Etherification Reaction of 2-Naphtol with Ethanol Using Dealuminated Beta Zeolite

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ABSTRACT

Zeolite H-beta was modified by treatment with oxalic acid solution (0.01, 0.05, 0.1, 0.5 and 1 M). Conversion showed similar trend until 0.1 M oxalic acid treatments. In the case of 0.5M and 1M oxalic acid treatments, the conversion decreased with reaction time because of small Al contents. NH3-TPD profiles of H-Beta with different oxalic acid treatment showed that the total acid amount decreased with increasing oxalic acid concentration.

Keywords: Beta zeolite; Dealumination; Etherification; 2-Naphtol

INTRODUCTION

The ether products of 2-naphthol are very attractive due to their extensive applications as perfumery and flavoring compounds in the fine chemical industry. It is traditionally manufactured from 2-naphthol and alcohol such as methanol, ethanol and iso-butanol in the presence of sulfuric acid as the homogeneous catalyst. However, the drawbacks of such a process, based on homogeneous catalysis system, include corrosion, safety hazards, separation procedures, and environmental problem. Therefore, many researchers have attempted to utilize solid acid catalysts instead of sulfuric acid, in order to find an eco-friendly process for etherification.

Yadav et al. [1] reported that etherification of 2-naphthol with methanol using modified clays and sulfated zirconia. According to their results, the
dodecatungstophosphoric acid supported on K-10 clay was found to be best. The rates of etherification with other aliphatic alcohols over the same catalyst at 150 °C were in the following order n-BuOH > 2-PrOH > MeOH > EtOH > n-PrOH. Chen et al. [2] reported the production of 2-naphthyl methyl ether using sulfated mesoporous material. They suggested etherification activity as follows: sulfated Al-MCM-41 ~ USY > H2SO4 > Al-MCM-41 > Silica-Alumin > H-ZSM-5 > γ-Alumina, which was similar trend with the acid strength of catalysts.

Zeolites are also one of excellent candidates for homogenous catalyst, which can replace the homogeneous system, due to their solid acidity, constricted pore shape and redox property. We have found that beta zeolite exhibit an excellent catalytic activity and selectivity for production of 2-naphthyl ethyl ether. In the present work, we have aimed to find an effect of aluminum content within the frameworks of beta zeolite on the catalytic activity and stability, using dealuminated beta zeolite. Moreover, we demonstrate the active site for the etherification reaction.

### EXPERIMENTAL

NH4-Beta (Tosoh) was converted to H-form by calcination at 550°C for 4h. The H-Beta zeolite was treated with oxalic acid using a proportion of 1 g zeolite per 20 ml solution. The acid treatment was carried out at room temperature for 5min. The concentration of oxalic acid was varied systematically from 0.01 to 1M. The suspension was then washed with deionized water and dried in an oven at 393K overnight. The samples were then calcined at 550 °C for 4 h at a heating rate of 1°C/min under shallow bed conditions.

The catalytic etherification of 2-naphthol (Kanto chemical, 98.5%) with ethanol (Samchun, 95%) at 180°C was carried out at atmospheric pressure using a fixed-bed vertical flow reactor (catalyst weight 0.1g). A mixture of 2-naphthol and ethanol with a molar ratio of 1:10 was introduced into the reactor by means of a syringe pump (feed flow: 1ml/h) with a WHSV (Weight Hourly Space Velocity) of 1h⁻¹. Reactor temperature was measured using K-type thermocouple around catalyst bed. The temperature of catalyst bed had reached 180°C then syringe pump injection started. Sample were withdrawn every 30min for analysis during 5h.

The analysis was carried out by gas chromatography (Young-Lin 600D) by using a flame ionization detector. HP-5 capillary column was used for analysis. Reactants, products and their synthetic mixtures were used to calibrate the chromatograms and to deduce quantitative information. For FT-IR study, samples of 12mg were pressed into self-supported wafers. These wafers were mounted in an
infrared vacuum cell with calcium fluoride windows. Then samples were degassed at 500°C for 1h. Pyridine (99.9% HPLC grade, Sigma) vapor was introduced into the cell at room temperature. The cell elevated to 200°C and kept for 30min; the samples were then evacuated at the same temperature for 30min. In order to investigate the acid strength, desorption of pyridine was performed by evacuation at 200, 300, 400°C, respectively. All the FT-IR spectra were measured at room temperature. The FT-IR spectra were recorded by using a Nicolet Magna IR 550 spectrometer over the range of 1400-4000cm⁻¹ with 4cm⁻¹ resolution. The NH₃-TPD spectra were recorded using a flow-through microreactor system equipped with a thermal conductivity detector (TCD). Data were collected and processed by a computer. About 300mg of sample was activated in flowing O₂ at 600°C for 1h, and then switched to a He flow. After the sample was cooled to 100°C, the He flow was switched to a flow of 1% NH₃/He for 1h. Then the weakly adsorbed NH₃ was removed by purging He flow for 1h. The reactor temperature was ramped up to about 600°C at a rate of 10°C/min, while a He flow of 40cm³/min was passing through the reactor and the TCD.

RESULTS AND DISCUSSION

Figure 1 shows the results of 2-naphthol etherification with ethanol over zeolite H-Beta with oxalic acid treatment. Etherification activity has similar trend until 0.1 M oxalic acid treatments. With increasing the concentration of oxalic acid, the aluminum content of H-Beta decreases. In case of 0.5 M and 1 M oxalic acid
treatments, the activity rapidly decreased with reaction time.

Figure 2 shows the selectivity of 2-naphthyl ethyl ether. As the oxalic acid concentration increases, the selectivity of 2-naphthyl ethyl ether increases. In this case, H-Beta treated with 1 M oxalic acid shows the highest selectivity, compared with that of H-Beta without treatment.

