

Effect of Element Modifications on Catalytic Performance of Zeolites

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Abstract— Various modification methods have been applied to enhance the shape selectivity of HZSM-5 zeolites. In general, the modifications aim at suppressing secondary reactions occurring on the external surface and/or at hindering the diffusion of undesired products out of the pores of the zeolites. In this paper we decide to review the most important elements and investigate the effect of these modifications on catalytic performance and acidity of zeolite catalysts, especially HZSM-5, that has been done until now. Generally, these groups of elements include rare earth elements, transition metals, alkali earth metals. After further comparison of the results, we can conclude that rare earth elements, especially Ce, are one of the most important group, in periodic table, among the others, for enhancing the catalytic performance and selectivity of HZSM-5. They not only increase the olefin yield, but also suppress the aromatic formation.

Index Terms— Modifications, Catalytic Performance, Acidity, HZSM-5

1. INTRODUCTION

Light olefins and diolefins such as ethylene, propylene, butenes and butadiens are considered the backbone of the petrochemical industry. The most prevalent technologies for producing these precursors are Steam Cracking and recently Fluid Catalytic Cracking Using ZSM-5 zeolite containing catalysts [10]. The market demand for ethylene and propylene in the year 2000 was 89 and 51 million metric tons, respectively. It is expected that the demand for ethylene and propylene by the year 2010 will increase to about 140 and 90 million Mt, respectively [11]. However, with the current olefin technologies, it is becoming increasingly difficult and costly to satisfy the market demands and meet the stringent environmental regulations [1]. Thus, it is imperative that we develop a new alternative to improve the production of light olefins. Thermo-Catalytic Cracking has been recognized as a promising alternative route for light olefins production and has been extensively studied since 1998, although it is important to synthesize a catalyst which has high selectivity and stability for industrial application. Japan carried out a national project named “catalytic cracking of naphtha” and developed MFI zeolite catalysts modified by lanthanum oxide and phosphorus; however, its commercial application was not reported [2].

Thus far, many modification methods have been applied to

enhance the shape selectivity of HZSM-5 zeolites [13-19]. The modifications mainly focus on suppressing secondary reactions occurring on the external surface and/or hindering the diffusion of undesired products coming out of the pores of zeolites. Thus, the deactivation of the acid sites on the external surface (blocking active sites for secondary reactions) and/or the narrowing of the pore openings of HZSM-5 (enlarging difficulties in the diffusivities of isomers) will improve the shape selectivity of HZSM-5 zeolites. Post-synthesis modification by chemical vapor deposition (CVD) of silicon alkoxides, such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS), is one of the most effective methods to enhance the shape selectivity of HZSM-5 zeolites [12]. Another group of modifications include catalysts modified with rare earth elements, transition metals, and alkali earth metals.

2. RARE EARTH ELEMENTS

Rare earth (RE) elements are very important components of the commercial catalysts for the process of catalytic cracking of hydrocarbons (FCC). RE cations such as La^{3+} and Ce^{3+} occupy different sites in the zeolite faujasite even in hydrated and dehydrated forms. Although there have been some studies concerning the RE element modification on the catalytic performances of ZSM-5 for the cracking of hydrocarbon, there have been few reports on the HZSM-5 ones, for the cracking of light hydrocarbons (C_3 and C_4 hydrocarbon) [4,5]. Moreover, the nature of RE modification on the catalytic performances for the cracking of hydrocarbon is still under discussion. On one hand, some researchers think that the addition of RE elements modified the acidity of the HZSM-5 sample, thus affecting its catalytic performance for the cracking of hydrocarbon [6, 4]. On the other hand, it is generally accepted that the introduction of RE elements modifies the basicity of ZSM-5 zeolite, as RE oxides usually possess some basic characters. Wakui et al. [16] have investigated the effect La, Ce, Pr, and Sm on the catalytic behavior of HZSM-5 zeolite for n-butane cracking by NH_3 -TPD and CO_2 -TPD, and have found that basic sites have been newly generated on the catalyst surface by rare earth loading, although the acid character of the catalyst is almost not affected by the modification.

Recently, Xiaoning et al. investigated the effect of a series of RE/HZSM-5 catalyst, containing 7.54% RE (La, Ce, Pr, Nd, Sm, Eu or Gd) on acidity and catalytic performance, for catalytic cracking of n-butane [3]. The results (figure 1) show that the total alkene yield was increased, especially the propene yield, which increased by about 10% more than the unmodified HZSM-5. The optimal propene yield at 600°C reached 25.9%, 25.2%, and 25.2% over Nd/HZSM-5,

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Ce/HZSM-5, and La/HZSM-5, respectively.

