

論文 / 著書情報  
Article / Book Information

題目(和文)	ゼオライトの触媒機能解明に向けた赤外分光法による種々の触媒特性評価
Title(English)	Characterization of several catalytic properties for understanding zeolite catalysis by infrared spectroscopy
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

## 論文要旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学 応用化学	系 コース	申請学位 (専攻分野)： Academic Degree Requested	博士 Doctor of	( 理学 )
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words )

This thesis is entitled “Characterization of several catalytic properties for understanding zeolite catalysis by infrared spectroscopy”. The main purpose of this study is to clarify the catalytic properties of zeolite using infrared (IR) spectroscopy. Especially, I focus on “Acidity at high temperature region (chapter 2)”, “Basicity of lattice oxygen atoms (chapter 3)” and “Confinement effect (chapter 4)”.

The first chapter is the general introduction. The fundamental knowledge of zeolite chemistry and the conventional characterization method of zeolite catalysis are introduced. In addition, the recent studies of zeolite chemistry are summarized, and the motivation of this study is described.

In chapter 2, the behavior of the acidic OH groups on zeolites at high temperatures was observed, and the acidity of zeolite at high temperatures was characterized by *in-situ* IR measurement. The decreases in integrated intensity and the shifts in the peak-top frequency to lower frequency side of the acidic OH groups were detected with increasing temperatures. These changes were completely reversible depending on temperatures. The decrease of integrated intensity means the increase of the amount of the dissociated sites, and the behavior of the intensity decrease was different between higher (573–773 K) and lower (398–548 K) temperature regions. Therefore, the proton-hopping mechanism was elucidated by density functional theory (DFT) calculations. Two types of proton-hopping mechanisms existed in equilibrium between bonded and dissociated states; the localized hopping around four oxygen atoms in the same Al site and the free hopping over the zeolite framework. Their distribution changed depending on temperature regions. In addition, the dissociation enthalpy of acidic OH groups was estimated. The estimated enthalpy increased in the order **CHA** < **MFI** < **MOR**. Moreover, zeolites with smaller dissociation enthalpy resulted in higher activity for the H/D isotope exchange reaction of methane as one of the model acid-catalyzed reactions. In other words, the dissociation enthalpy could be used as a characterization factor for the acidity of zeolite at high temperatures.

In chapter 3, I succeeded the characterization of the basic lattice oxygen in proton-form zeolite by CO<sub>2</sub> probe IR method. In CO<sub>2</sub> adsorption, some absorption bands of adsorbed CO<sub>2</sub> species on lattice oxygens, acidic OH groups, alkaline metal cations and extra-framework Al species were observed, and their IR bands could be identified by CO<sub>2</sub> adsorption on various types of zeolites. The lattice basic oxygens existed in (AlO<sub>4</sub>)<sup>-</sup> units of zeolite framework, and the number and the strength of basic lattice oxygens were affected by the environment of the central Al atoms. As a result, they were different depending on the zeolite topology. Zeolite with many types of T sites such as **MFI** showed plural IR bands of adsorbed CO<sub>2</sub> species (2370–2350 cm<sup>-1</sup>) due to the presence of various types of basic lattice oxygens in comparison with

zeolites with less types of T sites represented by **MOR** and **CHA**. In addition, the quantitative relationship between the basic lattice oxygens and Brønsted acid sites was confirmed by CO<sub>2</sub> adsorption on NH<sub>3</sub>-preadsorbed samples, which revealed that the base site exists as the acid-base pair site. From these results, *in-situ* IR measurement with CO<sub>2</sub> probe method can be regarded as one of the powerful methods for the characterization of the basicity of lattice oxygens on proton-form zeolites.

In chapter 4, the cation vibration on zeolite was investigated by *in-situ* far-IR measurement to understand the confinement effect. Generally, the cation vibration has been observed using high energy beam source and high sensitive detector. In this study, I optimized the measurement conditions to observe the cation vibration using the conventional and commercial *in-situ* far-IR systems. Consequently, the cation vibration of alkaline metal cations on zeolites could be observed, where the peak-top frequency of the cation vibration with the same type of cation depended on the zeolite topology. This result indicates that the cation in the micropore of zeolite is affected by the confinement effect. The cation vibrations of a series of alkaline metal cation-form Y and **CHA**-type zeolites were compared. The comparison revealed that the confinement effect affects the force constant of the cation vibration, which means differences in the strength of the cation-anion interaction between alkaline metal cations and lattice oxygens. Moreover, the observation of the cation vibration was expanded to the molecular cation vibrations such as ammonium and pyridinium cations. In the case of the molecular cation vibration, the presence of the confinement effect was suggested as well as alkaline metal cation vibration. Therefore, I experimentally probed the presence of the confinement effect in zeolite micropore.

The final chapter summarized this study.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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