

Chemical Oscillation in ZSM-5 dealumination

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Introduction

ZSM-5 is widely used as excellent selective catalyst in novel material synthesis and the petrochemical industry. However, its active lifetime and applications are limited due to structure dealumination when used at high temperatures, particularly in gaseous atmospheres or steam which leads to decreased activity and selectivity [1-3]. Some work has been reported to date on the theoretical basis of the dealumination process and its dependence on process conditions. The conditions controlling dealumination have been identified via mathematical model and calculations made of the degree of dealumination under specific representative conditions[4-7]. Little work has been reported the relation of dealumination process with the changing of surface alumination concentration, still little work has been reported the relation of surface alumination concentration with actual reaction performance. In the present paper, we have found that the changing of ZSM-5's surface alumination concentration abide by chemical oscillation under high temperatures or steam atmospheres. Correspondingly, the conversion and yield of chemical reaction all changing abide by chemical oscillation. Our aim is to improve understanding of the dealumination process and the rule of changing in chemical reaction.

Materials and Methods

The zeolite HZSM-5(Si/Al=10) was used after pressing and cracking. Hydrothermal treatment of samples were performed at 923K with WHSV 1h⁻¹ flowing steam in fixed bed. The naphtha cracking reaction was used to test the HZSM-5 sample at 923k with WHSV 1h⁻¹ flowing steam and the weight ratio of oil/H₂O as 1:1 in fixed bed. The catalyst hydrothermal treated was characterized by XPS. The reaction production was analyzed by HP-6890 gas chromatograph(GC) with a capillary column of HP-Al₂O₃/KCl and a FID detector, the product yield was calculated by the normalization of GC analysis results.

Results and Discussion

The XPS data of the hydrothermal treatment catalysts were given in Fig.1, from which we knew the catalysts surface aluminium concentration was high at first. As the treatment time increased, it decreased rapidly before the first inflexion. Then, the surface aluminium concentration increased and got the highest value when treated for 4 hours, and then decreased gradually as time going on. During the whole course, the surface dealumination concentration changed according to a special rule with different hydrothermal treatment time. Thus chemical oscillation was formed.

Naphtha catalytic cracking with the same sample was carried out under homologous flow steam conditions. The detail of light olefin yield with the steam function time was shown in Fig.2. As the reaction time increasing, the yield change of light olefins abides by a certain rule, which was identical to that of XPS test. Comparing the two figures, we knew that the yield of

light olefins was positive correlative with the surface aluminium concentration. The latter higher, the former higher, and vice versa.

Through IR spectrum, NH₃-TPD, Al-NMR et.al. characterization and the yield change test of light olefin without steam, we concluded that the chemical oscillation of yield and conversion were caused by the chemical oscillation of surface aluminium concentration of catalyst.

Significance

This work proves that the surface aluminium concentration of catalyst changes under high temperature or steam atmosphere, which causes the changes of yield and conversion of chemical reactions. They are all special chemical oscillations.

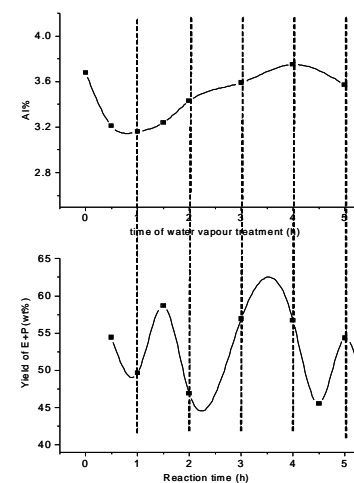


Figure 1. XPS data of catalyst for different time of hydrothermal treatment.

Figure 2. The yield of ethylene and propylene for different reaction time.

References

1. G. J. Hutchings, A. Burrows and C. Rhodes, J. Chem. Soc. Farad. Trans. 3593, 93(1997).
2. Y. N. Wang, X. W. Guo and C. Zhang, Catal. Lett. 209, 107(2006).
3. J. C. Groen and L. A. A. Peffer, Micropor. Mesopor. Mater. 1, 60(2003).
4. G.W.Ma, J.W.Teng and Z.K. Xie, Mater. Sci.& Techn. 10, 24(2008).
5. S. Sen, R. R. Wusirika and R. E. Youngman: Micropor. Mesopor. Mater. 217, 87(2006).
6. D. G. Wei, J. L. Zhou and B. J. Zhang: J. Molec. Catal. (Chin) 445, 10(1997).
7. W. Reschetilowski, W.-D. Einicke and M. Jusek: Appl. Catal. 15, 56(1989).