong acidity is, as shown in Fig. 3, therefore $SO_4{}^{2-} > WO_3 > MoO_3 > V_2O_5$. On the other hand, the sequence of support oxide to accommodate the monolayer is $SnO_2 > ZrO_2 > TiO_2 > Al_2O_3$, though the case of loaded vanadium oxide might be ordered in a different way. A combination of $SO_4{}^{2-}$ on SnO_2 would be the strongest acid catalyst based on this summary, and in fact this is consistent with the measurements by Matsuhashi et al. [11].

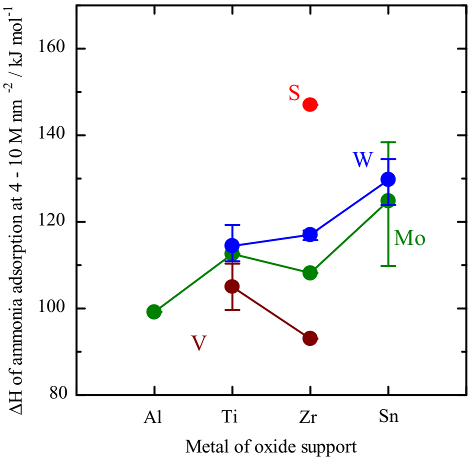

Fig. 3. ΔH of ammonia adsorption on the monolayer with metal surface concentration, 4–10 metals nm^{-2}.

Acid site is created on the cluster compound in this region, as discussed above. Therefore, not only the structure but also electric configuration of the cluster would determine the strength of the acid site. Structure of the monolayer must be similar to the crystal of metal oxide, fundamentally. However, it can be modified due to the influence by the basal plane of support. Therefore, the structure is optimized by the interaction between them. Electric configuration is also determined by the electric properties of loaded metal oxide and support. Most simply, electro-negativity of the cations of metal oxide and support may determine the strength of acidity. However, electro-negativity cannot explain the sequence of the strength of acid site correctly. It would be explained more precisely from the electronic interaction between metal oxide monolayer and support based on the precise structure model. Further study on this problem should be carried out using a quantum chemical calculation.

Structure of the acid site, Lewis or Brønsted acid site, is particularly important, however it is not fully proven yet mainly due to the difficulty in IR study caused by the low transmittance. We confirmed however some of metal oxide monolayer as the Brønsted acid site. An example that has been proven is WO_3 monolayer on ZrO_2 to show the Brønsted acidity. On the sulfate anion on zirconia, the structure is strongly dependent on the concentration of metal oxide, as described below.

Complex behavior was observed on the V_2O_5/TiO_2 (anatase). Vanadium oxide is readily reduced, and shows different solid acidity independent on the surface oxidation states. Fig. 4 shows the TPD of ammonia on the V_2O_5/TiO_2 with 4.4 V nm^{-2}. TPD spectrum on the oxidized one showed two-spike pattern, one desorption at 460 K and another at 610 K. However, it changed drastically by simply evacuation or by flowing hydrogen, thus showing one desorption at 520 K. TPD of ammonia using infrared spectroscopy was applied to reveal the structure of acid site of ammonia desorption. In this study, only the weight of catalyst was decreased to one-tenth of the usual TPD experiment, and IR was taken successively during the elevation of temperature from 353 to 873 K. The background spectra without adsorption of ammonia were taken successively at the

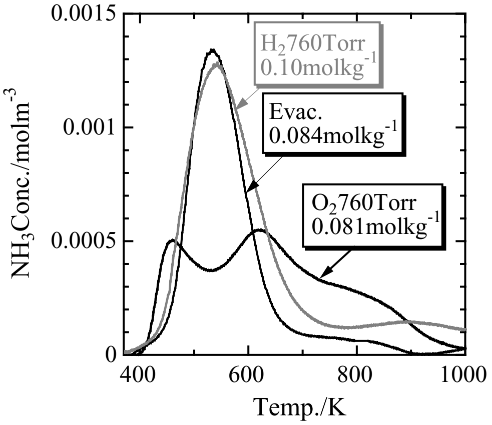

Fig. 4. TPD of ammonia on V_2O_5/TiO_2, oxidized, reduced or evacuated before adsorption of ammonia.

same region of temperature, and difference spectra were calculated by subtracting the latter from the former. Differentiation of thus calculated IR intensity with respect to temperature of the bed gives us the TPD spectrum of adsorbed species, from which the structure of acid site is able to be determined. Fig. 5 shows the TPD-IR on the vanadium oxide monolayer. IR of adsorbed ammonia showed absorptions at 1423 and 1241 cm^{-1}, which were ascribable to Brønsted and Lewis type adsorbed species of ammonia, respectively. IR intensity of Brønsted band disappeared at about 400 K and that of Lewis band at 520 K. Temperature of the disappearance was therefore lower than that of usual TPD, 460 and 610 K, respectively. Theoretical equation for the TPD of ammonia, which was derived under the conditions of freely occurring of re-adsorption of ammonia, however predicts the difference of temperature correctly. Therefore, the low temperature desorption of ammonia was ascribable to the acid site of Brønsted type, while the high temperature desorption to Lewis type. One single desorption of ammonia on the reduced catalyst was proven to be the Lewis type (IR evidence is not shown). Vanadium oxide loaded on titania therefore showed the complex behavior which depended on the oxidation states [8].

