Enhancement of Catalytic Cracking Activity of Steam Treated HZSM-5 Zeolite by Acid-leaching

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In this investigation HZSM-5 samples having silica/alumina (Si/Al₂) ratios of 32, 40 and 45, respectively, have been steam treated under severe conditions, and followed by acid-leaching with HCl solution. The samples thus obtained have been characterized by X-ray diffraction and X-ray photo-electron spectroscopy, as well as by cracking of hexadecane and adsorption of hexane. The results show that the steam treatment causes the HZSM-5 samples to become dealuminated. The lower the Si/Al₂ ratios of the initial HZSM-5 samples, the greater the dealumination, causing cracking activities of the HZSM-5 samples to decrease. Cracking activity of the HZSM-5 with the lower Si/Al₂ ratio was lower than that having higher Si/Al₂ ratio, after the steam treatment. The acid-leaching treatment can enhance activity of the steam treated HZSM-5. Removal of extra framework aluminum in the zeolite, formed by steam treatment, might be one of factors leading to enhancement of the activity of the steam treated samples by acid-leaching.

1. Introduction

In cases of refining of residual oils, the FCC (fluid catalytic cracking) catalyst has to be discharged from the devices, from time to time, to control preferable activity levels and selectivities in conditions of metal deposition, etc. Some available methods for demetallizing the FCC catalyst are highly complicated¹)-⁴).

A preliminary investigation, which was conducted in this laboratory, shows that if the contents of nickel and iron are high and that of vanadium is low in the residual oil (as that from China’s crude oil), the demetallization procedure may be greatly simplified⁵). Acid treatment, for example, can not only substantially reduce the content of nickel and iron deposited on the FCC catalyst (composed of ultra-stable Y zeolite and silica-alumina matrix), thus depressing its dehydrogenation effect, but also can restore, noticeably, its cracking activity.

If the acid treatment could be applied commercially for the reactivation of spent FCC catalyst blended with additive-catalyst, the information concerning the effect of the acid treatment on the cracking of hydrocarbon fractions over steam treated ZSM-5 zeolite is also helpful, because ZSM-5 zeolite is used as an active component of the additive-catalyst to boost octane number of gasoline with its effectiveness to selectively crack straight chain hydrocarbon fractions of low octane numbers. In addition, ZSM-5 zeolite is subjected to severe dealumination in an environment of high temperature and presence of steam in the devices.

2. Experimental

The HZSM-5 was obtained by treating NaZSM-5, having crystallinity of ≥90% (from Dept. of Chem., Nankai Univ., synthesized without template), with HCl solution (0.1 mol/dm³), three times, followed by washing and drying.

The Si/Al₂ ratios, bulk and surface, of the samples were measured by the method described in section 6.

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Assessment of the cracking activity and the analyses of the product were conducted in accordance with the methods presented in section 7.

The reactant is normal hexadecane (n-C₁₆); cracking temperature, 653 K; catalyst/reactant ratio, 3.3 mg/µl; and catalyst amount for each run, 20 mg. The activity is expressed in terms of conversion of n-C₁₆. The activity referred to in this investigation is always that of the initial one. Prior to the assessment, the sample was activated at 773 K for 10 h, in order to obtain reproducible data.

The acid-leaching was completed by refluxing the steam treated HZSM-5 with HCl solution (0.1 mol/dm³) several times, for 1.5 h each, and...
then filtered and washed with decationized water until Cl−-free, and finally dried and tableted, for assessment of cracking reactivity.

The samples were designated HZSM-5(N), HZSM-5(N)S and HZSM-5(N)SLn, respectively. The letter N refers to Si/Al2 ratio of the initial HZSM-5, the subscript S, the steam treated sample; SL, the steamed sample, subjected to acid-leaching; n, the times of the acid-leaching conducted.

3. Results and Discussion

3.1 X-Ray Diffraction and Silica/Alumina Ratio

X-Ray diffraction patterns of HZSM-5(32) and HZSM-5(32)s are illustrated in Fig. 1. The bulk and the surface Si/Al2 ratios of the samples are listed in Table 1. These results strongly suggest dealumination of HZSM-5 by the steam treatment.

From Fig. 1, it is seen that after the steam treatment the two peaks at 2θ of 24.3° and 29.0°, respectively, are split into two components, showing transformation of the crystalline structure, from orthorhombic to monoclinic. The transformation is associated with an increased Si/Al2 ratio of the framework caused by the dealumination of the zeolite framework. The same distinction between the patterns of the initial and the steam treated samples is also observed on the samples of the two other Si/Al2 ratios.

The surface Si/Al2 ratio of the steam treated HZSM-5 is lower than that of the initial one. Some of the Al extracted from the framework during the steam treatment seems to migrate to the zeolite surface, producing aluminum surface rich zeolites. Accordingly, the surface Si/Al2 ratio of HZSM-5 drops after the steam treatment.

