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# Zeolites-catalyzed alkylation of isobutane with 2-butene: Influence of acidic properties

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The influence of acidity properties of zeolites on the alkylation of isobutane with 2-butene was studied using ultrastable Y (USY) zeolites. Most zeolites possessed almost comparable hydrogen transfer activity except for USY-30, which has the lowest acid site density. On the other hand, the strength of acid sites increased with degrees of dealumination. During the alkylation, a maximum in catalytic activity for certain Si/Al ratios were observed. This behavior is believed to be a result of a balanced level of acidic properties between the concentration and strength of Brønsted acid sites. It can prohibit the formation of heavy carbonaceous materials that deactivate the zeolites.

**KEY WORDS:** alkylation; USY zeolite; hydrogen transfer; Brønsted acid sites.

## 1. Introduction

The alkylation of isobutane with butenes has been used to produce a clean high-octane gasoline compound of low volatility [1]. However, current industrial processes with liquid acid catalysts should be replaced because of their hazardous nature. From this point of view, acidic solid materials have been intensively studied as alternative catalysts for this reaction [2]. Even though they displayed adequate activity and selectivity, most catalysts deactivated rapidly. The numerous efforts to overcome this drawback are reported in the literature [1, 2]. Especially, zeolites have been widely studied as a potential alkylation catalyst with intensive characterization to identify their desirable properties for the reaction [3–17]. However, the correlation between the physicochemical properties of zeolites and catalytic performance has reminded unclear. So far, it is known that the catalytic activity depends strongly on Brønsted acid sites.

It has been proposed that the way to improve its stability is to increase the concentration of Brønsted acid sites [2, 10, 11]. Stocker *et al.* indicated that only strong Brønsted acid sites were catalytically active [8], while Diaz-Mendoza *et al.* suggested that Brønsted acid sites with intermediate strength play an important role in alkylation [12]. Corma *et al.* [3] have not found any direct correlation between type of acid sites and catalytic activity for this reaction. Recently, Feller *et al.* [17] found a strong correlation between the fraction of strong Brønsted acid sites and catalyst life time. In this study, we carried out the alkylation of isobutane with 2-butene using USY zeolites with various Si/Al ratios ranging from 2.5 to 30. Especially, acidic properties of zeolites were examined to investigate their influence on the catalytic performance in this reaction.

## 2. Experimental

### 2.1. Catalyst preparation

A series of Y zeolites with Si/Al ratios ranging from 2.5 to 30 were obtained from Zeolyst International (formerly PQ Corporation). Zeolyst International prepared the higher Si/Al samples by controlled steam treatment followed by lean acid leaching of the parent Y faujasite. Ammonium forms of the zeolites were obtained by cation exchange with 2 N $NH_4Cl$ solution at 90 °C for 4 h. Finally, the zeolites were converted to their protonated forms by calcination in air at 500 °C for 1 h.

### 2.2. Catalysts characterization

The estimation of crystallinity was done based on the height of the main crystallographic XRD peaks obtained by a Siemens D500 X-ray Diffractometer using $CuK_\alpha$ radiation (wavelength 1.5406 Å). The BET surface area of zeolites was determined from the nitrogen isotherms at 77 K measured in a Micromeritics ASAP 2010 apparatus. The bulk Si/Al ratios of the zeolites were determined by inductively coupled plasma (ICP) emission spectroscopy. The STPD experiments were performed to determine the acid site concentration and have been described elsewhere [18, 19]. FT-IR spectroscopy was used to assign the ammonia desorption peaks to Brønsted or Lewis acid sites. The spectra were

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recorded using an IR cell with CaF2 windows and equipped for continuous flow of gases in a Bio-Rad FTS-40 spectrophotometer. The procedure used was described in detail previously [19]. The hydrogen transfer activity was determined by *n*-Hexane cracking experiment as described elsewhere [14].

