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Catalysis Today 87 (2003) 195–203
CATALYSIS TODAY
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Preparation and characterization of zeolite catalysts for etherification reaction

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Abstract

Catalytic etherification of 2-naphthol with ethanol has been carried out over a series of solid-acid catalysts such as H-Beta, H-MOR and H-ZSM-5 using a flow-type reactor. H-Beta zeolite shows higher conversion and catalytic stability than other catalysts for the production of 2-naphthyl ethyl ether, which may be correlated to the amount and strength of acid sites. H-Beta zeolites with different Si/Al ratios show that conversion decreases with increasing Si/Al ratios. The NH_3-TPD profiles indicate that the weak acidity decreases more sharply with increase in Si/Al ratios, compared with the strong acidity. The influences of ethanol/2-naphthol molar ratios, reaction temperature, and space velocity with respect to catalytic activities are investigated for H-Beta zeolite in the present work.

Keywords: Beta zeolite; Dealumination; 2-Naphthol; Etherification; NH_3-TPD; Pyridine IR

1. Introduction

Catalysis is viewed as a benefactor in the development of eco-friendly processes. There are several processes in the fine chemical industry which employ catalytic routes in order to make them eco-friendly and cost effective. The ethers of 2-naphthol are very attractive due to their extensive applications in the fine chemical industry. The alkyl ethers of 2-naphthol, particularly methyl, ethyl, and isobutyl ethers known as Yara Yara (or nerolin-1), Bromelia (or nerolin-2, Nerolin Bromelia), and Fragrol (or Nerolin-Fragrol), respectively, are important perfumery and flavoring compounds [1,2]. The current practice for the manufacture of these ethers is based on homogeneous acid-catalyzed reactions which are out of consonance with the worldwide thrust on eco-friendly processes. For example, 2-naphthyl methyl ether is traditionally manufactured from 2-naphthol and methanol in the presence of sulfuric acid. The drawbacks of such a process include corrosion, safety hazards in handling and disposal of the acid, separation procedures, and environmental problems due to the use of sulfuric acid. Zeolites are one of the excellent candidates for the replacement of the homogeneous system, due to their solid acidity, constricted pore shape and redox property [1–8].

Yadav and Krishnan [1] have reported the etherification of 2-naphthol with methanol using modified clays, sulfated zirconia and dodecatungstophosphoric acid supported on K-10 clay. The rates of etherification with other aliphatic alcohols over the

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doi:10.1016/j.cattod.2003.10.006

same catalyst at 150 °C are in the following order: *n*-BuOH > 2-PrOH > MeOH > EtOH > *n*-PrOH. Chen et al. [2] have synthesized 2-naphthyl methyl ether using sulfated mesoporous materials. They have suggested etherification activity as follows: SO_4^{2-}/Al-MCM-41 ≈ USY > H_2SO_4 > Al-MCM-41 > silica–alumina > H-ZSM-5 > γ-alumina. This order is similar to the trend in the acid strength of the catalysts. Sulfuric acid modification of Al-MCM-41 enhances both catalyst acidity and the catalytic activity. However, they have carried out the etherification reaction under batch conditions, where it may be difficult to show the catalytic stability. Generally the catalysts may lose the activity during the reaction due to the coke formation, even though the initial activity is high. Therefore, finding an excellent solid catalyst without deactivation, stability and the investigation of active sites for etherification using a flow-type reactor are still a challenge.

In the present work, the etherification reaction of 2-naphthol with ethanol using several kinds of zeolite catalysts under the flow condition of reactants has been studied in detail. The influences of ethanol/2-naphthol molar ratios, reaction temperature, and space velocity on the catalytic activity have been investigated. The characterization of the catalysts and the correlation between catalytic activity and acidity have been performed using NH_3-TPD, TGA/DSC and pyridine IR experiments. Also, we have discussed about the active sites responsible and deactivation of the catalysts for the etherification reaction by using dealuminated H-Beta zeolites.

