Combined Method of Ammonia IRMS-TPD Experiment and DFT Calculation to Characterize Zeolite Acidity

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Our recently developed potential characterization method for studying the zeolite acidity is reviewed. In this method, ammonia TPD is a principle technique and first the principle of the method was explained. In order to overcome the drawback existed in the usual TPD, IRMS-TPD method was developed, in which IR and MS were measured simultaneously to monitor the thermal behavior of ammonia molecules on the surface and in the gas phase. The developed method made it possible not only to measure the Brønsted and Lewis acid sites individually but also to clarify the distribution of Brønsted acid sites. In addition, DFT calculations were carried out to confirm the obtained information of the Brønsted acidity. Based on these studies, a new technique was developed by combining the IRMS-TPD experiment and DFT calculation to precisely characterize the zeolite acidity. Using the developed method, the modified Y zeolites active for the cracking of hydrocarbons were studied.

Keywords
Zeolite, Acidity, Temperature programmed desorption, Infrared spectroscopy, Density functional theory, Catalytic cracking

1. Introduction

Dynamic and multiple characterization techniques are being performed recently to investigate the structures and properties of catalysts and their roles in the catalysis. For example, spectroscopy measurements such as infrared spectroscopy (IR) and nuclear magnetic resonance (NMR), adsorption, test reactions, extended X-ray absorption fine structure (EXAFS) etc. are frequently utilized. Structures and properties of the catalysts are studied, and the obtained information is applied to examining the catalytic activity. Because various techniques are today available for use, selection of the appropriate and effective method among various proposed techniques is important. Purpose of our study is to characterize the zeolite acidity, to apply the obtained information to understanding the catalysis, and further to develop new catalysts by utilizing thus created ideas for the catalyst design. In our study, ammonia temperature-programmed desorption (TPD) is a principal technique, which is combined with IR spectroscopy and density functional theory (DFT) calculation. First, the principle of the ammonia TPD is mentioned. A fundamental equation for ammonia TPD is derived. Based on the proposed technique, numbers and strengths of acid sites on various zeolites have been measured. Then, a new technique of IRMS-TPD is proposed, and the study of the distribution of Brønsted acidity on some zeolites is explained. DFT calculation is studied to support the experimental findings on the strength of the acid sites. Finally, our interests are directed to applications of this method to the study on catalysts and catalysis over the zeolite catalysts.

2. What We Know from the Ammonia TPD

Ammonia TPD is a technique for the characterization of acidity. Ammonia is adsorbed on the evacuated sample, followed by elevation the bed temperature linearly with time, and the evolved gas is monitored with MS (mass spectroscopy) or TCD (thermal conductivity detector). Intensity of the evolved ammonia is plotted against the temperature, and the thermal behavior of ammonia desorption is revealed, which we call ammonia TPD spectrum. Number of the acid site is measured from the amount of desorbed ammonia which had been directly adsorbed on the acid site, strength is evaluated from the thermal behavior, and the heat of ammonia adsorption as an index of the strength is determined.

Detailed experimental procedure is not elucidated in the present paper, since much more precise explanation was described in our previous reviews. Ammonia TPD is usually controlled by the equilibrium between ammonia molecules in the gas phase and on the surface.
Re-adsorption of ammonia occurs freely. It is usually difficult to be free from the equilibrium control. Two simple fundamentals, i.e., material balance and Gibbs free energy equilibrium equation, give us an equation to show the gas concentration \( C_e \) of ammonia related with temperature during the TPD experiment,

\[
C_e = -\frac{\beta A_0 W}{F} \frac{\Delta \theta}{\Delta T} = \frac{\theta}{1-\theta} \frac{P_0}{RT} e^{\frac{\Delta H}{RT}} e^{\frac{\Delta S}{R}}
\]

