

HYDROXYL GROUP STUDIES BY FTIR AND CATALYTIC ACTIVITY OF DEALUMINATED ZSM-5 ZEOLITE FOR ETHYLENE CONVERSION

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ABSTRACT

The hydroxyl groups of ZSM-5 and dealuminated ZSM-5 zeolites can be determined by FT-IR spectroscopy technique. All zeolites are having three types of hydroxyl group, i.e. terminal silanol and site defect (3744 cm^{-1}), non-framework aluminium (3669 cm^{-1}), and framework aluminium (3609 cm^{-1}). Intensity of 3609 cm^{-1} , 3669 cm^{-1} , and 3744 cm^{-1} bands of dealuminated ZSM-5 zeolites are decreases. Dealumination of ZSM-5 increases ethylene conversion but decreases gasoline selectivity. The amount of aluminium in the zeolite framework and purity of zeolite has a role in the ethylene conversion to liquid hydrocarbons process.

Keywords: Dealumination, ZSM-5, Hydroxyl group, FTIR, Ethylene.

INTRODUCTION

Fourier Transform Infrared (FT-IR) Spectroscopy has been extensively used in the study of acidity in zeolites and modified zeolites. The near-IR region ($4000\text{-}3000\text{ cm}^{-1}$) gives valuable information on the nature or origin of different types of OH groups. The hydroxyls in zeolite lattices can be classified into two groups according to their acidity and origin, i.e.: (i) located on the structural defects or amorphous extra-framework materials, non-acidic or weakly acidic properties, (ii) attached to the zeolite framework, strong acidic properties.

Major group frequencies are those associated with the presence of so called double rings ($650\text{-}500\text{ cm}^{-1}$), pore opening modes ($450\text{-}300\text{ cm}^{-1}$) and characteristic symmetric and antisymmetric TOT modes of these linkages are observed at $750\text{-}820\text{ cm}^{-1}$ and $1050\text{-}1150\text{ cm}^{-1}$ respectively. Subtle changes in these bands have correlated with variation in the Si/Al ratio and with the exchange cation.

The high frequency ($4000\text{-}2000\text{ cm}^{-1}$) spectral region associated with the OH vibrations and CH stretching vibrations or organics. After vacuum activation at $200\text{-}400^\circ\text{C}$ most of the adsorbed water is removed. After activation at 400°C it sometimes exhibits weak bands near 3745 and 3690 cm^{-1} . The 3690 cm^{-1} band has been attributed to the presence of traces of water, which interact with the Na^+ ions. The 3745 cm^{-1} band is attributed to terminal isolated SiOH groups (3747 cm^{-1} in SiO_2), either on the external surface of the zeolite, or more probably to traces of occluded SiO_2 as an impurity. The 3600 cm^{-1} (Bronsted acidic Al site in ZSM-5) band decreases in intensity as the Si/Al ratio increases. At the same time, a strong band grew at 3740 cm^{-1} (sharp) and at 3500 cm^{-1} (broad) which they argued were due to true SiOH species in high silica ZSM-5.

The purpose of this study is to dealuminate the ZSM-5 zeolite and to examine the acidity of dealuminated ZSM-5 by FT-IR measurement. Infrared spectra were determined using a Shimadzu FTIR 8000 series. The catalytic activity of zeolites was carried by quartz reactor for oligomerization of ethylene.

The proposed reaction path for ethylene reaction over ZSM-5 and dealuminated ZSM-5 catalysts is shown in Figure 1. The oligomerization of ethylene and cracking of oligomers processes are dependent on the zeolite acidity [1,2]. If the zeolite acidity is weak, then the oligomerization of olefins to oligomers (path 1) is difficult. In contrast, if the zeolite acidity is high, the oligomerization of olefins to oligomers and the cracking of oligomers to CO_x (path 2) are less difficult.

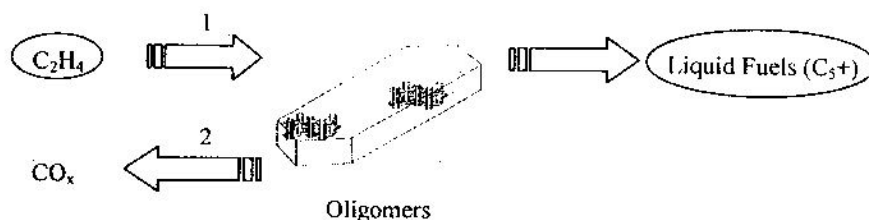


Figure 1: The proposed reaction path for ethylene reaction over ZSM-5 zeolite catalysts.