2. Experimental

2.1. Preparation of catalysts

The following zeolites were used in the present work: NH_4-Beta (Tosoh Corp., 620 m^2/g, Si/Al = 13), H-MOR (Tosoh Corp., 403 m^2/g, Si/Al = 20) and Na-ZSM-5 (334 m^2/g, Si/Al = 18). NH_4-Beta was converted to H-form by calcination under static air condition at 550 °C for 4 h. H-MOR was used without further treatment. In order to obtain H-ZSM-5, Na-ZSM-5 was ion-exchanged with 0.1 M aqueous solution of ammonium chloride (1 g of zeolite in 20 ml of solution) at room temperature, and followed by filtration and washing with doubly distilled water. The process was repeated three times to maximize the ion-exchange level. Subsequently, NH_4-ZSM-5 was calcined under static air condition at 550 °C for 4 h.

For dealumination of H-Beta zeolite, the zeolite was treated with oxalic acid solutions (0.01, 0.1 and 0.5 M). Typically, 1 g of H-Beta zeolite was slurred with 20 ml of oxalic acid solution for 1 h at room temperature, using magnetic stirrer. The samples were then filtered, washed with doubly distilled water, and dried in an oven at 120 °C overnight. Subsequently, the samples were calcined at 550 °C for 4 h in air at a heating rate of 1 °C/min under shallow bed conditions.

2.2. Materials characterization

Aluminum contents of the zeolite catalysts were determined by elemental analysis using ICP instrument. Temperature programmed desorption (TPD) spectra of ammonia were recorded using a flow-through microreactor system equipped with a thermal conductivity detector (TCD). Three hundred milligrams of sample in the reactor was activated in O_2 flow at 600 °C for 1 h before the TPD measurement and then switched over to the He flow. After the sample was cooled to 100 °C, it was switched to a flow of 1% NH_3/He for 1 h for adsorption of NH_3. Then, the physically adsorbed NH_3 was removed by purging with He at 100 °C for 1 h. The reactor temperature was ramped up to 600 °C at a rate of 10 °C/min, while the He flow of 40 cm^3/min was passing through the reactor and the TCD. FT-IR spectra were recorded in a Nicolet Magna IR 550 spectrometer. A self-supported wafer of 12 mg with a diameter of 12 mm was placed in an infrared cell, which was made of quartz with CaF_2 windows and connected to a vacuum system. The wafer was evacuated at 400 °C up to $P = 10^{-5}$ Torr for 2 h. After cooling to room temperature, the samples were exposed to pyridine vapor for 1 h and subsequently evacuated at 200 °C. The spectra (32 scans, 4 cm^{-1} resolution) were recorded after evacuation at desired temperature for 1 h. Thermogravimetric analysis (TGA) curves were obtained in flowing nitrogen or air on TGA2050 (TA instruments) with a temperature increasing rate of 10 °C/min in the range of 30–700 °C.

2.3. Catalytic reaction

Catalytic etherification of 2-naphthol (Kanto Chem., 98.5%) with ethanol (Samchun Chem., 95%) was carried out at atmospheric pressure using a fixed-bed down flow vertical reactor (catalyst weight = 0.1 g) at 180 °C. Typically, a mixture of 2-naphthol and ethanol with a molar ratio of 1:10 was fed into the reactor using a calibrated syringe pump. Weight hourly space velocity (WHSV) was $1\,h^{-1}$. Reaction temperature was measured using K-type thermocouple attached around catalyst bed. The products were collected every 30 min for analysis over a period of 5 h and analyzed by a gas chromatography (Younglin 600D) using a flame ionization detector and a HP-5 capillary column. Reactants, products and their synthetic mixtures were used to calibrate the chromatograms and to deduce quantitative information.

3. Results and discussion

Fig. 1 shows the etherification activities of 2-naphthol with ethanol over the zeolite catalysts, H-Beta (Si/Al = 13), H-MOR (Si/Al = 20) and H-ZSM-5 (Si/Al = 18) at 180 °C. The products were collected from the flow-type reactor after 2 h. The conversion of 2-naphthol is calculated from the amount of 2-naphthol converted. As shown in Fig. 1, the H-Beta exhibits the higher activity in converting 2-naphthol to 2-naphthyl ethyl ether as compared to H-MOR and H-ZSM-5 catalysts which are low.