The carbonaceous materials were also characterized by temperature-programmed oxidation (TPO). The spent zeolite was loaded into a stainless steel reactor and heated to 550 °C at the rate of 5 °C/min, in a high purity stream of oxygen (4.2% $O_2$ in helium). The $CO_2$ evolved was analyzed using a MKS PPT-RGA quadrapole mass spectrometer. The amount of carbonaceous material remaining in the zeolite after reaction was measured by thermogravimetric analysis (PerkinElmer TGA7). The carbonaceous material on the catalyst was combusted at a temperature increase rate of 5 °C/min to 550 °C under a flow of oxygen (20 cc/min) and the weight change of the catalyst during oxidation was measured. The ratio of this weight difference to the weight of the catalyst yielded the weight percent of carbonaceous material in the catalyst.

### 2.3. Catalytic experiments

The alkylation of isobutane with 2-butene was carried out in a high pressure, fixed bed reactor. The catalyst (1 g, dry basis) was loaded into a stainless steel tube and was heated to 550 °C under a flow of $N_2$ (30 $cm^3$/min) for 2 h followed by a flow of $O_2$ (30 $cm^3$/min) at 450 °C for 2 h. The reactor was then cooled to 80 °C and then pressurized to 300 psig with $N_2$. For each run, a pure isobutane was introduced into the system by an ISCO syringe pump (model 100 DM), and then a mixture of isobutane and 2-butene (i/o molar ratio of 20, the olefin WHSV of 0.5 $h^{-1}$) was pumped into the system by another ISCO syringe pump (model 500 D) to prevent a chromatographic sorption/reaction of 2-butene on the zeolites. Thereafter, samples were collected periodically and stored in a 16-port valve with heating system (Vici-Valco). These samples were analyzed using an HP 6890 GC/FID. A more detailed description of the qualitative and quantitative analyses can be found elsewhere [13–16].

## 3. Results and discussion

### 3.1. Characterization of catalysts

The physicochemical properties of USY zeolite samples are given in table 1. It can be seen that the dealumination procedures used on USY zeolites resulted in a decrease in their crystallinities and BET surface area as measured by XRD and ASAP, respectively. Further removal of aluminum from the USY-30 sample is not practical as it results in a catalyst that is only partially crystalline. Such samples are not sufficiently crystalline to allow meaningful interpretation of catalytic data and thus are not useful for this study. Of course the differentiation between partially crystalline and sufficiently crystalline samples is arbitrary; for the purposes of this study, any sample with a measured % cystallinity of greater than at least 70 is considered sufficiently crystalline.

The number and strength of the acid sites in the zeolites were characterized by $NH_3$-stepwise temperature programmed desorption (STPD). It was observed that the total number of ammonia molecules desorbed from the catalyst during ammonia STPD is proportional to the total number of aluminum atoms (see table 2). The distribution of acid strength over USY zeolites is also shown quantitatively in table 2. Five peaks were observed when the STPD took place from 150 to 540°C. The results of the zeolites with different Si/Al ratios showed that the decrease of the aluminum contents monotonically increases the portion of the strong acid sites from which $NH_3$ desorbs at elevated temperature over USY zeolites. This indicates an increase of strength of the acid sites. For zeolites where the aluminum distribution in the pores varies locally and/or the pore network is not uniform (small pores are connected with relatively large voids), the acid site strength can vary significantly with respect to the Si/Al ratio and dealumination methods. Other researchers have also mentioned that the increase in Si/Al ratio corresponds to an increase in the number of aluminum atoms with zero next-nearest neighbors (0-NNN) and the strength of the acid sites increases [20].

The IR absorption spectra of the USY samples are shown in figure 1. The large peak at 1445 $cm^{-1}$ was due to ammonia adsorbed on Brønsted acid sites (asymmetric $NH_4^+$ bending) and decreased with increasing desorption temperature for all samples. Over USY-15 and USY-30 samples, this peak remained relatively large even after desorption at 440 °C. Over the USY-2.5 and USY-6 samples, while, this peak significantly decreased at this desorption temperature. This indicates that the strength of the Brønsted acid sites increased with increasing dealumination. In particular, after desorption at 540 °C, the peak at 1445 $cm^{-1}$ significantly disappears for the zeolite samples with larger number of acid sites. This is in a good agreement with STPD results.