EXPERIMENTAL

Dealuminate ZSM-5 zeolite by treating ZSM-5 with 1 N HCl solution under temperature 80°C and various dealumination time, as name DZ_1 (12 hours), DZ_2 (2 x 12 hours), and DZ_3 (3 x 12 hours). Infrared spectra were determined using a Shimadzu FTIR 8000 series. A sample zeolite was loaded into an infrared cell which was capable of air evacuation, and programmed heating.

The mid infrared spectra (1500-400 cm^{-1}) were recorded on a Shimadzu FTIR 8000 series using the KBr pellet technique. Infrared spectrums for hydroxyl group were also recorded on a Shimadzu FTIR 8000. An IR spectrum was acquired in the absorbance mode at 25°C in the wave number between 4000-1300 cm^{-1} , and 2 cm^{-1} resolutions.

Thin wafers of 13 mm diameter was made by pressing about 10 mg of fine zeolite powder under 5 ton pressure for 15 seconds. The thin wafer was placed in a ring type sample holder and transferred into the IR cell equipped with CaF_2 window. The IR cell containing zeolite wafer was placed to the vacuum system (1×10^{-8} mbar pressure). For hydroxyl group analyst, every zeolite samples were dehydrated at 400°C for 5 hours under vacuum system. The infrared spectra of these samples were recorded at room temperature.

The performance of the catalysts is tested for ethylene conversion to liquid hydrocarbons (LHC) via a single step reaction in a fixed-bed micro reactor [3]. Ethylene with 99.9% purity was reacted at atmospheric pressure and temperature of 400°C at ethylene flow rate 50 ml/m. The reactor was first preheated at 400°C under a 100-ml/min-nitrogen stream for two hours to activate the catalyst. The reaction products were separated into liquid and gas fraction through ice-trap. A Gas Chromatography with FID and HP-1 capillary column was used to analyze the gas and liquid products [4].

RESULTS AND DISCUSSIONS

Infrared Spectra of The Framework

The FT-IR analysis is shown in Figure 2. For a more precise characterization of the known IR spectra of same ZSM-5 zeolite the mid infrared spectra (1500-400 cm^{-1}) of a series were recorded including both synthetic and natural materials. Especially the structure sensitive absorption around 1200 cm^{-1} and 550 cm^{-1} are of interest to differentiate zeolite types [5]. All samples show bands at about 546 and 1223 cm^{-1} , this indicates that no change crystal ZSM-5 structure. The spectra of ZSM-5 exhibits a band at 1398 cm^{-1} which is typical of ammonium ions. After dealumination, this band disappeared indicating that hydrogen replaced ammonium.

At 1099 cm^{-1} frequency band, assigned to the asymmetric stretching of framework Si-O-Si or Si-O-Al bonds [6], there is significant frequency shift or decrease in the intensity framework (Figure 2). This indicates that there is significant change in the number of those forming framework bonds. 1099 cm^{-1} frequency band of DZ_1 is lowest than the others. This suggests that more aluminium atoms are removed from zeolite framework.

For the determination of the estimated purity of especially ZSM-5 is using the IR optical density ratio of the 546 and 454 cm^{-1} bands of zeolite [7]. According to earlier reports and our present finding the optical density ratio of the 547 and 446 cm^{-1} bands of ZSM-5, DZ_1, DZ_2, and DZ_3 is 0.815, 0.845, 0.829, and 0.828, respectively. Thus, it can be concluded from the infrared spectra that no destruction of the zeolite framework occurred upon dealumination.