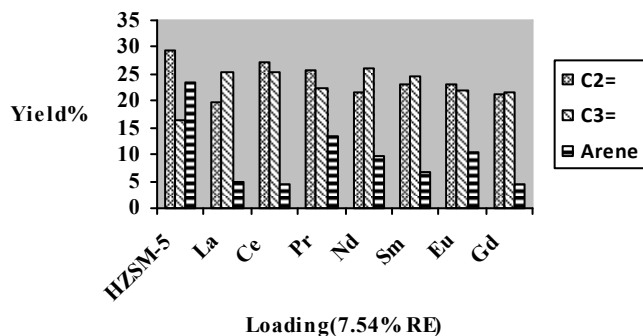


Fig.1- Effect of rare earth elements on catalytic performance for catalytic Cracking of n-butane at 600°C

In addition, it was obvious that the yield of aromatics over rare earth modified catalysts was greatly decreased. Therefore, the modification of rare earth metal on HZSM-5 was favorable for the formation of propene and suppression of aromatics. Although the effect of RE-Loading on generating the new basic sites is apparently the major cause of the lower aromatics formation and it is not due to increased acidity.

Figure 2 shows the acid amount of RE/HZSM-5 in detail after NH₃-TPD [3]. Except for the Gd modified HZSM-5 sample, the total number of acid sites of RE-modified samples is greater than that of the HZSM-5 sample, as shown in figure 2. Moreover, the ratio of L/B of RE-modified HZSM-5 samples is bigger than that of HZSM-5 (figure 3). At the same time, both the total yield and total selectivity to olefins are much higher than that of the unmodified HZSM-5 sample. These results indicate that the promoting effect of light rare earth metal on the catalytic performances for the catalytic cracking of butane is closely related to the modification of rare earth metal on the acidity of HZSM-5. In other words, the acidic properties of RE-HZSM-5 samples play an important role in the catalytic cracking of butane. And the suitable ratio of L/B is favorable for obtaining high yields of olefins.

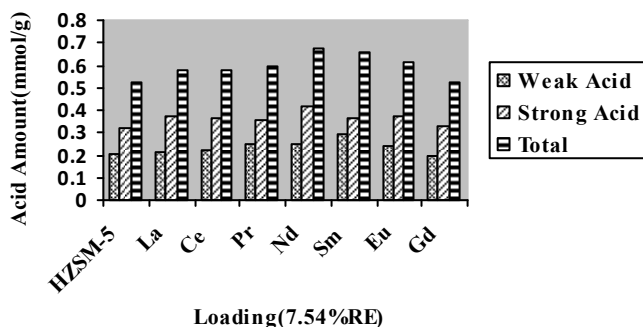


Fig.2- Effect of RE on acidity of HZSM-5

It could be found on the Gd/HZSM-5 catalyst, that there was no significant change of acid amount when compared with the parent HZSM-5, only with weak acid strength increasing and strong acid strength lessening. It is probably because of the specific electron configuration structure of Gd³⁺. In the series of light rare earth cations (RE³⁺), the electron configuration structure is in a half-occupied state, and no empty f orbit in the Gd³⁺ cation. However, there are empty f orbitals in the other light rare earth metal cations (RE³⁺). Therefore, the empty f orbit is important for the modification of the acidity of the HZSM-5 zeolite. The empty f orbitals can at least provide some positions for the formation

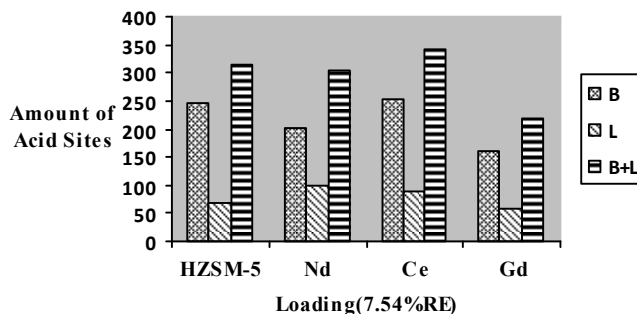


Fig.3- Effect of RE on Bronsted and Lewis acidic sites (μmol.gr⁻¹).

of Lewis acidic sites.

The best propylene yield poses to Nd/HZSM-5 (Fig. 1). For Nd/HZSM-5, the amount and strength of weak acid and strong acid greatly increased, especially for its strong acidity. For Ce/HZSM-5, it showed medium acid amount and strength, but it exhibited the highest ethene yield and optimal yield of total olefins. For La/HZSM-5, the amount of acidity does not change enormously but its ethylene and propylene yield is medium. It indicates that suitable amount of acid sites is favorable for catalytic cracking. Also La-loading generated basic sites on the surface. The readsorption of the cracking products, such basic compounds as ethylene, propylene, and butanes, are probably suppressed as the surface basicity of the catalyst increases, and this is apparently the major cause of the lower aromatics formation[2].