### 3.2. Catalytic activity

The 2-butene conversion as a function of time on stream for USYs of different Si/Al ratios is presented in

Table 1
Physicochemical characteristics of USY zeolites samples

| Zeolite | Sample name | Si/Al ratio (Bulk) | BET area ($m^2$/g) | Crystallinity (%) |
|---|---|---|---|---|
| CBV-100 | USY-2.5 | 2.5 | 854 | 100 |
| CBV-712 | USY-6 | 6.0 | 779 | 83 |
| CBV-740 | USY-15 | 15.0 | 714 | 73 |
| CBV-760 | USY-30 | 30.0 | 705 | 72 |

Table 2
Acidic characteristics of zeolite samples

| Sample | # Acid Site ($NH_3$-STPD, mmol/g) | % Distribution of five peak areas ($NH_3$-STPD) | | | | |
|---|---|---|---|---|---|---|
| | | 180 °C | 250 °C | 350 °C | 440 °C | 540 °C |
| USY-2.5 | 2.21 | 10.4 | 35.4 | 38.7 | 11.1 | 4.4 |
| USY-6 | 0.99 | 10.5 | 28.5 | 39.7 | 12.9 | 8.4 |
| USY-15 | 0.79 | 6.5 | 20.7 | 42.5 | 16.4 | 13.9 |
| USY-30 | 0.40 | 6.2 | 19.8 | 41.9 | 17.5 | 14.6 |