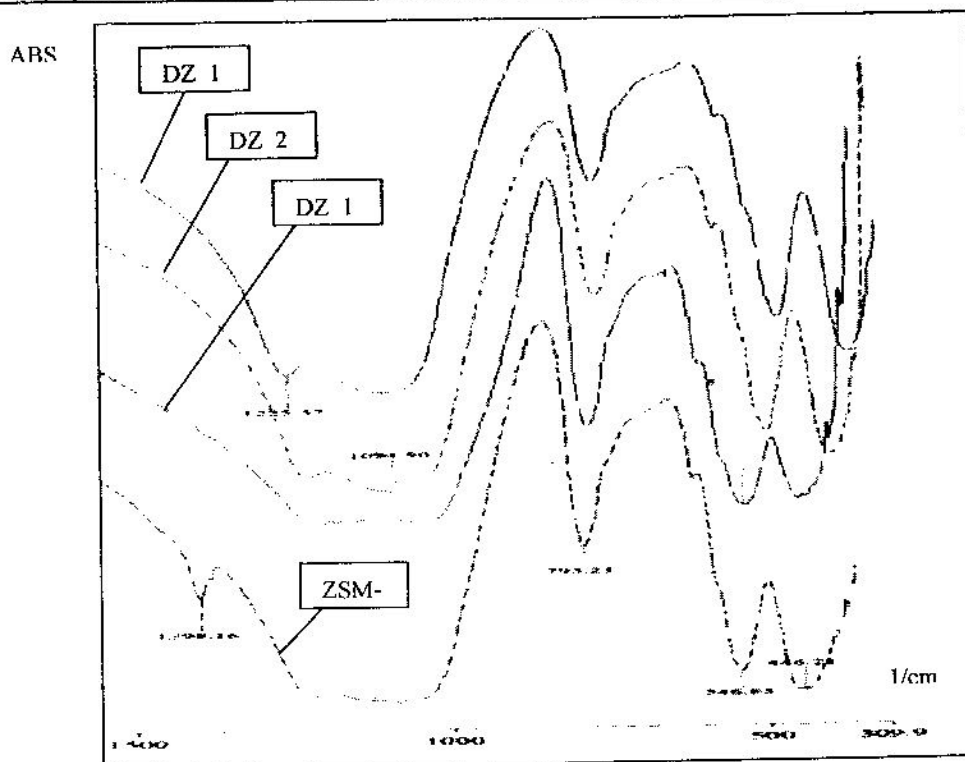


Figure 2. The mid infrared spectra (1500-400 cm^{-1}) of ZSM-5 and dealuminated ZSM-5.

Infrared Spectra of The OH Groups

The vibrations (OH) region of the IR spectrum of ZSM-5 contains bands at around 3600 and 3740 cm^{-1} [8,9]. The typical stretching vibrational band of the bridging OH groups bonded to tetrahedrally coordinated framework aluminium is located at around 3610 cm^{-1} , as shown figure 3 (A) [10]. The band at 3660 cm^{-1} is assigned hydroxyl group located at non-framework Al sites. This is similar with earlier investigators [11]. Authors reported that a band at 3649 cm^{-1} was ascribed to OH groups on non-framework aluminium species, as shown Figure 3 (B). The band at 3736 cm^{-1} is assigned terminal silanol groups attached to the framework [9]. Generally, the appearance of this band is an indication of the decrease in crystallinity due to the increasing number of terminal Si-OH groups per unit cell.

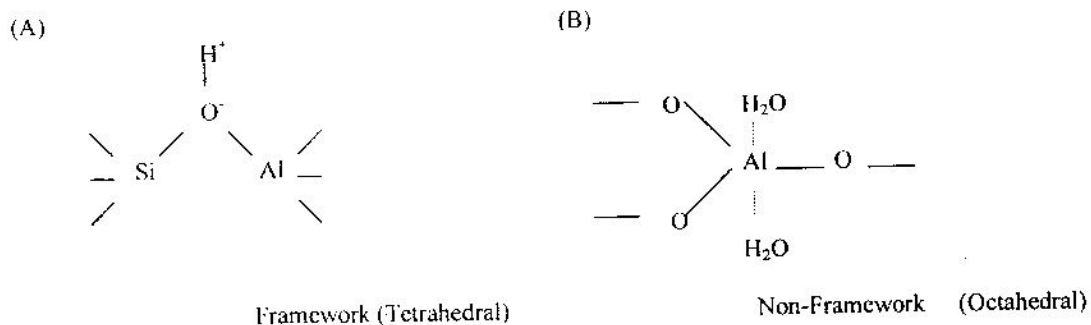


Figure 3. Structure of two types of terminal hydroxyl group.

