



表面改質による天然ゼオライト触媒の高活性化

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Enhancement of Catalytic Activity of Natural Zeolites by Surface Modification for 1-Butene Isomerization

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Catalytic activity of some natural zeolite (NZ) samples has been examined using 1-butene isomerization in a closed-circulating system as a test reaction. A remarkable improvement in the activity was observed after modification of the samples. Samples treated by aqueous ammonium solutions (1 M) gave relatively higher activities than that by mineral acid solutions (1 M). X-ray diffraction powder patterns suggested that, the zeolite crystalline structure is well preserved in the case of the ammonium solution-treated samples, whereas partial structural deterioration occurred in the acid-modified ones. Ammonia temperature desorption study indicated an increase in the concentration and strength of surface acidity resulting from the modification, whilst IR spectra of adsorbed pyridine on the catalyst, revealed the presence of both Bronsted and Lewis acid sites. Some of the modified samples (particularly NZ-YK, NZ-Y and NZ-O) showed catalytic activities higher than amorphous Al_2O_3 and HMordenite, but relatively lower than HZSM-5.

Keywords: Catalytic Activity, Surface Modification, Natural Zeolite (NZ), Isomerization

1. INTRODUCTION

Natural zeolites (NZs) have mainly been utilized from time past as molecular sieves and ion exchangers. However, their usage as industrial catalysts is very much limited compared to the synthetic ones owing to their relatively low catalytic activity and their small pore sizes¹⁾. Nevertheless, some natural zeolites have been applied as catalysts or carriers in industry. For instance, it has been reported that, for the selectoforming process, nickel supported on erionite or erionite/clinoptilolite have been employed as catalysts²⁾. This is a process in which, straight chain paraffins are selectively cracked from reformer product mixtures including, naphthenes, aromatics, or isoparaffins³⁾.

Furthermore, frantic research efforts are being made to

employ natural zeolites as effective catalysts or supports in the petroleum industry. Sako et al⁴⁾ reported that, natural clinoptilolite modified by mineral acids and ammonium salts, was found to be efficient for catalyzing the conversion of methanol to olefins, which are precursors for the Mobil olefins-to-gasoline and distillates (MOGD) process. Recently, the proton form of natural clinoptilolite, has been noted as an effective catalyst for the skeletal isomerization of n-butenes to isobutene⁵⁾. This product, is a primary ingredient for the synthesis of MTBE (methyltert.-butylether) and ETBE (ethyltert.-butylether), which are environmentally friendly octane-number enhancers for the reformulated gasoline.

Development of highly active natural zeolites catalysts may be attractive in view of its low cost. In this paper, the catalytic properties of some natural zeolites, after activation through surface modification is investigated.

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2. EXPERIMENTAL

(a) Catalyst Materials

Natural zeolite (NZ) samples examined were obtained from some locations in the Hokkaido prefecture of Japan, namely Yoichi (Y and YK), Oshamambe (O), Matsumae (M) and Kushiro (K). They were labelled as NZ-YK (and NZ-Y), NZ-O, NZ-M and NZ-K, respectively.

(b) Sample Treatment

(i) Ion-Exchange Method: Samples were ion-exchanged with various solutions namely NH_4Cl , $[\text{NH}_4]_2\text{SO}_4$, HCl and H_2SO_4 (1 M each). One treatment was made by soaking the sample at room temperature and the other at about 100°C under refluxing conditions. In each case, a 10 g sample was treated with 250 ml of the reagent for a period of 24 hours. The samples were then filtered and washed with distilled water until free from the corresponding anion. This was followed by drying at 120°C overnight and calcination at 500°C and other temperatures for 3 hours.

(ii) Impregnation Method: 2 g sample of H-YK (protonated form of NZ-YK) was impregnated with aqueous solutions of FeSO_4 , CuSO_4 , $\text{Zr}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$ to yield 5 wt% catalysts. The resulting catalysts, were dried at 120°C and calcined at temperatures ranging from 200°C to 500°C for 3 hours.

(c) Reaction System and Procedure

A closed-circulatory system was used as a reactor for the isomerization of 1-butene (which was a chosen test reaction) over the various catalysts. Prior to reaction, each catalyst was activated under evacuation at its calcination temperature for 2 hours. The reaction was conducted at 25°C using 50 mg catalyst sample and 40 torr of 1-butene. A gas chromatograph equipped with a 4 m long column with propylene carbonate and TCD was employed for the analysis of the products.