where \( \beta, A_0, W, F, \) and \( \theta \) are heating rate (K·s\(^{-1}\)), number of acid site (mol·kg\(^{-1}\)), weight of the sample (kg), flow rate of the carrier gas (m\(^3\)·s\(^{-1}\)), and coverage by adsorbed ammonia (—), respectively. \( P_0, R \) and \( T \) are standard pressure (10\(^5\) Pa), gas constant (8.31 J·K\(^{-1}\)·mol\(^{-1}\)) and temperature (K). \( \Delta H \) and \( \Delta S \) denote enthalpy and entropy changes upon desorption of ammonia, respectively. \( \Delta S \) consists of two entropy terms, \( \Delta S \) (phase transformation) and \( \Delta S \) (physical mixing), and the former \( \Delta S \) due to the phase transformation, i.e., desorption, is almost equal to \( \Delta S \) upon vaporization of liquid ammonia.

The dependence of peak temperature on the \( W/F \) ratio was an important evidence to experimentally confirm the equilibrium conditions of the ammonia TPD\(^3\). Entropy change upon desorption which equals to that of the vaporization implies that the translational energy only changes upon desorption, which sounds reasonable for the physical chemistry of gaseous molecule. Therefore, \( \Delta S \) (desorption) is a constant parameter, and \( \Delta S \) (physical mixing) can be calculated from the concentration of desorbed ammonia in the gas phase. Thus, \( \Delta S \) can be regarded as a constant. Under the conditions, only \( A_0 \) and \( \Delta H \) (i.e., number and strength of acid site, respectively) are unknown parameters in the above equation for ammonia TPD. Therefore, a theoretical spectrum (curve) of TPD can be calculated with a set of assumed \( A_0 \) and \( \Delta H \). Fitting of the simulated curve to the experimental TPD spectrum gives us the solutions of two parameters. This is the method of quantitative determination of number and strength of acid sites by means of ammonia TPD experiment\(^3\).

Actually, the curve fitting can be carried out using an "Excel" software on a personal computer. We open the Excel format work-sheet in our web-site\(^4\), which you can utilize for the measurements.

After this method was applied to various zeolites, we arrived at two simple and important conclusions\(^5\), i.e.,

(1) Number of the acid site is equal to number of Al atoms in the framework.

(2) Strength does not depend on the concentration of acid site but on the structure of zeolite species.

3. What We Know from the IRMS-TPD

However, the usual (conventional) ammonia TPD contains a serious drawback as a method of characterization. No information on the structure of acid site is available. In other words, it is impossible to differentiate between Brønsted and Lewis acid sites. Additional experiments e.g., IR measurements of adsorbed pyridine, are therefore required to identify the structure.

In order to overcome the drawback, we developed a new method, IRMS-TPD, in which both IR and MS are working together to monitor the change of concentration of ammonia on the surface and in the gas phase, respectively, and the origin of desorbed ammonia can be discriminated to identify Lewis and Brønsted acid sites. The IR measurements during the ammonia TPD have already been studied, but to our knowledge no study for the simultaneous measurements of IR and MS was reported. By combining the IR and MS measurements, very precise and informative study becomes available, because IR affords us qualitative information principally but quantitative study is not easy, and on the other hand MS measures the intensity quantitatively. It must be noted therefore that the present measurement can give us information which cannot be obtained with any other methods.

Figure 1 shows the structure of Y zeolite which we mention mainly in the present paper. It is constructed from the sodalite cage and double six rings, and the super cage of 13 Å (1 Å = 10\(^{-10}\) m) in diameter is formed on which the catalysis and adsorption occur. Y zeolite is utilized in the petroleum refinery process, and contributes greatly to our human society. The acid sites located in the Y zeolite are still now being studied, but not yet fully understood because of the complex property.

An example of the experimental finding of IRMS-TPD is at first elucidated. Figure 2 shows the difference spectra obtained during ammonia TPD on the Y zeolite\(^5\). Zeolite NH\(_4\)Y was evacuated to convert into HY, and ammonia TPD was directly measured without
Reference shows the IR spectrum of Y zeolite before ammonia adsorption.