The etherification of 2-naphthol being an acid-catalyzed reaction, it is meaningful when the conversion of 2-naphthol is correlated to the strength and amount of the acid sites. NH_3-TPD profiles for the zeolite catalysts are shown in Fig. 2. The NH_3-TPD is a useful method to determine the surface acidity of solid-acid materials [9,10]. The amount of desorbed ammonia directly relates to as the amount of the acid sites on the sample. The strength of the acid sites can also be determined by desorption temperature. It is known that higher the ammonia desorption temperature, stronger is the acid sites. For H-Beta, the TPD curve shows a gradual rise with a maxima at 230 °C and thereafter declines with a smaller peak appearing at 370 °C. The existence of two TPD peaks means that the H-Beta has weak as well as strong acid sites. The H-MOR and H-ZSM-5 also show two peaks in the TPD profiles. The positions of weak acid sites for the H-MOR and H-ZSM-5 are very similar with that of the H-Beta, while the strong acid sites are shown at different positions. The strong acid sites of the H-MOR and H-ZSM-5 appear around 500 and 440 °C, respectively. The H-MOR exhibits relatively small amount of weak acid sites at 230 °C compared to those of H-Beta and H-ZSM-5. Although the acid amount of the H-ZSM-5

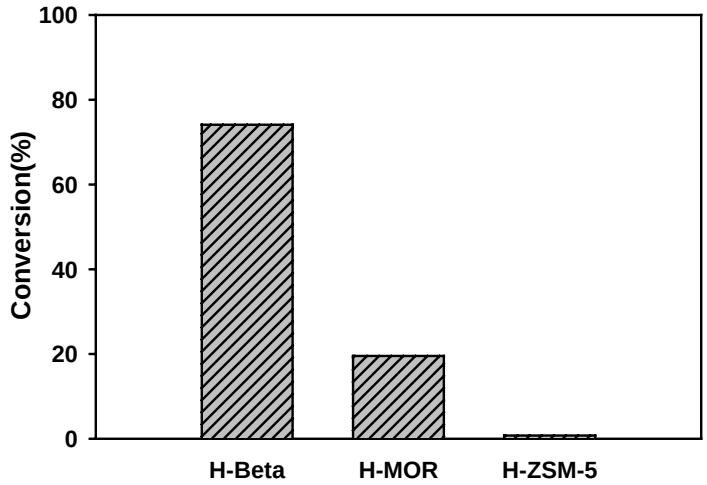

Fig. 1. Etherification activity of zeolite catalysts from 2-naphthol and ethanol. The reaction was carried out at 180 °C and the products were collected after 2 h.

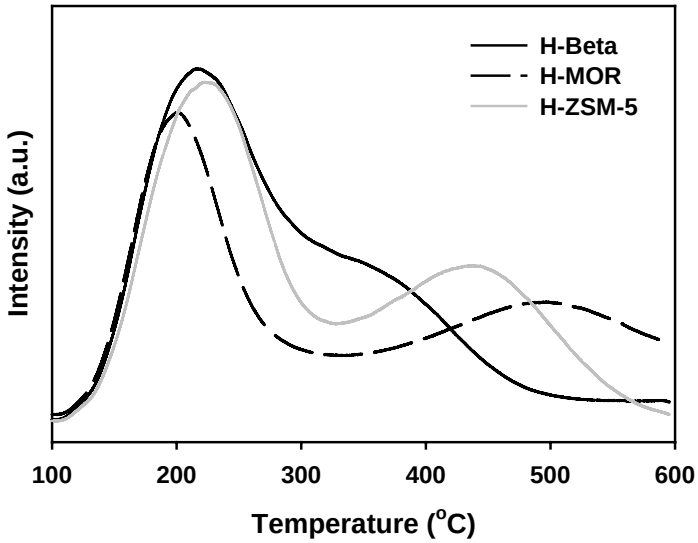

Fig. 2. NH_3-TPD profiles of the zeolite catalysts used in the present works.

is highest among the zeolite catalysts and its strength of the strong acid site is higher than that of the H-Beta, but shows the least catalytic activity (as in Fig. 1). This is due to the small pore size of the material which hinders both the entrance of 2-naphthol and the product formation. However, the activity is much less than that of the H-Beta in the case of the H-MOR, even though the density and strength of the strong acid sites are higher. This may be due to the lower amount of the weak acid site compared with other zeolites. Indeed, the initial activity of the H-MOR within 30 min is up to 50%. However, the catalytic activity is decreases dramatically with reaction time and this may be due to the coke formation. From these observations, it is inferred that both the weak and strong acid sites are the active sites for the etherification and the strong acid sites get deactivated during the course of reaction by coke formation.