(d) Characterization

In order to study the effects of the modification, particularly the ion-exchange, on the samples and the nature of catalysts produced, NZ-YK, which is known to consist of mainly clinoptilolite, was selected for characterization. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku Gergeflex XRD instrument using $\text{CuK}\alpha$ radiation to study the structure of sample NZ-YK before and after modification. Specifically, unmodified YK and those modified by $[\text{NH}_4]_2\text{SO}_4$ and mineral acids at about 100°C were considered.

Temperature programmed desorption (TPD) of NH_3 was also conducted after pretreating 0.1 g sample for 1 hour at 500°C under vacuum to study the surface acidity of the catalyst. A $20^\circ\text{C}/\text{min}$ heating rate of NH_3 desorption from 100°C to 550°C was used. Fourier Transform Infra-red (FTIR) spectroscopy was used to study the nature of acid sites on H-YK using pyridine as a probing adsorbate molecule. A self-supporting disc of the sample, was outgassed at 500°C for 2 hours, after which 10 torr pyridine was introduced for 30 minutes at 150°C , followed by desorption at the same temperature for 30 minutes.

3. RESULTS AND DISCUSSION

3.1. Catalyst Activation

Figures 1 (a), (b), (c) and (d) depict some of the typical results for the conversions and product selectivities obtained in the isomerization of 1-butene over the catalysts. As shown, prior to modification, the samples were inactive for the reaction under the present reaction conditions. This observation, is consistent with the fact that, potassium form of clinoptilolite was found to be practically inactive for isomerizing n-butene isomers⁶⁾.

In general, all the catalysts, especially NZ-YK, NZ-Y and NZ-O, showed a remarkable improvement in their catalytic activities. It is known that double bond isomerization is an acid sensitive reaction. We assume that, the treatment given to the samples led to an increase in the concentration of acid sites as well as the amount of strong acid sites. The cis to trans-2-butene ratio observed was generally close to unity. It is therefore noted that Bronsted acidity is responsible for this reaction⁷⁾. The cases with cis to trans ratios deviating from unity are due to the pore size of the zeolites. Ritcher et al⁸⁾ indicated that, in the isomerization of 1-butene over Bronsted-acid sites in small pore zeolites, selectivity of cis and trans 2-butene is influenced by the pore size of the molecular sieve. The preferential conversion of the secondary butylcarbenium-ion intermediate into the trans isomer leads to cis/trans ratios lower than 1. This is caused by the steric constraints and the slow diffusion of the bulkier cis isomer out of the pores of the zeolite.