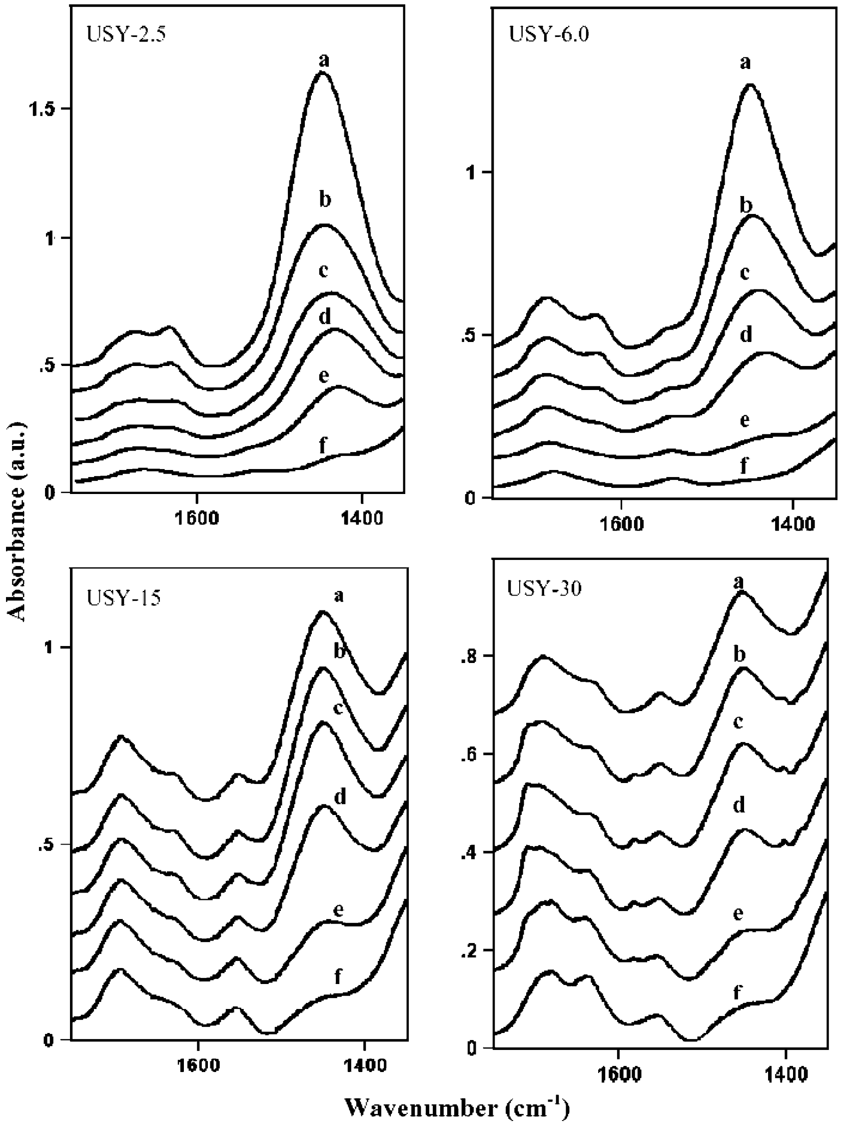

Figure 1. The FT-IR spectra of USY zeolites. Spectra were obtained after desorption at (a) 150, (b) 180, (c) 250, (d) 350, (e) 440, and (f) 540 °C.

figure 2. It has been known that the aluminum content of the zeolite was the key factor controlling its activity in alkylation of isobutane with butenes [2, 10, 11]. The large contents of aluminum were found to be necessary for improving the stability of the zeolites. In contrast to the results, it was observed that an existence of optimum USY zeolite with a certain Si/Al ratios in alkylation (see figure 2). The result could be attributed to two factors which are responsible for preventing deactivation of zeolites. The first factor is a hydrogen transfer activity related with the concentration of Brønsted acid sites. The zeolites with high hydrogen transfer reaction (HTR)

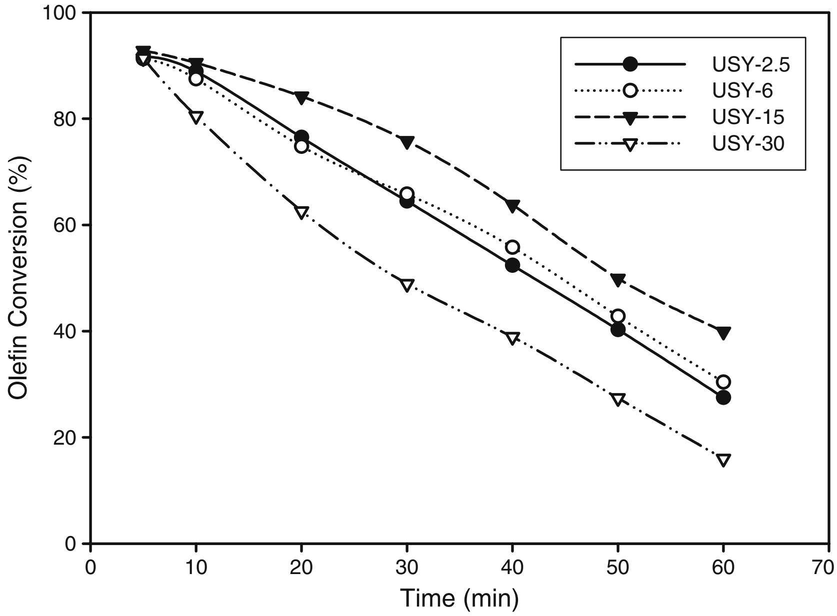

Figure 2. Olefin conversion for USY zeolites as function of time on stream. Reactions were performed at 80 °C and 300 psi ($WHSV_{olefin} = 0.5\ h^{-1}$, $i/o_{molar} = 20$).

capability from isobutane are very desirable because they favor the transformation of secondary carbenium ions to tertiary carbenium ions and the formation of primary products, trimethylpentanes (TMPs), from i-$C_8$ carbocations [1]. In addition, the zeolites with higher HTR allow the fast hydrogenation of the intermediate octyl-cations followed by their desorption. However, with the decrease in the hydrogen transfer activity, large alkyl cations by consecutive condensation reaction (e.g. oligormerization) are formed. These alkyl cations are related to the formation of bulky carbonaceous materials that deactivates zeolites. Hence, the hydrogen transfer reactions are required to complete the alkylation mechanism. The comparison of hydrogen transfer capabilities over these zeolites is shown in figure 3. The relative hydrogen transfer activity is defined by the ratio between the rate constant for zeolites and that for a reference sample; for this case, USY-2.5 is considered as reference. From the result, it was obviously seen that USY-30 deactivated rapidly due to its lower hydrogen transfer activity. However, USY-2.5 lost its activity quickly even though it possesses higher hydrogen transfer activity.