Fig. 3 shows the TGA curves in air flow for the H-Beta and H-MOR catalysts after the etherification reaction is over at 180 °C for 2 h. A weight loss below 150 °C corresponds to the desorption of physically adsorbed water and residual organics. A notable weight loss in the TGA curve begins at 400 °C which may be due to the decomposition of coke formed during the course of reaction. As shown in Fig. 3, the H-MOR exhibits larger amount of the weight loss after 400 °C as compared to that of H-Beta. In case of the H-MOR, there is an additional weight loss in the range of 150–400 °C. This weight loss may come from the residual reactants or products which are strongly adsorbed on the active sites. The existence of coke and the strongly adsorbed organics may cause the catalyst deactivation which coincides with the etherification activities of the catalysts.

Fig. 4 shows FT-IR spectra for the H-Beta and H-MOR after adsorption of pyridine and subsequent evacuation at 200 °C. In the region of 1400–1600 cm^{-1}, several bands due to C–C stretching vibrations of pyridine are observed. FT-IR analysis of the adsorbed pyridine allows a clear distinction between Brønsted and Lewis acid sites. IR bands appearing at 1455 and 1546 cm^{-1} can be assigned to the adsorbed pyridinium ions on the Brønsted sites and the pyridine coordinated to Lewis acid sites, respectively [11,12]. The band at 1490 cm^{-1} is due to the pyridine adsorbed on both Brønsted and Lewis acid sites. As shown in Fig. 4, the H-Beta exhibits higher peak intensities for both Brønsted and Lewis acid sites as compared to H-MOR. This is in good agreement with the results of catalytic activity (in Fig. 1) and NH_3-TPD (in Fig. 2). Moreover, the IR results in Fig. 4 indicate that H-Beta has higher portion of Lewis acid sites than H-MOR from comparison of intensity ratios between Lewis and Brønsted acid sites.

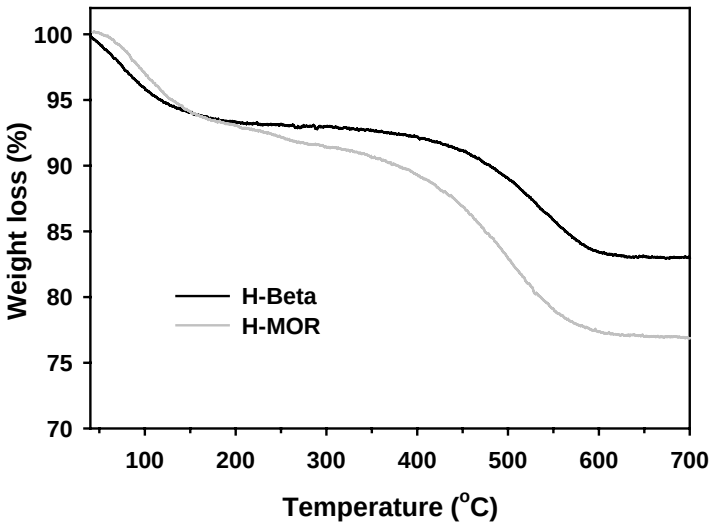

Fig. 3. TGA profiles for the H-Beta and H-MOR catalysts, obtained after the etherification reaction at 180 °C for 2 h, in air flow.

The effect of reaction temperature on the catalytic activity on the H-Beta catalyst is shown in Fig. 5. The etherification reactions were carried out in the temperature range of 140–220 °C. It is clearly seen that the conversion increases with temperature until 180 °C and decreases thereafter. This is in agreement with Yadav and Krishnan [1] and Selvraj et al. [8] who also have reported a similar behavior in their respective studies. The decrease in catalytic activity after 180 °C in our present study may be due to the deactivation of the catalyst by the coke formation arising at high temperature. The influence of molar ratio of ethanol to 2-naphthol on etherification is shown in Fig. 6. The conversion of 2-naphthol gradually increases with increase in the molar ratio and reaches to a maximum of 10. Beyond this, the addition of more ethanol does not affect on the activity. Fig. 7 shows the conversion versus WHSV after the reaction run of 1 h. The WHSV is changed by varying the feed rate of the reactant mixture by keeping constant amount of catalyst. Until the WHSV is 2, there is no change in the 2-naphthol conversion but when WHSV increases to 4, the conversion decreases to about from 78 to 35%. This suggests that less time is available for 2-naphthol to react with ethanol at higher space velocity and hence causes a decrease in the conversion of 2-naphthol [13].