3. TRANSITION METALS

This group is placed in the middle of the periodic table and contains metals such as Cu, Zn, Mg. Wakui et al. investigated Co/HZSM-5 catalyst for dehydrogenative cracking reaction of n-butane at low conversions (<20%)[7]. The results of their investigation are shown in figures 4, 5. With Co/HZSM-5 catalyst, the selectivity of butane was enhanced, which is considered to be due to the dehydrogenation activity of cobalt in the catalyst. A higher selectivity of ethylene was obtained using 5%Co/HZSM-5 as the catalyst.

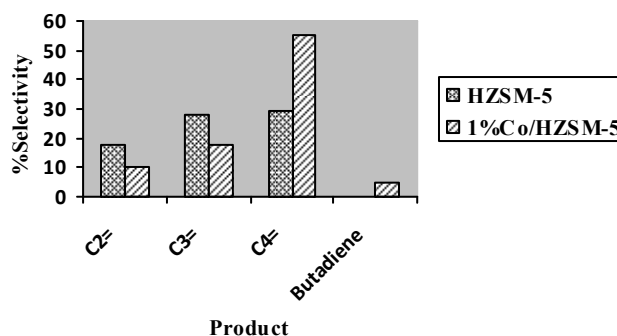


Fig.4- Effect of 1%Co on selectivity of butane

Jiangyin et al. investigated the effect of different amount of Cr loading (0-0.231mmol/g) on catalytic performance over HZSM-5 for the cracking of isobutene (figure 6) [8]. These results demonstrate that a small amount of Cr (0.004-0.038mmol/g) played an important role of modification, not only did it enhance the reactivity for the catalytic cracking of isobutane, but also increased the selectivity of olefins, especially the selectivities to ethylene. One reason is that a trace amount of Cr alters the acidity of the HZSM-5 catalysts. The suitable strength and amounts of

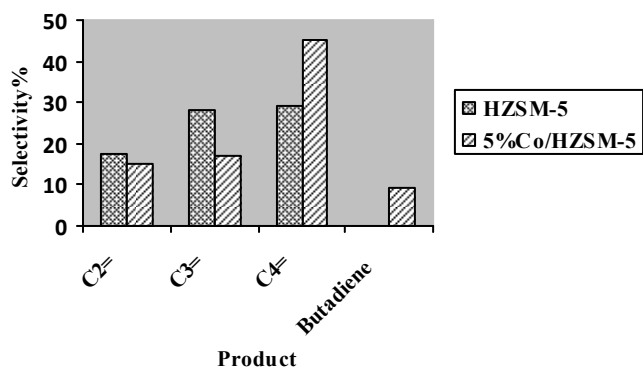


Fig.5- Effect of 5%Co on selectivity of butane

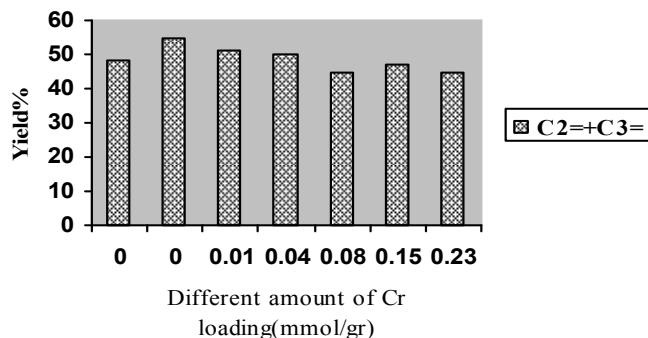


Fig.6- Effect of different amount of Cr loading on catalytic performance for catalytic cracking of isobutane

acidity of the catalysts are favorable for obtaining high selectivity to the light olefins in the catalytic cracking of isobutene. Another reason is that the presence of a little amount of Cr may be favorable for the dehydrogenation of isobutane to isobutene which are easier than isobutane to be cracked to light olefins.

Anunziata et al. studied HZSM-11 zeolite modified with zinc by ion exchange [9]. Zn tended to distribute itself uniformly in zeolite channels interacting with Bronsted acidic sites and produced new and stronger Lewis sites. In zinc loaded zeolites only Lewis acidic sites with high strength were obtained when the zinc content increased. Bronsted acidic sites were weak or medium strength. The reason is that zinc ions introduced in ZSM-11 zeolite by ammonium exchange decreased the concentration of the strongest Bronsted acidic sites [10] by blocking negatively charged tetrahedral AlO₄ groups.

4. ALKALI EARTH METALS

This group includes metals such as, Be, Mg, Ca, etc. Wakui et al. investigated the effect of Mg loading on catalytic performance in dehydrogenative cracking of n-butane over HZSM-5 [7]. With the use of Mg-ZSM-5, the ethylene selectivity was much larger than ethane (figure 7), suggesting that a different cracking mechanism is involved in the reaction using Mg-ZSM-5.