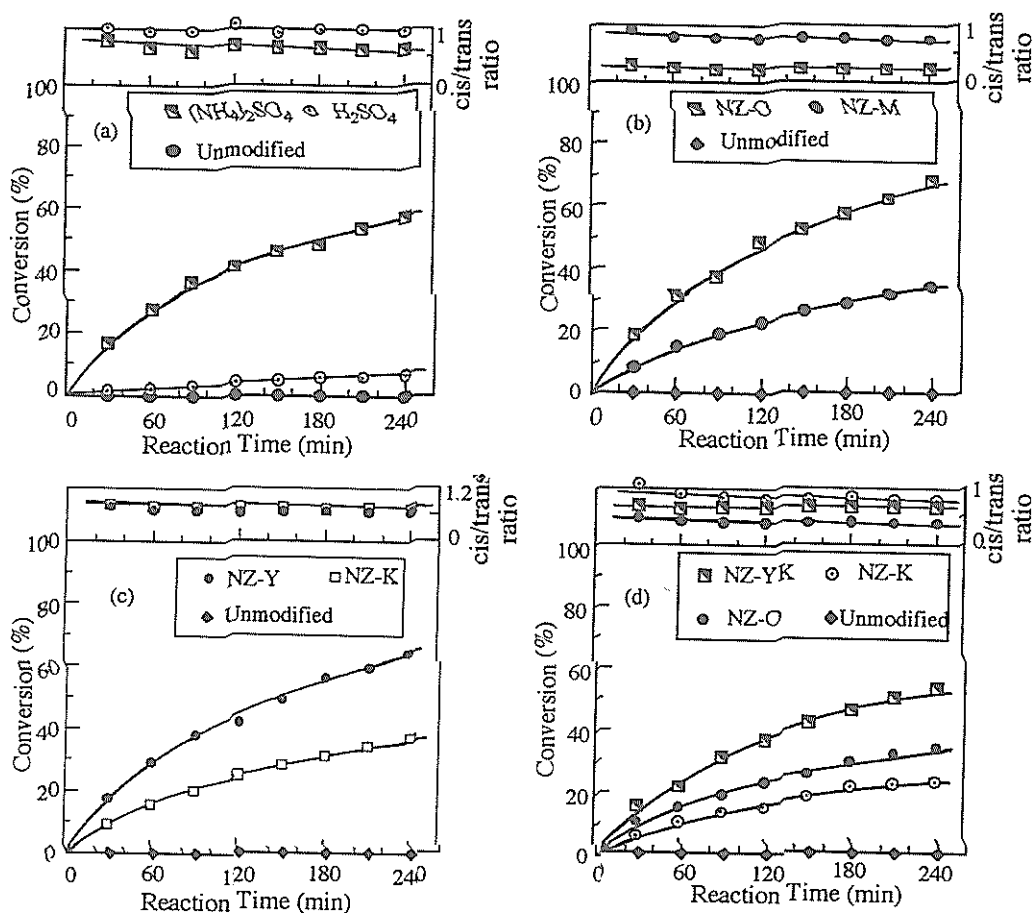


Figure 1. Conversion and product selectivity in 1-butene isomerization over modified natural zeolites. (a) NZ-YK modified by $(\text{NH}_4)_2\text{SO}_4$ and H_2SO_4 at 100°C ; (b) NZ-O and NZ-M modified by NH_4Cl at 100°C ; (c) NZ-Y and NZ-K modified by NH_4Cl at 100°C ; (d) NZ-YK, NZ-O and NZ-K modified by NH_4Cl at 25°C . (Catalyst weight = 50 mg; Reaction temperature = 25°C .)

3.2. Characterization

3.2.1 XRD Study

The XRD powder patterns (Figure 2) obtained show two prominent peaks, with the most significant peak located at diffraction line corresponding to $2\theta \approx 22.6^\circ$ and the other at about 9.9° . This pattern is typical of natural clinoptilolite as reported in the literature⁹. The diffraction pattern for ammonium solution-treated NZ-YK shows an increase in intensity relative to that of the original sample. On the other hand, that of the mineral acid-modified samples depict significant decrease in peak intensity.

These observations suggest that, the zeolite crystalline structure remains intact or is well preserved, when treated with ammonium solution. Conversely, structural deterioration and/or partial collapse occurs in the case of the mineral acid modification. Certainly, such important changes are expected to reflect on the catalytic activity of these samples as discussed later.

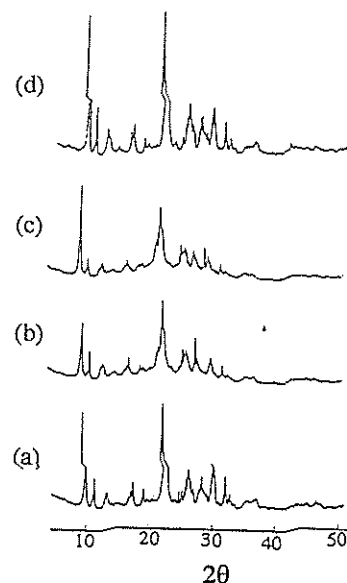


Figure 2. Powder XRD patterns of NZ-YK before and after modification.

(a) Unmodified NZ-YK; (b) Sample modified by H_2SO_4 (1 M); (c) Sample modified by HCl (1 M); (d) Sample modified by $[\text{NH}_4]_2\text{SO}_4$. Note: Reagent treatment was done at 100°C .

3.2.2 Temperature Programmed Desorption of NH_3

Ammonia TPD profiles for NZ-YK before and after modification with H_2SO_4 , HCl and $[\text{NH}_4]_2\text{SO}_4$ at 100°C and calcined at 500°C for 3 hours are shown in Figure 3. All the catalysts, except the unmodified sample, show two NH_3 desorption peaks,