This behavior is mainly attributed to the other factor related with cracking activity occurred from strong Brønsted acid sites. Considering alkylation reaction

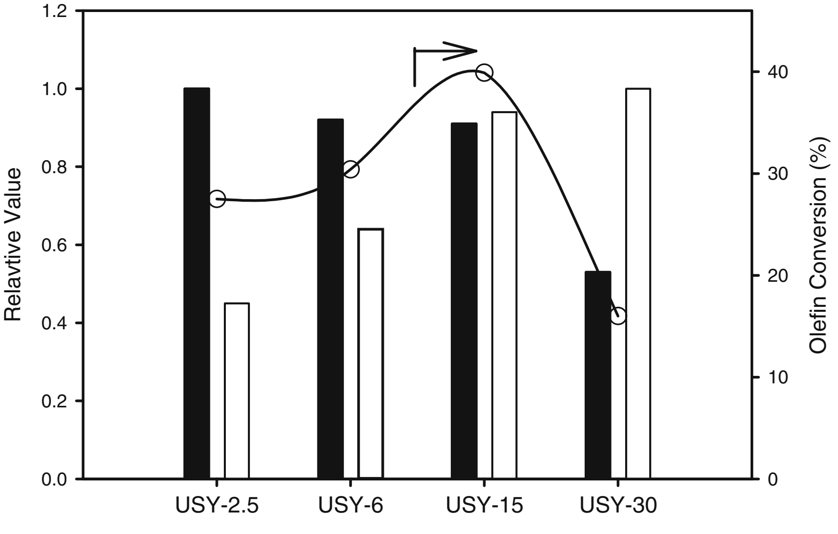

Figure 3. Relative hydrogen transfer activity (Black bar graph) and fraction of strong Brønsted acid sites (White bar graph), and olefin conversion (TOS = 60 min) of zeolites.

conditions, low temperature and liquid phase, minimizing the formation of the bulky materials is crucial to prolong the lifetime of zeolites catalyst. Based on the acidity characterization performed by STPD coupled with FT-IR, the concentration and relative strength of Brønsted and Lewis acid sites were determined. A strong correlation between the fraction of strong Brønsted acid sites (the ratio of number of strong Brønsted acid sites as measured above 450 °C to that of total Brønsted acid site) and catalytic activity was found except USY-30 sample as shown in figure 3. The relative fraction of strong Brønsted acid sites is defined by the ratio between the fraction of strong Brønsted acid sites of measured zeolite to that of reference sample; for this case, USY-30 is considered as reference. Indeed, the fraction of strong Brønsted acid sites over USY-2.5 was lower than USY-15 which is most active catalyst (see figure 3). The lower faction of strong Brønsted acid sites over USY-2.5 hardly prevented the formation of the bulky carbonaceous materials by oligomerization leading to the deactivation of zeolites by pore blocking. A similar trend can be found from the product distribution at the initial stage from the alkylation experiments as illustrated in table 3. The selectivity of cracking product (C5~C7) over USY-15 was relatively higher than other zeolites while that of oligomerization (olefins and heavy products) was less. The results can support well the fact discussed above.

Table 3

Initial products distribution over USY zeolites (time on stream = 5 - min). Reactions were performed at 80 °C and 300 psi ($WHSV_{olefin} = 0.5\ h^{-1}$)