Fig. 2 Difference IR Spectra of Adsorbed Ammonia Measured at 373 to 573 K during Ammonia TPD Experiment

exposing it to the atmosphere. This method of preparation of H-zeolite, i.e., in-situ preparation of H-form zeolite, is important to keep the zeolite structure fine and unperturbed and using this method the precise measurements of zeolite acidity become possible. Ammonia was adsorbed at 373 K, followed by the evacuation. Temperature was raised gradually from 373 K in a ramping rate of 10 K/min, and continued until no adsorbed ammonia was observed.

Very broad IR band observed at 3000 to 2000 cm\(^{-1}\) which is due to the combination of stretching vibrations of NH and zeolite framework cannot be utilized. A fine absorption was found at ca. 1430 cm\(^{-1}\), which was identified as the bending vibration of NH\(_4^+\). Additionally, a small absorption due to the bending vibration of NH\(_3\) was found at 1665 cm\(^{-1}\). IR is taken at every 10 K, areas of these absorptions are quantitatively measured at every temperature, and the differential change with respect to the temperature gives us the IR-TPD to be compared with the usual MS-TPD.

We have to take a notice to the changes of Brønsted OH also. Brønsted OH were all disappeared upon adsorption of ammonia and the difference between the spectra before and after the ammonia adsorption gave us the negative absorption profile shown in Fig. 2. By elevating the temperature, ammonia was gradually desorbed, and the intensity of OH recovered. Enlarged portion of the difference spectra in the OH region is shown in Fig. 3. Usually, two kinds of OH bands are observed and those of high and low wave numbers are ascribable to OH in the super and sodalite cages, respectively. However, these two OH bands were further split, and thus four OH bands were observed in the present study of IRMS-TPD.

All the T sites in the Y zeolite are equivalent in the structure. In other words, there is only one kind of T site in the Y zeolite. The T site is surrounded by four oxygen atoms in the tetrahedral configuration, and thereby four different Brønsted OHs are possible. Number 1 to 4 in Fig. 1 shows four kinds of oxygens which are different in the structure. However, a neutron diffraction study could not find the O4H\(^\text{8}\). It was reported in a literature\(^\text{9}\) that the band at the lowest wave number was identified as the O3H directing to the center of the double six rings. Therefore, we identified these four OH bands as O1H, O1’H, O2H and O3H from high to low wave number, respectively. O1H and O1’H are both located in the supercage but these may have different environments of neighbored Al concentration\(^\text{10}\). Intensities of OH bands were calculated after dividing into portions.

Figure 4 shows thus measured IR-TPD of NH\(_3\) and OH bands, together with the MS-measured TPD. The bending vibration of NH\(_4^+\) was regarded as consisting of three absorptions at 1496, 1369, and 1430 cm\(^{-1}\), but these were not identified yet. A relatively small band at 1665 cm\(^{-1}\) showed the different thermal behavior, and could be identified as NH\(_3\) weakly adsorbed. The OH band at 3526 cm\(^{-1}\) showed the thermal behavior different from other OH bands, and changed associated

with the NH$_3$ appeared at 1665 cm$^{-1}$. Because the O3H directs to the center of double 6 rings, adsorption of ammonia on the O3H may be strongly hindered. It is therefore speculated that ammonia is not stabilized as NH$_4^+$, and interacts with the O3H to inhibit the vibration. Sum of the IR-TPD of adsorbed NH$_4^+$ and NH$_3$ bands must be equal to the MS-TPD, and sum of the IR-TPD of OH must have the mirror-image correlation with them. However, because the IR absorption bands have different extinction coefficients, sum of the intensities of IR-TPD of ammonia are largely different from the MS-TPD, as found from Fig. 4. Parameters to cancel the difference in extinction coefficients are therefore required to match all the IR-TPD. Figure 5 shows the comparison between MS-TPD and corrected IR-TPD of ammonia and OH; parameters were selected to fulfill the requirement of the material balance. As mentioned above, it was considered that ammonia interacted with the O3H to become the adsorbed NH$_3$ at 1665 cm$^{-1}$, and NH$_4^+$ cation was stabilized at O1, O1’ and O2 sites. Thus, thermal behaviors of four kinds of Brønsted OH were revealed; and number and strength were determined individually based on the theoretical equation, as shown in Table 1.