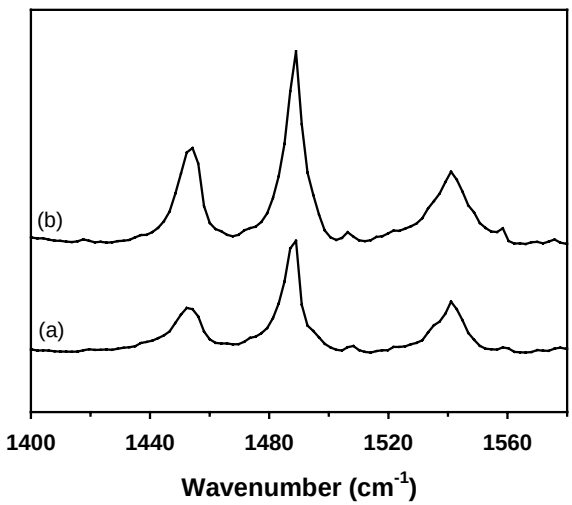

Fig. 4. Pyridine IR spectra for (a) H-MOR and (b) H-Beta, obtained after evacuation of the catalysts at 200 °C.

Fig. 8 shows the results of 2-naphthol etherification with ethanol over H-Beta zeolite with Si/Al ratios, which are prepared by dealumination using different amounts of oxalic acid. The increase in Si/Al ratios of the catalysts leads to a decrease in 2-naphthol conversion. When the aluminum content becomes small in the catalysts, the extent of contact of the reactants and/or products on the active sites decreases since the aluminum within the zeolite frameworks is the

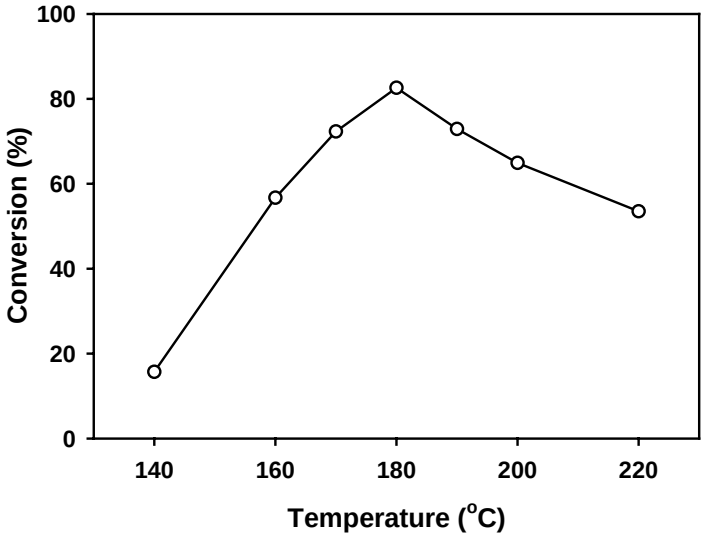

Fig. 5. Variation of conversion of 2-naphthol over H-Beta zeolite with the reaction temperature.

acid site. The catalytic activities also decrease with increasing Si/Al ratios. It is reasonable to suggest that the catalyst deactivation may be caused from the coke formation and the strong interaction between the active sites and the reactants and/or products.