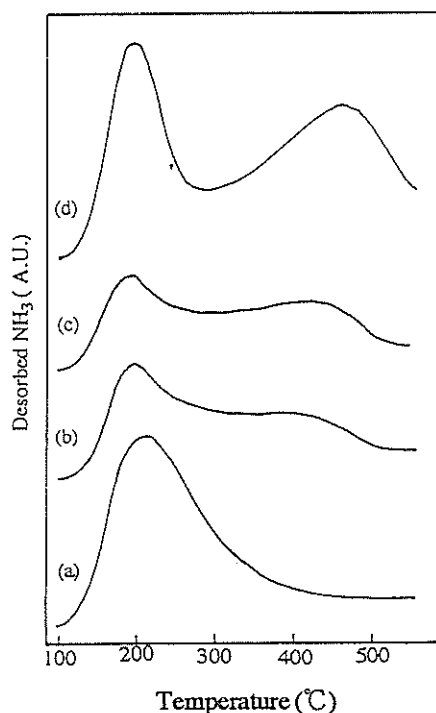


Figure 3. Profiles for temperature-programmed desorption of ammonia.

- (a) Unmodified NZ-YK.
 - (b) Sample modified by H_2SO_4 (1 M) at 100°C .
 - (c) Sample treated with HCl (1 M) at 100°C .
 - (d) Sample modified by $[\text{NH}_4]_2\text{SO}_4$ (1 M) at 100°C .
- All samples were calcined at 500°C for 3 hours.

which is characteristic of zeolites. The lower temperature desorption peak (around 200°C – 220°C), correspond to weak acid sites and the higher one (above 400°C) is ascribed to stronger acid sites (especially the Bronsted type)¹⁰. Thus, it is clear that, the unmodified sample (exhibiting a single peak at a low temperature), possesses only weak acid sites and hence could not catalyze the test reaction.

The increase in surface acidity as well as the concentration of strong acid sites as a result of the modification, accounts for the improvement in the catalytic activities of the zeolites. It should be noted, however, that the $[\text{NH}_4]_2\text{SO}_4$ modified catalyst has much higher concentration of stronger acid sites relative to that of mineral acid treated ones. This is in correlation with their catalytic activities.

3.2.3. IR Spectroscopy

Figure 4 depicts the infra-red spectra of pyridine adsorbed on

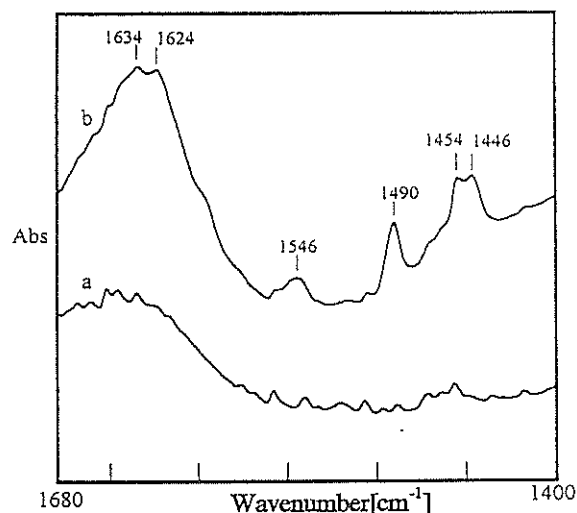


Figure 4. FTIR spectra of adsorbed pyridine on H-YK catalyst.

- (a) Sample after outgassing at 500°C for 2 hours.
- (b) Adsorption of pyridine (10 torr) at 150°C for 30 minutes, followed by desorption at the same temperature for 30 minutes.

H-YK catalyst. Desorption and evacuation of adsorbed pyridine at 150°C yielded a spectrum with absorption bands at 1546, 1490, 1454 and 1446 cm^{-1} . The 1546 cm^{-1} band is assigned to pyridinium ions bonded to Bronsted-acid sites whilst those of 1454 and 1446 cm^{-1} are attributed to coordinatively bonded pyridine at Lewis-acid sites. The absorption band at 1490 cm^{-1} is indicative of pyridine associated with both Bronsted and Lewis acid sites¹¹. It is therefore confirmed that both Bronsted and Lewis-acid sites are generated on the surface of the catalyst.

3.3. Treatment Reagent and Temperature Effect

Figures 5 (a) and (b) shows that, treatment by ammonium salts (NH_4Cl and $[\text{NH}_4]_2\text{SO}_4$) solution led to higher catalytic activities than that by the mineral acids except the case of NZ-K in which the HCl treatment at room temperature was the highest. Ion-exchange using NH_4^+ ion is reported to cause an appreciable decrease in the surface area whilst its dealumination effect is quite low. Thus, the Si/Al ratio is not significantly affected¹². Also, a 1M HCl treatment given to a zeolite like clinoptilolite, caused an increase in both the surface area and the Si/Al ratio⁴. Given these facts, the possible reason for the ineffectiveness of the mineral acids could be attributed to the collapse of part of the zeolite structure with the consequent substantial decrease in the surface acidity. This is clearly evident in the powder XRD pattern of mineral acid treated NZ-YK as in Figure 2 above, depicting diffraction lines with lower intensity, relative to the unmodified sample.