![](image)

**Fig. 2.** Selectivity of 2-naphthyl ethyl ether for H-Beta treated with oxalic acid

Temperature-programmed desorption of ammonia is a useful method to determine the surface acid sites of solid acids. The amount of desorbed ammonia can be considered as the amount of the acid sites on the sample. The strength of the acid sites can also be determined by desorption temperature. The higher the ammonia desorption temperature is, the stronger the acid sites are. NH$_3$-TPD profiles of H-Beta of different SiO$_2$/Al$_2$O$_3$ ratios are illustrated in Figure 3. In general, as the oxalic acid concentration is increased, the amount of total acid sites is decreased. There are two ammonia TPD peaks in the profiles, which means there are weak acid sites and strong acid sites on the zeolites. On H-Beta of 0.01M oxalic acid treatment, weak acid sites are dominant and strong acid sites just form a little shoulder peak. As the oxalic acid concentration is increased, the amount of weak acid sites decreases more quickly than the amount of strong acid sites. For the H-Beta of 0.5M oxalic acid treatments, strong acid sites form the main peak on the NH$_3$-TPD profiles. As the oxalic acid concentration is increased, the tops of the two ammonia TPD peaks also shift to lower temperatures.
FT-IR spectra of pyridine adsorbed on different H-Beta zeolite are compared at 200°C in Figures 4. As shown in Figures 4, the area of the FT-IR signals of pyridine decreased as the oxalic acid concentration is increased, which indicates the amount of acid sites in the H-Beta zeolites decreases as the aluminum content in zeolites decreases. IR signals of pyridinium ions (1546 and 1636 cm\(^{-1}\)), which are formed by interaction of pyridine and Brønsted acid sites, exist in all IR spectra even at high temperature. IR signals of pyridine adsorbed on Lewis acid sites (1455 and 1621 cm\(^{-1}\)) also exist in all IR spectra at different temperatures. With decreasing aluminum content, reactant and/or product contact opportunity is more decreased. We think that the catalyst deactivation is caused from strong interaction between active site and reactant and/or product. With contacting reactant and/or product, coke deposit more increased. From NH\(_3\)-TPD results, the oxalic acid concentration were increased, the amount of total acid sites was decreased. Etherification reaction closely related to acid amount with H-Beta zeolite.

Collignon et al. [3] reported on the gas phase synthesis of MTBE from methanol and isobutene over dealuminated zolites. The contribution of the external surface of the zeolites to the reaction has been discussed. In the case of H-Y zeolites, they showed that extraframework Al species (\(^{27}\)Al NMR signal at 30 ppm) have detrimental effect on the reaction. Also they studied on comparative vapor phase synthesis of ETBE from ethanol and isobutene over different acid zeolites [4]. They concluded H-Beta zeolites, with higher external surface area, were more active than the other zeolites. The highest yields of ETBE were obtained for beta samples with
high Brønsted acid content and low SiOH/AlOHSi ratio. Collignon et al. [5] studied liquid phase synthesis of MTBE from methanol and isobutene over acid zeolites and Amberlyst-15. The catalytic activity of the zeolites is related to the external specific surface area, and to the concentration of bridging hydroxyls and silanol groups in the mesopores. A zeolite H-Beta sample with a Si/Al ratio of 36 has an optimum silanol and bridging hydroxyl content leading to stoichiometric methanol and isobutene adsorption, highest activity and MTBE yields. Honglin Wang et al. [6] studied surface acidity of H-Beta and its catalytic activity for alkylation of benzene with propylene. They concluded that the catalytic activity of H-Beta zeolites is in direct proportion to the acidic amount of the zeolite in general. H-Beta zeolite of SiO$_2$/Al$_2$O$_3$=27 which contains the highest amount of Brønsted acid sites as indicated by FT-IR spectra of adsorbed pyridine, is the most reactive catalyst in the alkylation reaction. Selvaraj et al.[7] synthesized ethyl 2-naphthyl ether(neroline) using SO$_4^{2-}$/Al-MCM-41 mesoporous molecular sieves. The yield of ethyl 2-naphthyl ether follows the decreasing order: SO$_4^{2-}$/Al-MCM-41=USY>H$_2$SO$_4$>H-Beta>Al-MCM-41> silica-alumina>H-ZSM-5.

Fig. 4. FT-IR spectra of H-Beta treated with oxalic acid after pyridine adsorption.
Based on the results from FT-IR of adsorbed pyridine, TPD of the ammonia and those reported elsewhere, the catalyst acid strength also exhibits a similar trend, except H-ZSM-5 zeolite. The non-framework aluminum existing in the intrachannel space is supposed to increase the catalyst due to the increase of Lewis acidity. Li-Wen Chen et al. [2] showed that synthesis of 2-naphthyl methyl ether using sulfated mesoporous molecular sieve Al-MCM-41. The catalytic results were compared with those obtained by using sulfuric acid, amorphous silica-alumina, r-alumina, USY and H-ZSM-5 zeolites. The sulfated Al-MCM-41 catalyst forms the exclusive product of 2-naphthyl methyl ether and has much higher yields than other catalysts, except USY. The non-framework aluminum existing in the intrachannel space of Al-MCM-41 probably causes the enhancement of catalyst activity. The catalytic results are correlated to the acidity, the surface area and the pore size of the catalysts.

CONCLUSION

Zeolite H-Beta was modified using oxalic acid treatment. In case of 0.5 M and 1 M oxalic acid treatments, the conversion decreased with reaction time because of small Al contents. NH₃-TPD profiles of H-Beta with different oxalic acid treatment showed total acid amount decreased with increasing oxalic acid concentration.

REFERENCES