NH_3-TPD profiles of H-Beta with different Si/Al ratios are illustrated in Fig. 9. There are two peaks in the profiles which mean weak and strong acid sites on the zeolites. As shown in Fig. 9, the total amounts of acid sites are sharply reduced with increasing the Si/Al ratios. In general, as the oxalic acid concentration increases, the amount of total acid sites decreases [14–16], which may cause the decrease of the initial catalytic activity. Fig. 9 shows that the weak acid sites

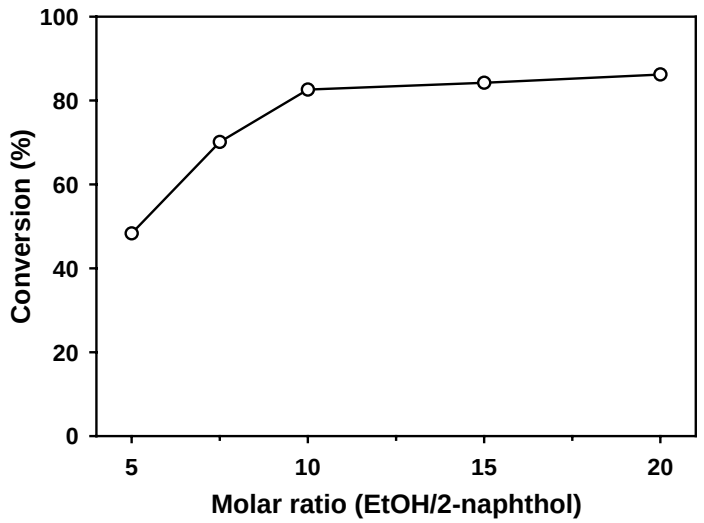

Fig. 6. Variation of conversion of 2-naphthol over H-Beta zeolite with the molar ratio of ethanol to 2-naphthol.

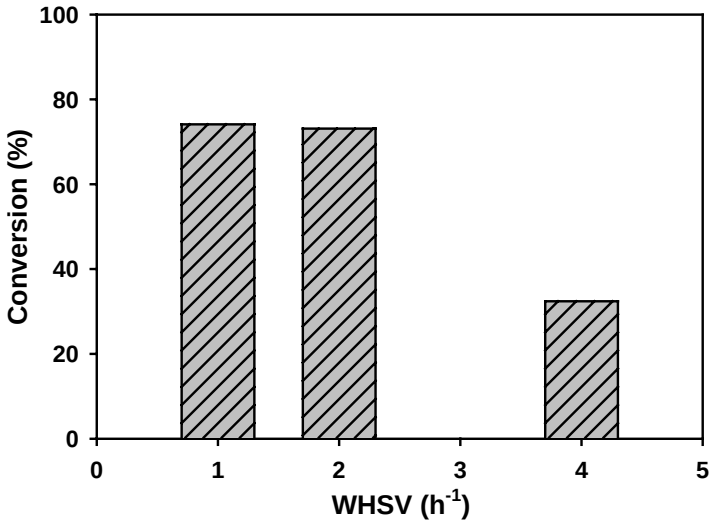

Fig. 7. Effect of WHSV on the etherification activity of H-Beta zeolite.

are dominant and strong acid sites just form a little shoulder peak, in case of the H-Beta with Si/Al = 13. As the Si/Al ratio increases, the amount of weak acid sites decreases more quickly than that of strong acid sites. When the Si/Al ratio reaches to 178, the amounts of both the weak and strong acid sites become similar. Fig. 10 represents the relation between the catalytic activity and the amounts of both weak and strong acid sites. The catalytic activity is highly dependent on the amount of weak acid sites in H-Beta zeolites, rather than the amount of strong acid sites. The strong acid sites may be easily affected by coke formation and due to strongly adsorbed organics as compared to the weak acid sites.

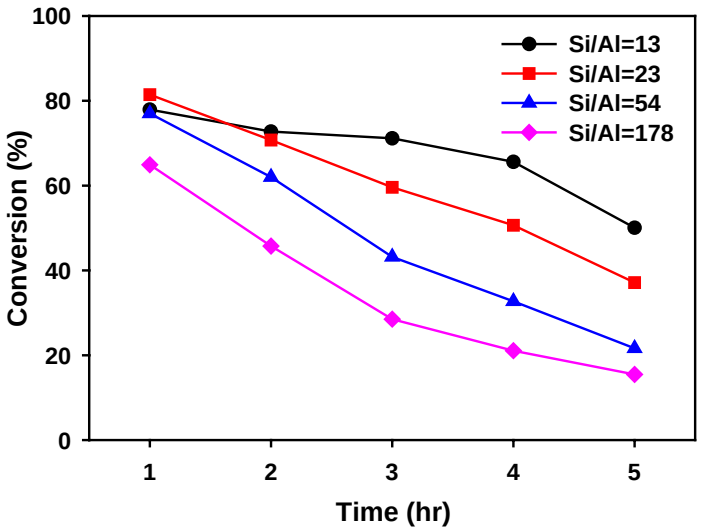

Fig. 8. Catalytic activities of H-Beta zeolites with different Si/Al ratios depending on reaction time.

