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Cyclopentadiene transformation over H-form zeolites: TPD and IR studies of the formation of a monomeric cyclopentenyl carbenium ion intermediate and its role in acid-catalyzed conversions

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Abstract

The adsorption and transformation of cyclopentadiene on HY and HZSM-5 zeolites were investigated by infrared (IR) spectroscopy and temperature-programmed desorption (TPD). The stoichiometric formation of monomeric cyclopentenyl carbenium ions ($C_5H_7^+$) was observed on the acidic sites in the supercages of zeolite HY and in the channels of zeolite HZSM-5 at room temperature, without formation of oligomerized cyclopentadiene. The IR spectra indicate that addition of quantitative cyclopentadiene led to the stoichiometric consumption of acidic OH groups. These cyclopentenyl carbocations formed in the supercages affected the vibration of the remaining OH groups at both high and low frequencies, resulting in a shift of the OH_{HF} from 3642 to 3530 cm^{-1} as well as a shift of the OH_{LF} from 3552 to 3500 cm^{-1}. The TPD-MS results reveal that the cyclopentadiene transformation on these H-form zeolites occurred at a temperature range of 473–800 K and followed a hydride ion-transfer pathway. The monomeric cyclopentenyl carbocation was the key intermediate initiating the cracking chain proceeding by the cationic mechanism.

Keywords: Infrared spectroscopy; Zeolite; Cyclopentadiene; Carbenium ion; Cracking

1. Introduction

Protonic zeolites are considered as one of the most attractive solid acid catalysts for a number of commercially important hydrocarbon transformation reactions in the petrochemical and fine chemicals industries, including olefin skeletal isomerization, alkene oligomerization, toluene disproportionation, benzene alkylation, paraffin isomerization, and cracking [1–3]. The catalytically active sites in zeolites have been not well described until now; however, the Si–OH–Al groups (i.e., Brönsted acid hydroxyl groups) in zeolites as proton donors are known to play a critical role in these hydrocarbon reactions. Numerous studies have been conducted on the adsorption and reaction of hydrocarbons on acid sites of zeolites to gain insight into the catalysis of zeolites [4–10]. It is generally accepted that the acid-catalyzed reactions of hydrocarbons on acid zeolites involve various elementary reactions, including proton addition, β-scission, oligomerization, skeletal isomerization, and hydrogen transfer, and each elementary transformation involves the formation of carbocations [11–13]. However, whether the carbocations act as transition states or as active intermediates remains under discussion [3].

Alkyl carbenium ion on zeolites has not been observed unambiguously up to now. These carbenium ions are only assumed to be formed and to act as reactive intermediates. However, several cyclic alkenyl carbenium ions, such as cyclopentenyl carbenium ions, have been found to persist in zeolites, mainly by Haw et al. using an *in situ* NMR technique [14,15]. Recently, Yang et al. also reported the formation of a few stable alkenyl carbenium ions in zeolites using *in situ* FT-IR and UV–vis spectroscopy at 150–573 K by the adsorption of cyclic precursors, including cyclopen-

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tene, 1-methylcyclopentene, methylenecyclopentane, cyclohexene, and 1,3-cyclohexadiene [16]. Haw et al. proposed that these cations not only are responsible for aromatic formation and coke deposition, but also play a catalytic role in some reactions, such as MTO/MTG processes [17]. Therefore, studying the formation and transformation of cyclopentenyl carbocation is very important to gain insight into the acidity, reactivity, and deactivation of zeolites.

Cyclopentadiene as a probe reactant is theoretically a perfect precursor of the cyclopentenyl carbenium ion. However, to the best of our knowledge, the detailed intrazeolite chemistry of cyclopentadiene has not been reported to date. The main objective of the present study was to evaluate the adsorption behavior and reactivity of cyclopentadiene on H-form zeolites HY and HZSM-5 and thus attempt to gain deeper insight into the formation mechanism of cyclopentenyl carbenium ions in these zeolites.

Fourier transform infrared spectroscopy (FT-IR) is another powerful technique for studying the surface chemistry of heterogeneous catalysis [18]. It often is used to study the adsorption of olefins on H-form zeolites [19–22], because it permits direct monitoring of the interaction between hydrocarbon molecules and active sites. In the present work, we studied the detailed intrazeolite chemistry of cyclopentadiene by *in situ* FT-IR in combination with temperature-programmed desorption (TPD). We found that cyclopentadiene adsorbed on these two zeolites can be protonated to form stable cyclopentenyl carbenium ions at room temperature. These cyclopentenyl carbocations are cracked to be hydrogen acceptor products by a hydride ion-transfer mechanism under catalysis of Brönsted acid sites with increasing temperature. The acid-catalyzed transformation mechanism of cyclopentadiene in protonic zeolites is discussed.