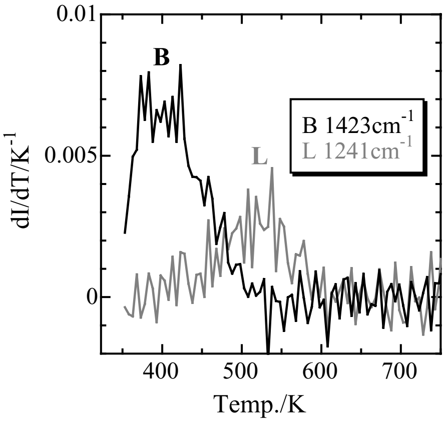

Fig. 5. TPD-IR of ammonia adsorbed on the oxidized V_2O_5/TiO_2.

3.3. *Catalytic activity on the monolayer*

Oxidation of methanol into formaldehyde proceeds selectively on the MoO_3 monolayer. MoO_3 covers the surface of all the supports, SnO_2, ZrO_2, TiO_2 and Al_2O_3, as the monolayer. Activity of MoO_3 for this reaction is enhanced by the loading, and the TOF (turnover frequency) depends on the support, i.e. on $SnO_2 > ZrO_2 > TiO_2 > Al_2O_3 >$ on unsupported MoO_3. Sequence of TOF is almost the same as that of acid strength [4]. Because of low transmittance of SnO_2-based catalyst, IR study was not undertaken, and the acid site is only expected to be Brønsted type. Methanol is selectively adsorbed on the Brønsted acid site as methoxide, and then oxidized into formaldehyde as a result of dehydrogenation by neighbored oxygen. Acid site affects the adsorption of the methoxide species, and the adsorption of reaction intermediate stimulates the reaction.

The WO_3/ZrO_2 showed the Brønsted acidity at the monolayer, and showed the activity of skeletal isomerization of butane [6]. Dependence of the activity on the loaded amount of tungsten clearly showed the volcano-relation against the loaded amount with the maximum at the full coverage monolayer. Number of acid site also has the same dependence on the loaded amount. These findings indicate strongly that catalytic activity is observed only on the monolayer of WO_3, and the acid site on the monolayer catalyzes the skeletal isomerization.

$SO_4{}^{2-}$ on zirconia is known as a super-solid acid catalyst. However, the chemical composition is often unreported. In our previous study [7], therefore, the loaded amount was carefully measured, and used for catalytic reactions as well as characterization. Two kinds of reaction catalyzed by the strong acid sites, Friedel–Crafts alkylation of benzene and skeletal isomerization of butane, were tested on these catalysts. Loaded amount of sulfuric acid was adjusted by changing the sulfuric acid content in the impregnation solution. In 2–15 wt.% of sulfuric acid in the solution, ca. 2.5 S nm^{-2} of the sulfur surface concentration was obtained constantly. An isolated species of sulfate anion was estimated from the surface concentration. In this range of sulfur concentration, the catalyst has not only the Lewis type acid character but also the activity of Friedel–Crafts alkylation. Catalytic activity and solid acidity are expected to be ascribable to on the surface of zirconia, because sulfate anions make zirconia electron deficient. Increase of the sulfuric acid above 15 wt.% remained sulfur more than 2.5 S nm^{-2} on the support. In this monolayer region with more than 2.5 S nm^{-2}, Brønsted acid site was created, and simultaneously the activity of skeletal isomerization of butane appeared. Therefore, the activity of skeletal isomerization is not found on the Lewis acid site, but on the Brønsted acid site. Clear change of acid character from Lewis to Brønsted acid site with increasing sulfur content made it possible to identify the structure as well as the catalysis.

It is claimed in the literature that isomerization of alkane occurs on the super-solid acid site. The super-solid acidity means the H_0 function less than -11.9. We measured the strength of acid site in a scale of ΔH of ammonia adsorption, and found about 200 and 160 kJ mol^{-1} in the sub-monolayer and monolayer regions, respectively. In order to relate the ΔH with the H_0 function, we derived a linear-form equation between them [6]:

$$H_0 = -1.75 \times 10^{-4} \Delta H + 15.9$$

From this relation, H_0 function -11.9 corresponds to ΔH value of 160 kJ mol^{-1}. Therefore, the sulfated zirconia catalyst which has 2.5 S nm^{-2} of the sulfur concentration and Lewis type character has the strong acid site which could be regarded as the super-solid acid site. However, the isomerization activity was not found in this region. Our analysis therefore has arrived at a conclusion that the skeletal isomerization proceeds on the Brønsted acid site without the super-solid acidity.

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