FT-IR Study of Characterization of Basicity of Lattice oxygen on Proton-form Zeolites using CO_2 Probe Method

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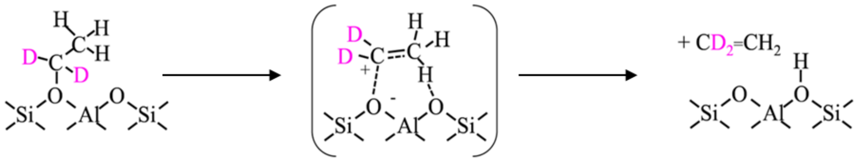
Abstract: The basicity of lattice oxygen of proton-form zeolite was characterized by low temperature (under room temperatures) CO_2 probe IR method. The basic lattice oxygen of proton-form zeolite existed around Al in $(AlO_4)^-$ units, and the number and the strength of base sites were affected by the environment of the central Al atoms in the framework. Consequently, various numbers and strength of basic sites appeared on several zeolite topologies. Zeolites with a large variety in T sites represented by **MFI** showed plural absorption bands of adsorbed molecular CO_2 (2370－2350 cm^{-1}) due to the presence of various types of basic sites in comparison with such zeolites with less types of T sites as **MOR** and **CHA**.

Keywords: Zeolite, lattice oxygen, Basicity.

1. Introduction

Proton-form zeolites have been used as solid acid practical catalysts for various reactions represented by catalytic cracking of hydrocarbons[1] and conversion of methanol to olefins reaction[2]. Generally, OH groups bridging to Al and Si atoms are recognized as active sites on proton-form zeolites for acid-catalyzed reactions. In addition, the contribution of lattice oxygen atoms to acid-catalyzed reactions is recently suggested[3], which proceed in concerted manners. The dehydration of ethanol to ethene over acidic OH groups of zeolites is one of the examples. When the reaction mechanism of the decomposition of ethoxy species was investigated using CH_3CD_2O-, it was verified that the abstraction of hydrogen from methyl groups of ethoxy groups by lattice oxygen was responsible (Scheme 1) [4]. In other words, zeolite lattice oxygens work as Brønsted base sites in combination with Brønsted acid sites. Thus, lattice oxygen adjacent to Al on proton-form zeolites may possess basicity and participate in several acid-catalyzed reactions. In this study, we focused on characterizing the basicity of lattice oxygen on proton-form zeolites. Infrared (IR) spectroscopy is one of the powerful methods for characterization of surface property of solid catalysts. Thus, we expected the stabilization of molecular adsorption of CO_2 at relatively low temperature, and attempted to characterize the basicity of lattice oxygen in proton-form zeolites.



Scheme 1 Proposed mechanism of decomposition of ethoxy species on zeolites.

2. Experimental

The self-supporting disks of each sample (20 mm diameter, 40 mg) were placed at the center of a quartz cell connected to a conventional closed gas circulation system. The samples were pretreated at 773 K for 1 h to remove the adsorbed species. IR spectra were recorded using a JASCO FT/IR-4100 spectrometer with an MCT detector. All spectra were collected as an average of 64 scans at resolution of 4 cm^{-1}. FTIR spectra of the pretreated samples were measured at several temperatures to use as background spectra. CO_2 was used as probe molecular for the characterization of basicity on zeolite lattice oxygen. The probe was introduced to IR cell, and IR spectra were measured after the pressure became constant, then introduction pressure of CO_2 was gradually increased at several pressures. Difference spectra were obtained by subtracting the background spectra from those measured after introduction of probe molecules.

3. Results and discussion

Figure 1a shows difference IR spectra of CO_2-exposed ZSM-5 at 173 K, followed by evacuation. These spectra were measured at several temperatures under evacuation. At 173 K, one negative band (3612 cm^{-1}) and three positive bands (3460, 2369 and 2349 cm^{-1}) were observed. The bands at 3612 and 3460 cm^{-1} are attributed to isolated and hydrogen-bonded acidic OH groups on ZSM-5, respectively. The conversion of the isolated to the hydrogen-bonded state of OH groups resulted in the downward and upward peaks. The band at 2369 and 2349 cm^{-1} are attributed to the OCO asymmetric stretching vibration of physically and chemically adsorbed CO_2 molecules on ZSM-5, respectively. Therefore, these results revealed that CO_2 adsorbed on proton-form zeolites in two fashions at 173 K. Increasing temperature to 198 K under evacuation, the bands of isolated and hydrogen bonded acidic OH groups simultaneously disappeared accompanied by the drastic loss in intensity of the band of physically adsorbed CO_2 due to desorption from acidic OH groups. On the other hand, the band at 2369 cm^{-1} remained, and some additional bands became apparent (Figure 1b). These results indicated that only chemical adsorption of CO_2 was observed without any interaction with acidic and non-acidic OH groups on ZSM-5 above 198 K. In addition, carbonate species were not observed in the all spectra, which was confirmed by the absence of any peaks at 1800－1400 cm^{-1}: CO_2 did not react to from carbonate species on ZSM-5 due to weak basicity, but adsorbed in a molecular fashion. Therefore, the chemisorption of CO_2 was suspected to occur on the basic lattice oxygen. In Figure 1b, four bands (2372, 2369, 2363 and 2355 cm^{-1}) were observed during increasing temperature under evacuation. Since all of them disappeared monotonously under evacuation at 348 K completely, they would be all assigned to molecularly adsorbed CO_2 on lattice oxygen in zeolite framework.

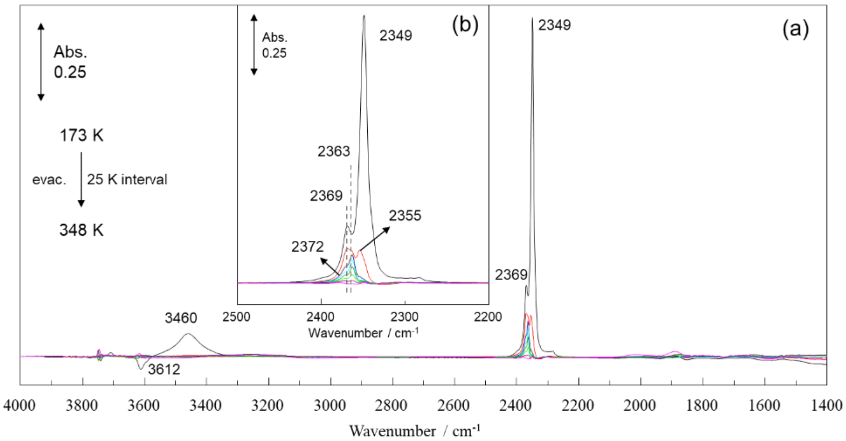


Figure 1 Difference IR spectra of adsorbed CO_2 species on ZSM-5 under evacuation from 173 to 348 K with 25 K interval, (a) 4000－1400 cm^{-1}, (b) 2500－2200 cm^{-1}.

4. Conclusions

The presence of basicity of lattice oxygen on proton-form zeolites was revealed by CO_{2-} probe IR method. The origin of the basic sites is the presence of Al in pair with Brønsted acid sites. In this method, the number of types of base site could be clarified by the number of IR bands of adsorbed CO_2. Since the experimental procedure is simple with no need to cool the sample, CO_2-probe IR method can be applicable for materials possessing weakly basic sites.

References

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