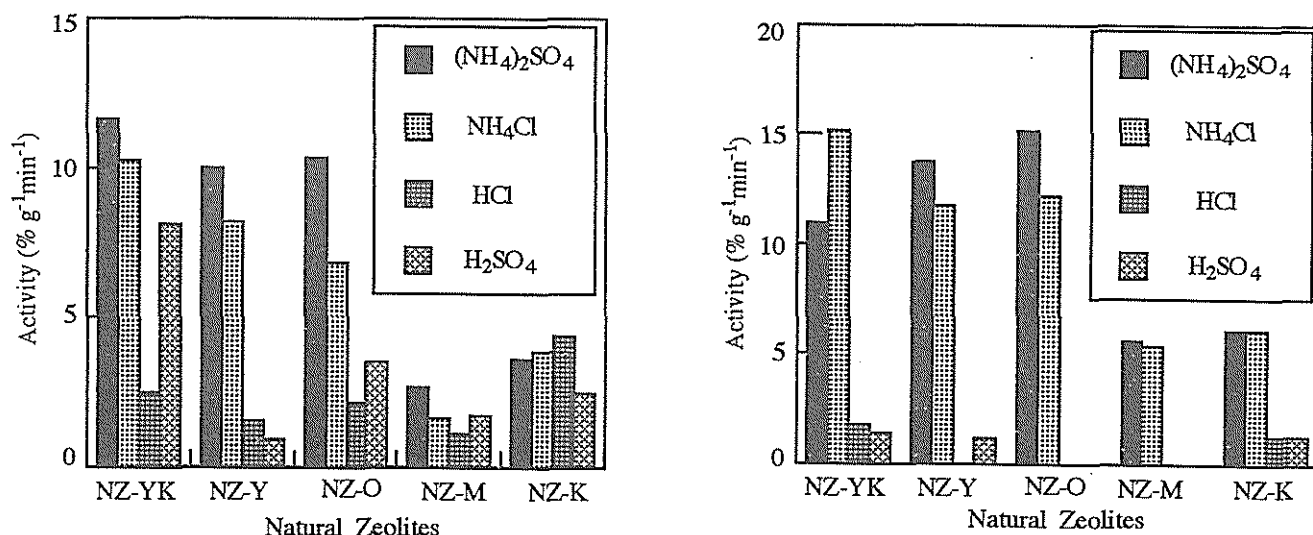


Figure 5. Activity of some natural zeolites modified at (a) room temperature and (b) 100°C in 1-butene isomerization. (Catalyst weight = 50 mg; Reaction temperature = 25°C). Note: Activity is based on analysis at 30 minutes.