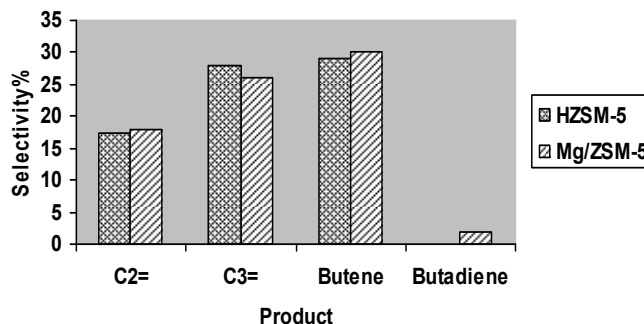


Fig.7- Effect of Mg loading on selectivity of n-butane

5. CONCLUSION

The ZSM-5 zeolite (SiO₂/Al₂O₃=200) catalyst modified by transition metals, such as Cu, Zn, and Ag, increased the aromatics yield and decreased the ethylene-plus-propylene yield due to the accelerated cyclodehydrogenation reaction. After the ZSM-5 zeolite was modified with alkali earth metals, the conversion of n-butane and consequently the olefin yield declined, although the formation of aromatics was suppressed. In contrast, ZSM-5 zeolites modified with rare earth elements showed high olefin yields as a consequence of the suppression of aromatic formation without any decrease in n-butane conversion. If propylene yield is favorable, the modifications which increase the amount and strength of weak acid and strong acid, especially for its strong acidity, is the best and for having high olefin yield the medium amount of acidic sites is favorable.

REFERENCES

- [1] Canada. Environmental Canada. Canada's Greenhouse Inventory report, <http://www.ec.gc.ca>
- [2] Y. Yoshimura, N. Kijima, T. Hayakawa, K. Murata, K. Suzuki, F. Mizukami, K. Matano, T. Konishi, Catalysis Surveys from Japan, Vol. 4, No. 2, 2000
- [3] Wang Xiaoning, Zhao, Zhen, Xu Chunming, Duan Aijun, Zhang Li, Jiang Guiyuan, J. Rare Earths, 25 (2007) 321-328
- [4] Aolewuyi Y G, Klocke D J, Buchanan J S. Effect of high-level additions of ZSM-5 to a fluid catalytic cracking (FCC) RE-USY catalyst J. Appl Catal A, 1995, 131: 121
- [5] Li B, Li S J, Li N. Structure and acidity of REHY zeolite in FCC catalyst J. Chi. J. Catal., 2005, 26: 301.
- [6] Argauer R J, Landolt G R. Crystalline zeolite ZSM-5 and method of preparing the same [PI. US Patent 3, 702886, 1972.
- [7] K. Wakui, K. Satoh, G. Sawada, K. Shiozawa, K. Matano, K. Suzuki, T. Hayakawa, Y. Yoshimura, K. Murata, F. Mizukami, Catalysis Letters, Vol. 81, No. 1-2, 2002
- [8] Jiangyin Lu, Zhen Zhao, Chunming XU, Aijun Duan, Pu Zhang, Catalysis Letters, Vol. 109, No. 1-2, 2006
- [9] Oscar A. Anunziata, Liliana B. Pierella, Catalysis Letters 19 (1993) 143-151
- [10] Nabil Al-Yassir (2007). Multifunctional Catalysts used in the Thermo-Catalytic Cracking of Hydrocarbon Feedstocks for the Production of Light Olefins, Concordia University, Montreal, Canada.
- [11] J. Mark Houdek, J. Andersen, Presented at the ARTC 8th Annual Meeting, UOP LLC, Kuala Lumpur, 2005
- [12] Shourong Zheng, Hilton R. Heydenrych, Andreas Jentys, A. Lercher, J. Phys. Chem. B 2002, 106, 9552-9558
- [13] Kaeding, W. W.; Chu, C.; Young, L. B.; Weinstein, B.; Butter, S. A. J. Catal. 1981, 67, 159.
- [14] Hibino, T.; Niwa, M.; Murakami, Y. J. Catal. 1991, 128, 551.
- [15] Ku'rschner, U.; Jerschke, H. G.; Schreier, E.; Vo'ltter, Appl. Catal. 1990, 57, 167.
- [16] Wang, I.; Ay, C. L.; Lee, B. J.; Chen, M. H. Appl. Catal. 1989, 54, 257.
- [17] Kaeding, W. W.; Chu, C.; Young, L. B.; Butter, S. A. J. Catal. 1981, 69, 392.
- [18] Tynjala, P.; Pakkanen, T. T. J. Mol. Catal. A 1997, 122, 159.
- [19] Fang, L. Y.; Liu, S. B.; Wang, I. J. Catal. 1999, 185, 33.