2. Experimental

NH_4Y zeolite, with a BET surface area of ca. 700 $m^2\,g^{-1}$ and a SiO_2/Al_2O_3 ratio of 5.1 was purchased from Alfa Aesar. NH_4ZSM-5 zeolite, with a SiO_2/Al_2O_3 ratio of 50, was purchased from Zeolyst international Ltd. The materials were pressed into self-supporting IR discs (18 mm diameter, 10–20 mg) and placed into an *in situ* IR cell with CaF_2 windows, followed by thermal treatment for NH_4Y zeolite at 673 K for 20 h and for NH_4ZSM-5 zeolite at 773 K for 20 h in a flowing oxygen atmosphere. This treatment removed all nitrogen from the solid disk (as indicated by IR) without destroying the structure (as verified by XRD), and the zeolites were considered pure HY and HZSM-5 samples.

Dicyclopentadiene of >98% purity was obtained from Aldrich, with 98.6% of the dicyclopentadiene in endo form and 1.4% in exo form. Cyclopentadiene was prepared by thermal cracking and distillation of the dicyclopentadiene.

IR spectra were recorded on a Nicolet 670 FTIR spectrometer with a DTGS detector at a resolution of 4 cm^{-1}. A total of 32 scans were performed to obtain each spectrum.

TPD experiments were performed on an Autochem 2920 automatic catalyst characterization system equipped with an Omnistar GSD 30103 mass spectrograph. The sample loading was 0.2 g. The flow rate of the supporting gas (He) was 20 $mL\,min^{-1}$, and the heating rate was 5 $K\,min^{-1}$.

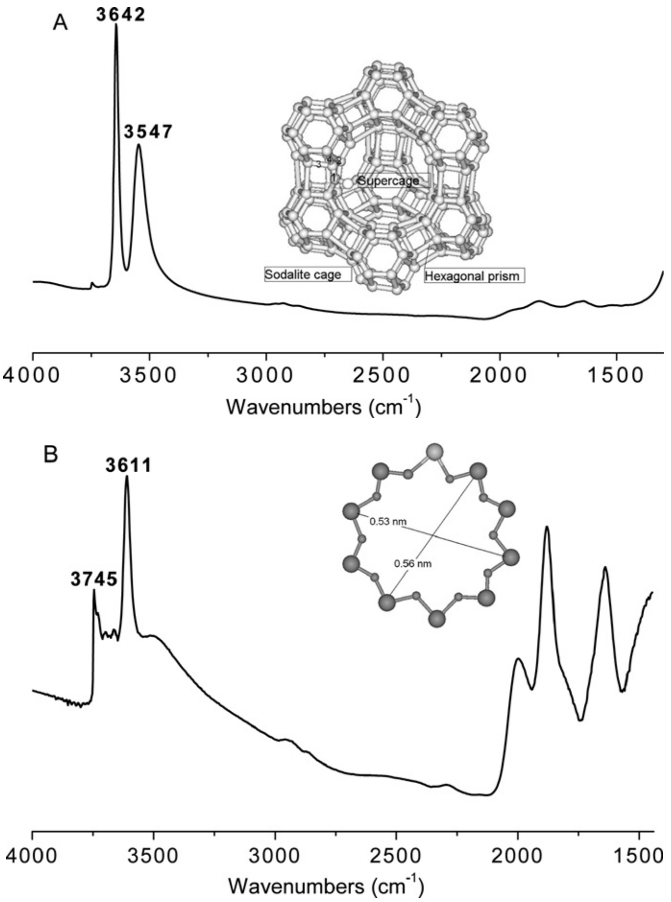

Fig. 1. (A) IR spectrum of HY zeolite and its framework structure. (B) IR spectrum of HZSM-5 zeolite and its open aperture of 10-membered ring along the [001] direction (main channel).

3. Results

3.1. Structural characteristics of HY and HZSM-5 zeolites

HY is a large-pore zeolite with a three-dimensional pore structure containing 1.25-nm-diameter supercages and 12-membered ring windows of approximately 0.75 nm. In Fig. 1A, four distinct crystallographic positions for the oxygen atoms of the framework are labeled 1–4; only the first three (O_1, O_2, and O_3) are proton positions [23]. The O_1H bond lies approximately in a plane of a 12-membered ring connecting the supercages of the structure, whereas the O_2H groups are in the plane of the six-membered ring of the sodalite units. The O_3H groups point inside the hexagonal prisms connecting the sodalite blocks [24]. After dehydration at 673 K for 3 h in vacuum, HY zeolite (ca. 13 mg disc with a diameter of 18 mm) exhibited three distinct hydroxyl bands at 3740, 3642 (high frequency [HF]), and 3547 cm^{-1} (low frequency [LF]) in the IR spectrum (Fig. 1A). Detailed data analysis reveals that the OH_{HF} band can be divided into two vibrations centered at 3642 and 3630 cm^{-1}, and that the OH_{LF} band also can be divided into three vibrations centered at 3552, 3530, and