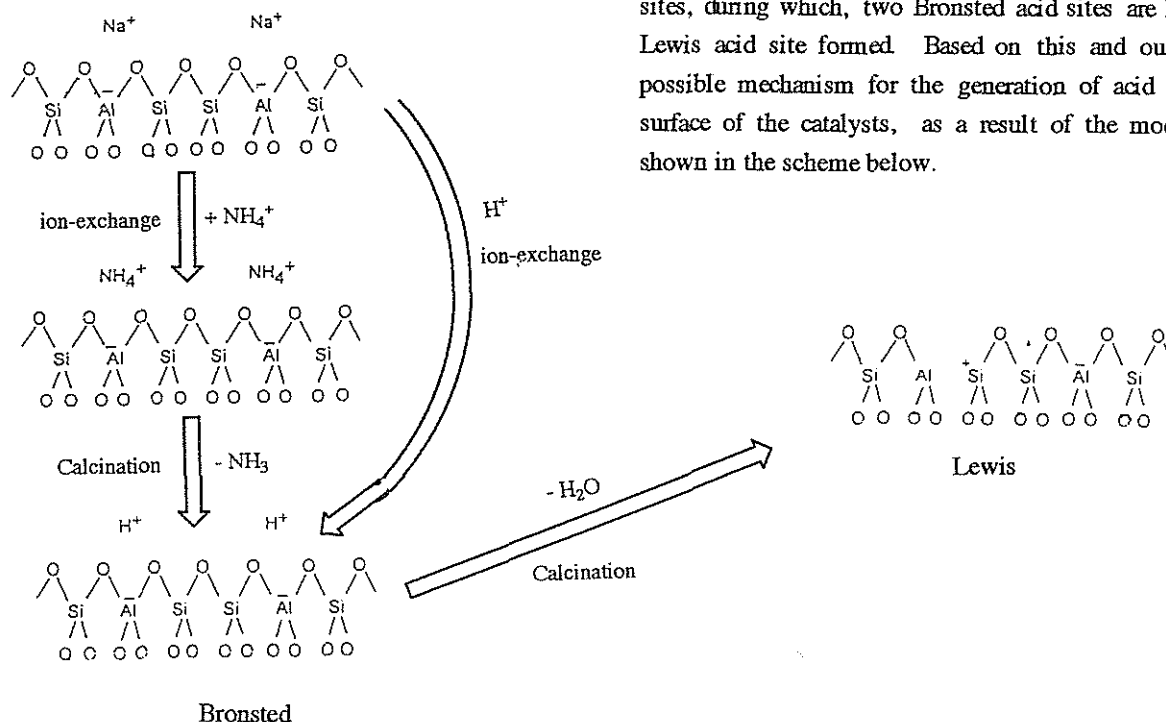
A comparison between of treatments at room temperature and 100°C, reveals that for the ammonium solution, treatment under the latter condition yields relatively more active catalysts. Treatment at room temperature is better when mineral acid is used as the reagent, since at higher temperature the zeolite structure is almost completely destroyed. This rendered NZ-Y, NZ-O and NZ-M completely inactive.

3.4. Mechanism for the generation of acid sites

Basically, cations especially alkali and alkaline earth metals residing in the pores of the zeolite, are exchanged for NH_4^+ or

H^+ ions in case of ammonium or mineral acid solution treatment, respectively. Most probably, the removal of impurities also occur during the treatment. Following calcination, the release of ammonia leaves the zeolite protonated. Thus, Bronsted acid sites are generated in the pores and on the surface. Progressive dehydration leads to the formation of Lewis acid sites. As mentioned above, from the FTIR results, both types of acid sites are formed.

Detrekoy et al.⁶ reported that, the deammoniation of the ammonium form of clinoptilolite, is complete at 400°C, forming the protonated zeolite. Dehydroxylation is said to occur above 400°C, leading to the formation of Lewis acid sites, during which, two Bronsted acid sites are lost for each Lewis acid site formed. Based on this and our results, a possible mechanism for the generation of acid sites on the surface of the catalysts, as a result of the modification, is shown in the scheme below.



Scheme 1. Possible mechanism for the generation of Bronsted and Lewis acid sites on the surface of the catalysts.

3.5. Impregnated Catalysts

As shown in Figure 6, the metal sulphate impregnated H-YK catalysts unexpectedly, showed lower activities than the supporting protonated zeolite. This is presumably due to the small pore size of the zeolite. As such, the metal ions do not get access into the pores instead they tend to block the channels thereby preventing the effective use of the active sites. The impregnation of $[\text{NH}_4]_2\text{SO}_4$ however, gave rise to a little higher activity. The increase is probably due to the presence of some residual SO_4^{2-} ions on the catalyst surface which by its electron-withdrawing effect strengthens the Bronsted acidity and also the increase in the number of protons originating from the NH_4^+ ions.

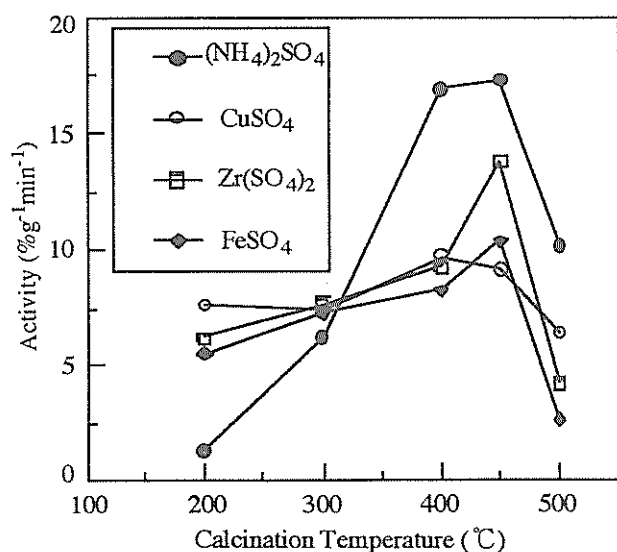


Figure 6. Catalytic activity of impregnated YK catalysts calcined at various temperatures in 1-butene isomerization.

