



Contribution ID: 21 Contribution code: Board 3

Type: Poster Presentation

Characterization of hydroxyl groups in zeolite defects using advanced temperature-programmed desorption

Monday, May 20, 2024 7:10 PM (20 minutes)

Zeolites are crystalline aluminosilicates that have a wide range of applications, including solid catalysts, adsorbents, and separation membranes. In zeolites, hydroxyl groups exist in various forms, including Brønsted acid sites (BAS), isolated hydroxyl groups, and hydroxyl groups in defects (Fig. 1a). Despite their significant impact on zeolite performance, it has been challenging to quantify and qualify each of them by conventional FT-IR and ^1H NMR methods [1,2]. Notably, hydroxyl groups in defects that are hydrogen-bonded to each other exhibit broad bands, making it difficult to assign clear peaks and perform absolute quantification. In this study, we propose employing advanced temperature-programmed desorption (TPD) heating up to 1600 °C under vacuum as a new analytical method to qualitatively and quantitatively analyze hydroxyl groups in zeolite defects. Fig. 1b shows the TPD profile of dealuminated Mordeinite (DeAl) in which hydroxyl groups in defects were generated by partly removing aluminum in the original Mordeinite. H_2O desorption was observed above 300 °C, and H_2 desorption started at temperatures above 600 °C, with complete elimination of all hydrogen by 1600 °C. The increase in the amount of OH groups due to dealumination determined by TPD was 1882 $\mu\text{mol/g}$. Considering the amount of Al removal determined by inductively coupled plasma (ICP) analysis, 2.4 hydroxyl groups per one Al defect on average were formed. Combined with the FT-IR results and DFT simulations, we found that pairs of hydroxyl groups forming strong hydrogen bonds in defects desorbed as H_2O , while distant pairs desorbed as H_2 at high temperatures. Therefore, advanced TPD up to 1600°C allows for the qualitative and quantitative determination of hydroxyl groups while discerning hydrogen bond strength, which is difficult with conventional analytical methods.

References:

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Primary author: SHIMIZU, Shunsuke (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Co-authors: Prof. NISHIHARA, Hiroto (Tohoku University); Dr OSUGA, Ryota (Hokkaido University); YOSHII, Takeharu (Tohoku University)

Presenter: SHIMIZU, Shunsuke (Institute of Multidisciplinary Research for Advanced Materials, Tohoku University)

Session Classification: Poster Session

Track Classification: Poster Presentations