Obviously, complex calculation steps after the experiment are required to quantitatively determine the number and strength of the acid sites. Therefore, experimental errors are counted for the obtained parameters of solid acid sites. However, any other methods cannot provide us such precise characterization data of the acid sites. IRMS-TPD of ammonia is therefore an advantageous method which makes it possible to measure the acid sites, directly and individually.

As mentioned above, overlapped OH bands may be divided into some portions during the ammonia TPD; and this is another advantage of this method. Interesting observation was found in the measurements of the USY (ultra-stable Y) zeolite$^{11}$). Our previous study on the USY successfully detected the OH which was hidden in the broad OH bands; the acid strength of the created OH in the USY was 137 kJ·mol$^{-1}$ and stronger than that of the Y zeolite by about 25 kJ·mol$^{-1}$; and the detected OH was regarded as the catalytically active site. Acidities on various zeolites were measured by this method, and the acid strength of Brønsted OH ($\Delta H$) and the IR band position were determined and summarized as shown in Fig. 6$^{12}$). We can identify a relation between them among the OH located in a pore of 12 to 8 members ring; i.e., the lower the wave number of OH, the stronger the $\Delta H$. The frequency of stretching vibration is proportional to the square root of force constant, and therefore the shift of the OH band position to the low frequency means the weakening and lengthening of the OH bond. At the conditions, the solid acidity becomes strong. Therefore, the relation obtained in the present study is supported strongly by the physical chemistry. Very scattered relations observed in the pore of 6 members ring may be caused by the hindrance of the small sized pore to the adsorption of ammonia and/or the hydrogen bonding of OH to the zeolite wall, and the $\Delta H$ and/or the band position may be varied.

The activities for catalytic cracking of octane on these zeolites were measured under the conditions of mono-molecular reaction, i.e., high temperature (773 K) and low partial pressure of octane (1.87 kPa), and the

### Table 1: Assignment, Number ($A_0$) and Strength ($\Delta H$) of OH on in-situ Prepared HY

<table>
<thead>
<tr>
<th>Band position [cm$^{-1}$]</th>
<th>Assignment</th>
<th>Position</th>
<th>$A_0$ [mol·kg$^{-1}$]</th>
<th>$\Delta H$ [kJ·mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3648</td>
<td>O1H</td>
<td>Super cage</td>
<td>0.58</td>
<td>108</td>
</tr>
<tr>
<td>3625</td>
<td>O1’H</td>
<td>Sodalite cage</td>
<td>0.57</td>
<td>110</td>
</tr>
<tr>
<td>3571</td>
<td>O2H</td>
<td>Sodalite cage</td>
<td>1.1</td>
<td>119</td>
</tr>
<tr>
<td>3526</td>
<td>O3H</td>
<td>Hexagonal prism</td>
<td>0.80</td>
<td>105</td>
</tr>
</tbody>
</table>

turn-over frequency (TOF) was determined from the reaction rate and the number of the active Brønsted OH. Thus determined the TOF depended strongly on the ΔH,
as shown in Fig. 7. This means that the Brønsted acid sites play a role of active site for the cracking, and it is suggested that the formation of the penta-coordinated carbonium cation is the rate-determining step of the reaction. This conclusion supported the mono-molecular reaction mechanism proposed by Haag and Dessau 13), and clearly shows that the strength of the acid site is a key parameter to decide the catalytic activity.

4. **DFT Calculation to Support the Experimental Observation**

We have measured the distribution of the Brønsted OH in a Y zeolite by means of IRMS-TPD of ammonia. A strong dependence of the heat of ammonia adsorption on the structure is clearly revealed by utilizing the advantage of new technique. In next step, theoretical calculation of the heat of ammonia adsorption was studied to support the experimental observation. Recently, various chemical subjects are studied by the density function theory calculation. In particular, some spectroscopic findings such as NMR are strongly supported by the DFT calculation. Very precise analysis becomes possible by obtaining not only the experimental observation but also the theoretical calculation.