(Catalyst weight = 50 mg; Reaction temperature = 25°C.)

Activity is based on analysis at 30 minutes.

Note: Catalysts contained 5 wt% of the sulphates indicated on the label.

3.6. Comparison with synthetic catalysts

Figure 7 indicates that, three of the natural zeolites studied, NZ-YK, NZ-Y and NZ-O have higher catalytic activities than the synthetic catalysts such as HMordenite and Al_2O_3 after modification. Also, modified NZ-Y which was calcined at 450 °C for 3 hours was more active than synthetic HY catalyst. In general, however, the activities of the natural zeolites were relatively lower than HZSM-5. The presence of excess cations in the pores of natural zeolites significantly limits the decationization and dealumination effect of the ion-exchange reagents. It is worthy of note, that, the presence of residual cations is evidenced by the IR band at 1446 cm^{-1} which is indicative of pyridine coordination with cationic sites- (Lewis acid sites)¹³.

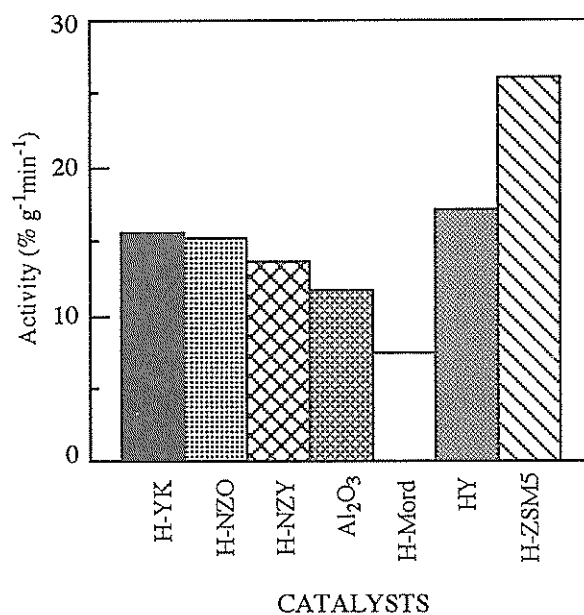


Figure 7. Comparison of the catalytic activities of modified natural zeolites and some synthetic catalysts in 1-butene isomerization.

(Catalyst weight = 50 mg; Reaction temperature = 25°C.)

Activity is based on analysis at 30 minutes.

4. CONCLUSION

The modification of natural zeolites by treatment with ammonium salt (especially NH_4Cl or $[\text{NH}_4]_2\text{SO}_4$) remarkably improves their catalytic activities by increasing the surface acidity as well as the concentration of strong Bronsted acid sites.

Though the natural zeolites studied showed relatively low catalytic activities, the fact that modified NZ-YK, NZ-Y and NZ-O have higher activities than some of the synthetic ones supports our suggestion earlier¹⁴ that there is a possibility of applying natural zeolites as catalysts for some acid-catalyzed hydrocarbon conversions in industry, in future.

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表面改質による天然ゼオライト触媒の高活性化

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1-ブテンの異性化反応をモデル反応として天然ゼオライトの触媒活性を調べた。天然ゼオライトは、改質処理を施すことによって触媒活性が改善された。X線回折パターンからアンモニウム塩水溶液処理したものは構造が破壊されていないが、酸水溶液処理したものは構造の一部が破壊されていることが示された。アンモニウム塩水溶液を用いた場合、酸水溶液を用いた場合よりも高活性を示した。アンモニアの昇温脱離を行なった結果、表面改質後の酸強度および濃度の増加が明らかとなった。ヒリジンを吸着させたIRの結果からLewis酸点とBronsted酸点が存在していることが分かった。 Al_2O_3 とHMordenite触媒よりも処理した天然ゼオライト(特にNZ-YK, NZ-YとNZ-O)のほうが高活性であったが、HZSM-5より低活性を示した。

キーワード： 触媒活性、表面改質、ゼオライト、異性化

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