| Sample | USY-2.5 | USY-6 | USY-15 | USY-30 |
|---|---|---|---|---|
| Olefin Conversion (%) | 91.5 | 91.6 | 92.4 | 90.8 |
| C5~C7 (wt%) | 40.3 | 41.2 | 45.6 | 30.4 |
| C8 (wt%) | 49.5 | 47.7 | 45.0 | 42.0 |
| $C9^+$ (wt%) | 10.2 | 11.1 | 9.4 | 27.6 |
| *C8 distribution* | | | | |
| TMPs (wt%) | 35.9 | 32.4 | 34.2 | 19.2 |
| 2,2,3-TMP | 3.1 | 2.4 | 2.4 | 0.7 |
| 2,2,4-TMP | 16.3 | 15.8 | 16.7 | 7.4 |
| 2,3,3-TMP | 7.6 | 6.7 | 6.4 | 4.3 |
| 2,3,4-TMP | 8.9 | 7.5 | 8.7 | 6.8 |
| DMHs (wt%) | 12.0 | 13.3 | 8.9 | 18.7 |
| 2,2-DMH | 0 | 0 | 0 | 0 |
| 2,3-DMH | 4.3 | 5.1 | 4.5 | 8.9 |
| 2,4-DMH | 3.4 | 3.9 | 2.8 | 4 |
| 2,5-DMH | 1.8 | 1.7 | 0.5 | 1.5 |
| 3,3-DMH | 0 | 0 | 0 | 0 |
| 3,4-DMH | 2.5 | 2.6 | 1.1 | 4.3 |
| C8 olefins (wt%) | 1.6 | 2.0 | 1.9 | 4.1 |

TPO experiments were performed to examine the combustion characteristics of the deposited coke inside pore. Two peaks are observed, which is a common pattern in these spectra (see figure 4). The first peak corresponds to coke burning below 300 °C, and the second peak occurred between 400 and 500 °C. It is well known that the second peak corresponds to coke that transformed from the original aliphatic materials to aromatic materials during TPO [21]. In all spectra of TPO, it can be observed that the height of second peak is higher than first peak and increased. The aliphatic materials deposited mainly inside the pore expansion of USY zeolite barely diffused out, and then became aromatics [21]. Especially, it was observed that the first peak of USY was relatively shifted to left-hand side. This means that relatively smaller carbonaceous materials were deposited in the

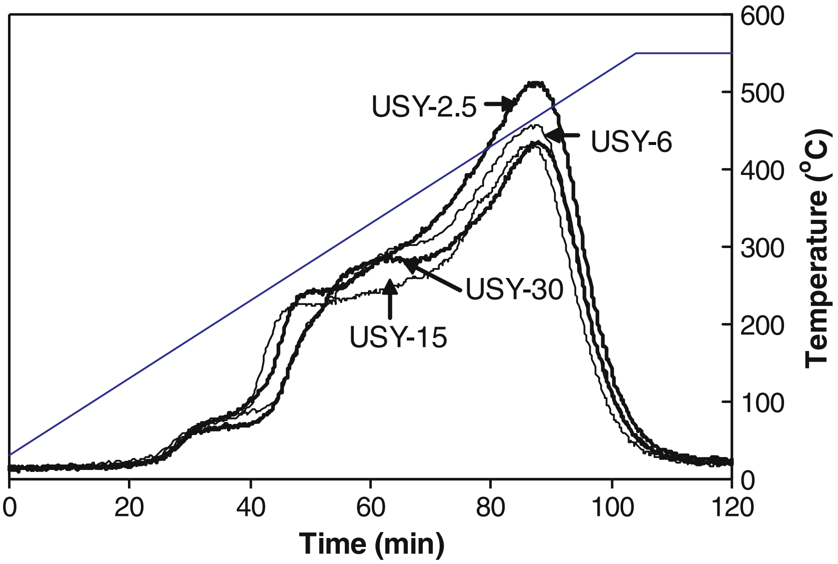

Figure 4. Temperature programmed oxidation of the carbonaceous materials deposited inside zeolites.