Our study using the DFT calculation was first applied to chabazite 14). Chabazite has a simple structure with only one kind of T-site like Y zeolite, and therefore the structure unit consists of relatively small number of atoms. DFT calculation was carried out with the chabazite model within the periodic boundary conditions. DMol3 software developed by Accelrys Co., was used, and the geometry optimization was based on a generalized gradient approximation (GGA) level using Hamprecht-Cohen-Tozer-Handy (HCTH) exchange and correlation functional. Total energies of ammonia (E_{NH3}), H-zeolite (E_{H-Z}), and zeolite with NH4+ (E_{NH4-Z}) were calculated, and the energy of ammonia adsorption was given by the equation, E_{ads} = E_{NH4-Z} - E_{NH3}. Actually, the energy of adsorption should be negative, but for the sake of simplicity, it is defined as a positive parameter. Because the calculated value of ammonia adsorption energy corresponds to ΔU, the ΔH was corrected due to the equation, ΔH = ΔU + RT. The correction was actually small.

As shown in **Table 2**, the calculated energy of ammonia adsorption agreed well with the experimentally determined ΔU, thus supporting strongly the IRMS-TPD measurements on chabazite. DFT calculation based on the periodic boundary models requires usually long time, and it is not easy to utilize. Therefore, a smaller embedded 8 T cluster model may be used in place of the rigid periodic boundary conditions model. In the calculation, the Brønsted acid sites consists of 8 atoms, Si, Al, and O, and surrounding zeolite structure was also taken into consideration. However, the 8 T cluster only was optimized in the calculation step. The E_{ads} for ammonia thus calculated for various zeolites agreed well with the measured ΔU, as shown in Fig. 815). Therefore, a coincidence between the energies of ammonia adsorption measured and calculated was confirmed. Furthermore, we have already studied the more precise calculation on zeolites FAU, MOR and BEA with the periodic boundary conditions, and arrived at the same conclusions16). Therefore, the IRMS-TPD experiments were strongly supported by the DFT calculations. Thus, we have a very powerful technique to characterize the zeolite acidity.
5. Trinity Study on the Zeolite Acidity: Examples

It is extremely interesting to study the zeolite acidity by means of the combined technique of IRMS-TPD and DFT calculation. We applied this method to the investigation of the modified Y zeolites active for the catalytic reaction\(^1\). Y zeolite is very poor in the catalytic reactions and has to be activated by the modification, e.g., ion exchange with alkaline earth cation or high temperature steaming to produce the USY (ultra-stable Y). The modified Y zeolites are active in the catalytic cracking, and have been utilized in the petroleum refinery process.

Ion exchange with Ba and Ca cations removed the OH bands at the low frequency preferentially; therefore, the O2H and/or O3H in the sodalite cage were found to be exchanged with such cations preferentially. IRMS-TPD measurements revealed that the strength of the O1H in the super cage was enhanced by the ion-exchange. In line with this, the turn-over frequency (rate/number of the Brønsted OH) increased. At ca. 40\% of the cation exchange, both the strength of Brønsted OH and the catalytic activity were enhanced most effectively.

According to X-ray analysis studies on the alkaline earth cation exchanged Y-zeolite, these cations were detected on the cation exchanged sites I, I’, and II\(^1\). Site I is located in the center of double 6 rings, I’ on the 6 member ring in the sodalite cage, and II on the 6 member ring directing to the super cage. Thus, as shown in Fig. 9, based on the model of Y zeolites with the exchanged cations on these sites, the energy of NH\(_4\)+ cation adsorption was calculated. As found from the Table 3, the calculated values for Y zeolite with the cations located at the positions I’ and II were similar to those measured experimentally. Therefore, it was concluded that, most probably, the alkaline earth metal cations located on these sites enhanced the acid strength of the O1H. These metal cations may play the role of electron withdrawing as the electron acceptor (i.e., Lewis acid site) to make the OH electron-deficient, thus enhancing the acid strength.