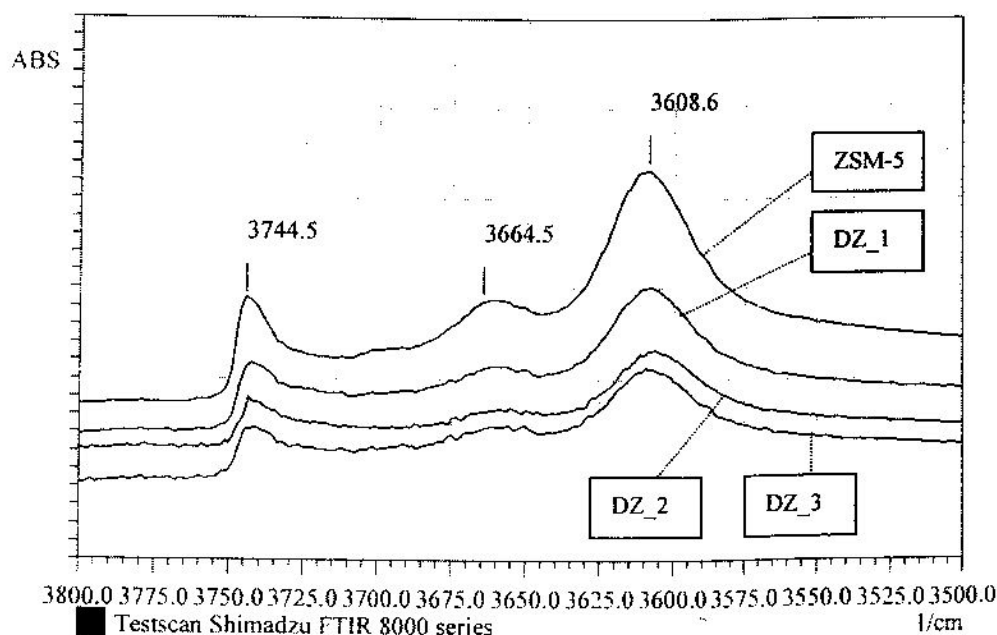


Figure 4. IR spectra in the hydroxyl stretch region of samples zeolite after dehydration at 400°C in 1×10^{-8} mbar during 2 hours.

The vibrations (OH) region of the IR spectrum of ZSM-5 and dealuminated ZSM-5 zeolite catalysts are shown on Figure 4. Figure 4 showed that all zeolites have bands at 3608 cm^{-1} , 3664 cm^{-1} , and 3744 cm^{-1} . This is indicated that all zeolites have aluminium framework, aluminium non-framework, and silanol.

Figure 5 demonstrated that the framework aluminium (3610 cm^{-1}) area of DZ_1, DZ_2, and DZ_3 (50.5, 40.5, and 14.6, respectively) are smaller than ZSM-5 (91.2). There is indicated that amount of framework aluminium decreases due to the extracted aluminium on zeolite framework to acidic solution. The non-framework aluminium (3660 cm^{-1}) area of DZ_1, DZ_2, and DZ_3 (13.3, 7.9, and 5.4, respectively) are smaller than ZSM-5 (26.9). There is indicated that amount of non-framework aluminium increases due to extraction of framework aluminium. The silanol (3743.6 cm^{-1}) are of DZ_1, DZ_2, and DZ_3 (12.7, 9.1, and 3.3, respectively) are smaller than ZSM-5 (24.8). There is probably due to the changed silanol group to amorphous.

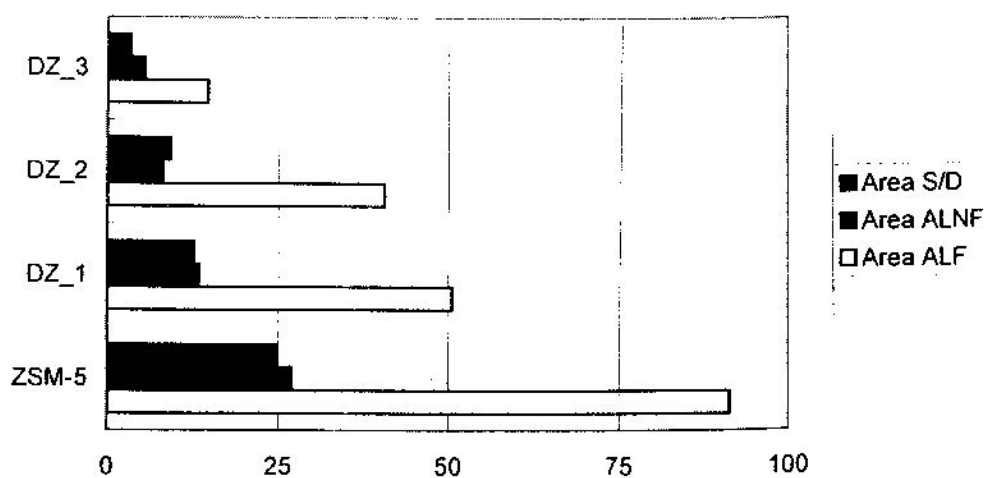


Figure 5. Integrated intensity of bands associated with bridging hydroxyls framework Al (ALF), extra-framework Al species (ALNF) and silanol group (S/D) in ZSM-5 and dealuminated ZSM-5.