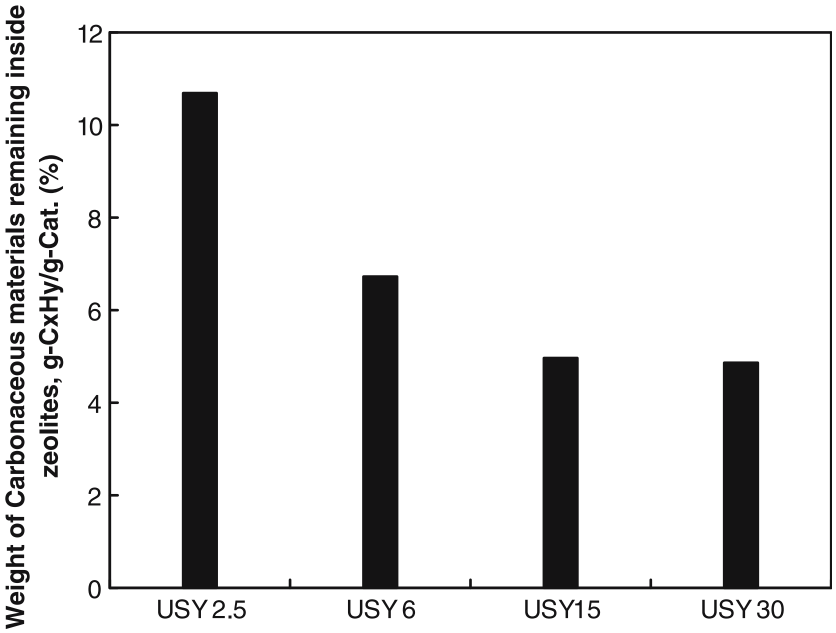

Figure 5. Weight percent of carbonaceous materials remaining inside zeolites after reaction.

zeolite pore. The result also well supports the reason that USY-15 showed the highest catalytic activity in this reaction. In the TGA analysis, it was observed that the amount of carbonaceous materials remaining inside the zeolites increased with the number of acid sites as illustrated in figure 5. It is well known that most carbonaceous materials formed inside zeolite pores are adsorbed on spent acid sites. However, one observed that the more time stable zeolites (USY-15) retained relatively less carbonaceous material during the alkylation reaction which is in agreement with earlier discussion.

The selectivities of the trimethylpentane isomers which are the desirable products of this reaction are presented as a function of time on stream (see figure 6). Since trimethylpentanes (TMPs) are the primary products from real alkylation of isobutane with 2-butane [1], the amount of TMPs can be taken as a measure of the alkylation activity of the zeolites. Indeed, the trend of TMPs distribution was comparable with that of

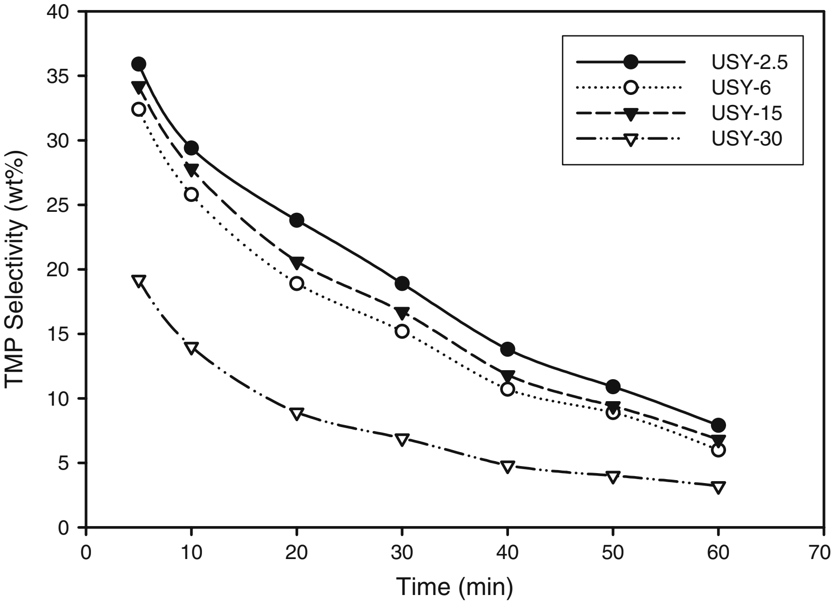

Figure 6. Selectivity of TMPs for USY zeolites as function of time on stream. Reactions were performed at 80 °C and 300 psi ($WHSV_{olefin} = 0.5\ h^{-1}$, $i/o_{molar} = 20$).

hydrogen transfer activity. This trend is directly related to the decrease in hydrogen transfer capability that results in the decrease of t-C4$^+$ surface species [22].