An extra-framework Al is created by the high temperature steaming of the NH\(_4\)Y zeolite, and the non-framework Al is requisite to produce the active USY zeolite. In the IRMS-TPD experiment on the USY, the IR band of the created OH was detected, and the ammonia adsorption heat on the OH was measured, as mentioned above\(^1\). These measured energy parameters, IR band position and \(\Delta H\) of ammonia adsorption, were supported by the DFT calculation within the periodic boundary conditions\(^5\). Therefore, the structure model of the Al-OH\(^2\)- located in the sodalite cage, which played the role of modified cation, was theoretically supported. It may be concluded that the Al-OH\(^2\)- cation is exchanged, and enhances the acid strength of O1H through the same mechanism above mentioned. The structure model and the activation mechanism in
Table 3  Ammonia Adsorption Energy ($E_{ads}$) Calculated by DFT Method and $\Delta H$ and $\Delta U$ of Ammonia Adsorption on the OH as NH$_4^+$ on HY (no), BaHY, CaHY and LaHY, where Ba$^{2+}$, Ca$^{2+}$, or LaOH$^{2+}$ is Assumed to be Exchanged in the Sites I, I' and II

<table>
<thead>
<tr>
<th>Metal cation</th>
<th>$E_{ads}$ (DFT) [kJ mol$^{-1}$]</th>
<th>$\Delta H$ (TPD) [kJ mol$^{-1}$]</th>
<th>$\Delta U$ (TPD) [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(no)</td>
<td>99</td>
<td>110</td>
<td>106</td>
</tr>
<tr>
<td>Ba</td>
<td>116</td>
<td>118</td>
<td>114</td>
</tr>
<tr>
<td>Ca</td>
<td>97</td>
<td>122</td>
<td>118</td>
</tr>
<tr>
<td>LaOH</td>
<td>—</td>
<td>118</td>
<td>114</td>
</tr>
</tbody>
</table>

the USY and alkaline cation exchanged Y have been studied previously by many researchers. Our conclusion based on the present combined method supports strongly the previously-adapted concept$^{20}$.

6. Summary and Future Study

As mentioned above, we can now utilize an advantageous method of IRMS-TPD of ammonia. By combining IR and MS measurements during the ammonia TPD, number and strength of Brønsted and Lewis acid sites are measured quantitatively. When the distribution of Brønsted OH is studied, these are measured individually to give the precise characterization data. Not only the number and strength but the structure of the Brønsted OH is analyzed with the newly developed technique. This is the most important advantage of this method, and such detailed characterization data could not be obtained with any other method. In addition, these experimental findings are supported by the theoretical DFT calculations. Therefore, we can discuss on the zeolite acidities from various view points to arrive at the best final conclusions.

Our purpose of the present study is not only to understand the acidity of zeolite but to study the cracking reaction. We have drawn a conclusion of the Brønsted acid site as the active site, as mentioned above. However, more precise and detail study may be required.

Computational study provides us the optimized parameters of bond angle and length of zeolite structures. We have often a fundamental question for the solid acidity, i.e., what parameters influence the strength of acid site? To solve the problem, we can utilize the provided geometrical parameters to analyze the relationship with the Brønsted acid strength.

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要旨
アンモニア IRMS-TPD 測定と密度汎関数計算の併用によるゼオライト酸性質のキャラクタリゼーション

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最近われわれが開発したゼオライト酸性質を研究する新しい方法をまとめた。この方法ではアンモニア昇温脱離（TPD）実験が中心となっており，はじめにその測定方法を説明した。この方法ではアンモニア TPD 測定がもつ欠点を克服する目的で，つぎに吸着および気相アンモニア分子の熱的挙動を同時に測定する IRMS-TPD 実験を開発した。この方法によって，ブレーンステッド酸とルイス酸を区別して測定すること，およびブレーンステッド酸点の分布を測定することができる。さらに，密度汎関数計算を行い，実験的に得られたブレーンステッド酸点の分布を確認した。この結果，実験と理論計算を併用する総合的な新しいゼオライト酸性質の研究方法を開発することができた。最後に，この方法を用いる修飾 Y ゼオライトの酸性質の研究を紹介した。