Relation between FTIR analyst result and catalyst performance

From FTIR studies indicated that the purity of zeolites is increased after dealumination, and the framework aluminium is decreased after dealumination.

The purity of the samples can be arranged as follows;

$$DZ_1 > DZ_2 > DZ_3 > ZSM-5$$

The framework aluminium (3610 cm^{-1}) area of the samples can be arranged as follows:

$$ZSM-5 > DZ_1 > DZ_2 > DZ_3$$

Ethylene Conversion of the catalysts can be summarized below:

$$DZ_1 > DZ_2 > DZ_3 > ZSM-5$$

Composition of liquid hydrocarbons product is shown on Figure 6, and can be summarized below:

$$C_{5-10} : ZSM-5 > DZ_2 > DZ_1 > DZ_3$$

$$C_{11-15} : DZ_3 > DZ_1 > DZ_2 > ZSM-5$$

This result demonstrated that the ethylene conversion has related with purity of zeolites. If the purity of zeolite is high, then the ethylene conversion becomes high. This is suggested that if the zeolite purity is high, then the zeolite surface area is high, hence the ethylene conversion is also high. For example, the ethylene conversion of DZ_1 is highest because its purity is highest. In contrast, the ethylene conversion of ZSM-5 is lowest because its purity is lowest.

The oligomerization and cracking processes are dependent on the zeolite acidity [1,2]. The self-addition of olefins to form dimmers, trimers, and low polymers is called oligomerization [12]. If Bronsted acidity strength of zeolite is strong, then the cracking of oligomers is easy. The amount of framework aluminium is related with the Bronsted strength. If the amount of framework aluminium is high, then the Bronsted strength is strong.

This result shown that the gasoline range (C_{5-10}) selectivity of ZSM-5 is the highest, because the amount of aluminium framework is highest, then the Bronsted strength is strongest than others. If the Bronsted strength is strong, then the C_{10} hydrocarbon cannot be oligomerized to C_{11} , but C_{10} hydrocarbon will be cracked to light hydrocarbons. Hence the C_{11-15} selectivity is the lowest. Thus, the successful production of gasoline from ethylene depends on the amount of aluminium in the zeolite framework and zeolite purity.

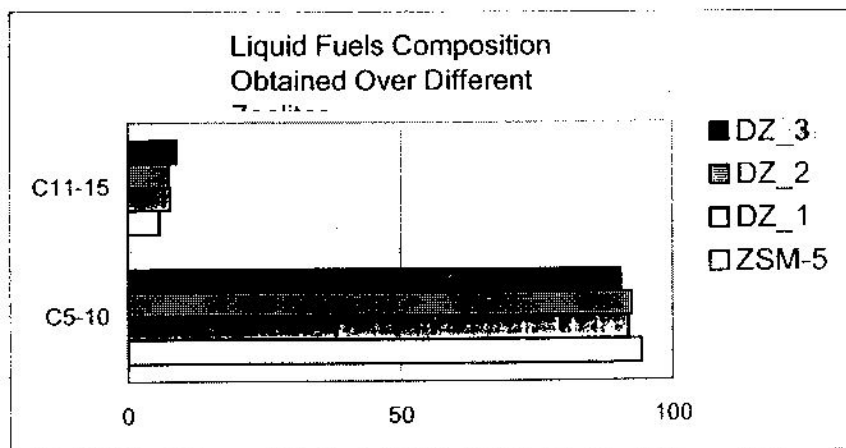


Figure 6. Composition of the liquid hydrocarbon fraction from ethylene conversion.

CONCLUSION

Fourier transform infrared (FT-IR) spectroscopy can be determine the zeolite acidity properties. Dealumination of ZSM-5 zeolite decreases of framework aluminium, non-framework aluminium, and silanol. However, the purity of zeolite increases after dealumination. Dealumination time has effect on framework aluminium, non-framework aluminium, silanol, and purity of zeolite. If dealumination time is increases, then removed framework aluminium, non-framework aluminium, and silanol is increases. Dealumination of ZSM-5 increases ethylene conversion but decreases gasoline selectivity. The amount of aluminium in the zeolite framework and purity of zeolite has a role in the ethylene conversion to liquid hydrocarbons process.

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