From Table 1, it is also seen that the Si/Al2 ratios of the final HZSM-5 (steamed and subsequently acid-leached) are close to each other, regardless of the magnitude of ratios of the initial HZSM-5. This implies that the lower the Si/Al2 ratios of the initial HZSM-5, the greater they are dealuminated. The greater dealumination of the initial HZSM-5 with lower Si/Al2 ratio may be attributed to its higher framework aluminum concentration, from the point of view of kinetics. This result was obtained by Sano, Suzuki and co-workers in 1987.

3.2 Catalytic Cracking of n-C16

The performance data of the samples in cracking are given in Table 2. It is shown in this table that steam treatment causes the cracking activity to drop. Two factors are known to be the causes for this phenomena. One is the loss of acidity of the HZSM-5 attributed to the dealumination; the other, the diffusional limitation affected by the extra framework aluminum (EFAL). In this way, the drop of the activity is still related to the dealumination of HZSM-5.

Table 2 also serves to illustrate that although the...
initial HZSM-5 with the low Si/Al2 ratio exhibits high cracking activity, after the steam treatment, its activity is lower than any of the other ones having higher Si/Al2 ratios, instead. This may be related to the fact that the lower the Si/Al2 ratio of the zeolite, the greater they are dealuminated. As mentioned above, dealumination of the zeolites causes loss of acidity, affecting activity of the zeolite. On the other hand, the EFAL sets the diffusional limitations to the reactants. Either of these two factors, therefore, leads to the drop of the cracking activity.

When a refinery is to consider the optimum Si/Al2 ratio of HZSM-5 to be used, the foregoing results may become valuable. The use of HZSM-5 having high Si/Al2 ratio seems to be preferable.

3.3 Acid-leaching

After the acid-leaching, one of the changes in the properties of the samples is featured by the increase of the Si/Al2 ratio, whether it be the surface or bulk (Table 1). This means that the acid-leaching removes some aluminum species in the steam treated zeolite. Since acid-leaching does not attack zeolitic framework, the removed aluminum would be the EFAL.

The second change is partial restoration of activity (Table 2). After triple acid-leaching, the cracking activity of steam treated HZSM-5 zeolite can be enhanced by 75—80% that of the initial HZSM-5 zeolite. The enhancement of the activity is related to the Si/Al2 ratio of the initial HZSM-5 zeolite: that is the lower the Si/Al2 ratio of the initial HZSM-5 zeolite, the greater the enhancement. This change may also be attributed to the removal of the EFAL. The explanation for this is given next.

3.4 Adsorption of Hexane

The steam treatment causes the adsorption amount of n-C6 on the HZSM-5 to diminish, whereas the acid-leaching serves to raise it again (Table 3). Moreover, there is parallelism between the changes of adsorption amount and cracking activity as a function of the acid-leaching time (Table 4).

These two facts, along with the two aforementioned, may imply that a part of EFAL, when migrating to the outer surface, is deposited near the entrance of the channels of the zeolite, thereby blocking or closing the pores of the zeolite, and yet another part may remain inside the channels. These would lead to limiting of the diffusion and to decrease of the adsorption amount. Since some active sites become inaccessible, the activity drops, too.

But the decreased activity observed after the steam treatment may come partially from clogging or closing of the pores of the zeolite by EFAL and partially from the loss of acidity. In other words, the real activity of the steam treated HZSM-5 zeolite should be higher than what it exhibits, considering aluminum concentration in its framework.

By multiple acid treatments, such EFAL is leached off gradually. Hence, the adsorption amount and the activity also increase gradually. Each time the steam treated HZSM-5 zeolite is acid-leached, the adsorption amount and the cracking activity are raised to some extent (Table 4). The increments of the adsorption amount and the cracking activity, however, diminish progressively. This implies that the enhancement of the activity, as well as the adsorption amount, of the steam treated HZSM-5 by acid-leaching is limited. Such limitation seems to signify the completion of removal of EFAL by acid-leaching.

4. Conclusion

Under severe hydrothermal conditions, the dealumination occurs in HZSM-5 having Si/Al2 ratios of 32, 40 and 45. Further, the lower the Si/Al2 ratios of the HZSM-5, the greater they dealuminated. The dealumination causes cracking activity of the HZSM-5 to drop. The rate of change of the cracking activity of the HZSM-5 is related with the Si/Al2 ratio of the initial HZSM-5. The lower the Si/Al2 ratio of the initial HZSM-5, the greater the drop of the cracking activity.

The acid-leaching can enhance the cracking activity of the steam treated HZSM-5. This phenomenon might be attributed to the removal of the
extra framework aluminum retarding the access of the reactants to the active sites.

References

Keywords
ZSM-5, Cracking, Acid leaching, Steam treatment, Dealumination