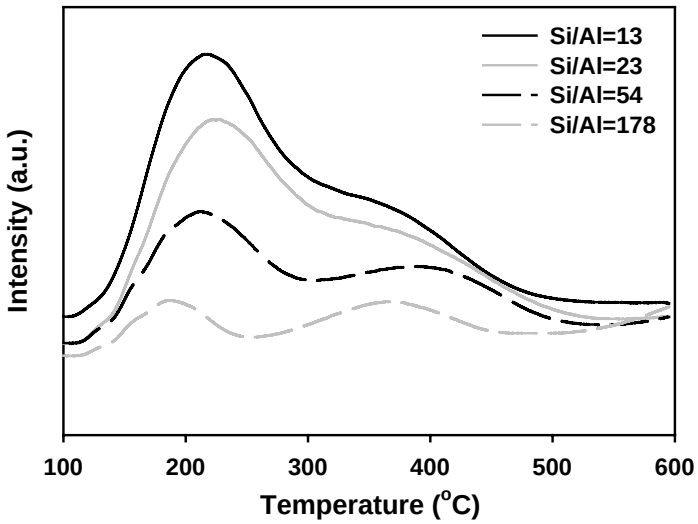

Fig. 9. NH_3-TPD profiles of H-Beta zeolites with different Si/Al ratios.

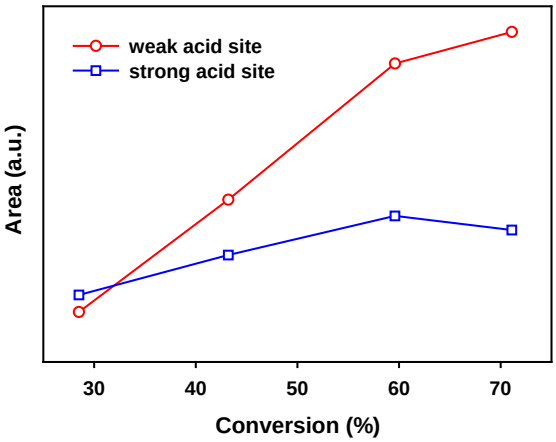

Fig. 10. Relation between the catalytic activity and the amounts of both weak and strong acid sites. The areas of acid sites are obtained by Gaussian peak analysis from Fig. 9, and the conversions of 2-naphthol after the reaction for 3 h are collected.

4. Conclusions

The catalytic etherification of 2-naphthol with ethanol has been studied over zeolite catalysts such as H-Beta, H-MOR and H-ZSM-5. H-Beta zeolite shows higher conversion than other catalysts for 2-naphthyl ethyl ether. NH_3-TPD, pyridine IR and TGA results indicate that the catalytic activity and deactivation are affected by the amount and strength of the acid sites in the catalysts. The influences of ethanol/2-naphthol molar ratios, reaction temperature, and space velocity on the catalytic activity were studied using H-Beta. The best optimized conditions were obtained at reaction temperature = 180 °C, WHSV = $1\,h^{-1}$, and ethanol/2-naphthol molar ratio = 10. Dealuminated H-Beta zeolites with different Si/Al ratios are obtained by oxalic acid show that the conversion decreases with increasing Si/Al ratios. The NH_3-TPD profiles indicate that total acid amount decreases with increase in Si/Al ratio and the weak acidity decreases more sharply as compared to the strong acidity. Etherification activity of 2-naphthol and ethanol may be affected by weak acid site. Deactivation of catalysts is caused by coke formation and strongly adsorbed organics present over the strong acid sites.

Acknowledgements

The authors are grateful for financial support by the Research Initiation Program at Ajou University (20012010) and Department of Molecular Science and Technology through Brain Korea 21 Project.

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