## 4. Conclusion

This study focused on the influence of acidic properties on the catalytic performance of ultrastable Y (USY) zeolites. The acidity of USY of variable Si/Al ratios has been characterized by $NH_3$-stepwise temperature programmed desorption (STPD) coupled with FT-IR. This technique allows us to quantify accurately the ammonia chemisorbed on acid sites of different strengths. The relative hydrogen transfer activity of zeolites was determined using the *n*-hexane cracking reaction. The hydrogen transfer activity slightly diminished with Si/Al ratios up to 15 and then significantly decreases with any increase in Si/Al ratio. In contrast to the common belief that a higher aluminum content zeolite is more active in alkylation reaction, we observed optimum Si/Al ratios of USY zeolites. This unexpected result can be attributed to the balanced level of acidity between the concentration and strength of Brønsted acid sites. Hence, the catalytic activity in alkylation of isobutane with 2-butene is strongly related to not only hydrogen transfer activity but also the fraction of strong Brønsted acid sites.

## References

[1] A. Corma and A. Martinez, Catal. Rev. Sci. Eng. 35 (1993) 483.
[2] J. Weitkamp and Y. Traa, in: *Handbook of Hetrogeneous Catalysis*, G. Ertl, H. Knozinger and J. Weitkamp (eds), Vol. 4 (VCH Verlagsgesellschaft mbH, Weinheim, 1997) p. 2039.
[3] A.W. Chester and Y.F. Chu, Zeolite 6 (1986) 195.
[4] A. Corma, A. Martinez and C. Martinez, Catal. Lett. 28 (1994) 187.
[5] M. Stocker, H. Mostad and T. Rorvik, Catal. Lett. 28 (1994) 203.
[6] F. Cardona, N.S. Gnep, M. Guisnet, G. Szabo and P. Nascimento, Appl. Catal. A: Gen. 128 (1995) 243.
[7] A. Corma, A. Martinez, P.A. Arroyo, J.L.F. Monteiro and E.F. Sousa-Aguiar, Appl. Catal. A: Gen. 142 (1996) 139.
[8] M. Stocker, H. Mostad, A. Karlsson, H. Junggreen and B. Hustad, Catal. Lett. 40 (1996) 51.
[9] D.E. Sherwood and R.J. Taylor, Appl. Catal. A: Gen. 155 (1997) 195.
[10] G.S. Nivarthy, Y. He, K. Seshan and J.A. Lercher, J. Catal. 176 (1998) 192.
[11] R. Loenders, P.A. Jacobs and J.A. Martens, J. Catal. 176 (1998) 545.
[12] F.A. Diaz-Mendoza, L. Pernett-Bolano and N. Cardona-Martinez, Thermochim. Acta. 312 (1998) 47.
[13] K. Yoo, E.C. Burckle and P.G. Smirniotis, Catal. Lett. 74 (2001) 85.
[14] K. Yoo and P.G. Smirniotis, Appl. Catal. A: Gen. 227 (2002) 171.
[15] K. Yoo, E.C. Burckle and P.G. Smirniotis, J. Catal. 211 (2002) 6.
[16] K. Yoo and P.G. Smirniotis, Appl. Catal. A: Gen. 246 (2003) 243.
[17] A. Feller, A. Guzman, I. Zuazo and J.A. Lercher, J. Catal. 224 (2004) 80.
[18] G.M. Robb, W. Zhang and P.G. Smirniotis, Micropor. Mesopor. Mat. 20 (1998) 307.
[19] W. Zhang, E.C. Burckle and P.G. Smirniotis, Micropor. Mesopor. Mat. 33 (1999) 173.
[20] J. Scherzer, Catal. Rev. Sci. Eng. 31(3) (1993) 215.
[21] C.A. Querini and E. Roa, Appl. Catal. A: Gen., 163 (1997) 199.
[22] A. Corma, A. Martinez and C. Martinez, J. Catal. 146 (1994) 185.