CATALYTIC PYROLYSIS OF N-HEXANE FOR ETHYLENE PRODUCTION OVER MORDENITE ZEOLITES MODIFIED BY METAL OXIDES

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Introduction

Thermal cracking (pyrolysis, or so-called steam cracking) of various hydrocarbons at high temperature (1073-1123 K) for the production of lower C_2-C_4 olefins has been one of the core processes in the petrochemical industry. Besides the large amount of energy consumed in this pyrolysis process, another disadvantage is the difficulty for this process to control the olefins formed, especially the lower yield to ethylene. Therefore, pyrolysis of hydrocarbons in the presence of catalysts[1-6], allowing preparation of lower olefins at lower temperature and with higher selectivity, is a subject of some studies.

The search for catalysts that promote hydrocarbon cracking started in the late 1960s. Till now, the catalysts found active to different extent can be typically classified into three types, *i.e.*, acidic catalysts (amorphous silica-alumina or zeolite crystalline), basic catalysts (such as CaO-SrO-Al_2O_3, KVO_3/corundum etc.) and transition metal oxide catalysts (*e.g.*, Cr_2O_3/Al_2O_3), which are used under the non-aerobic or aerobic conditions[3]. Three catalytic pyrolysis processes, namely Vniios process in Russia (using KVO_3/corundum catalyst), Asahi process in Japan and the deep catalytic cracking (DCC) process in China (both using ZSM-5 zeolite modified with Al and Cr), have been developed[6]. However, they are still far from replacing the conventional pyrolysis technique, and it is therefore worthy exploring approaches to finding highly efficient catalyst system for preparing C_2-C_4 olefins.

In this work, we studied the acid-base and catalytic properties of a series of Mordenite zeolites for the pyrolysis of n-hexane, and modified the least acidic Na^+ type Mordenite by supporting basic metal (such as alkali, alkaline earth) and reductive transition metal oxides. The reaction mechanisms for different catalysts have been discussed.

Experimental

Sample Preparation. Sodium-type Mordinite zeolite (NaM, the unit cell composition: $Na_{6.23}H_{0.02}Al_{6.25}Si_{41.75}O_{96}$) was purchased from HongGuang Molecular Sieve Co., Dalian, China. Three NaHM zeolite samples with different H^+ content were produced by ammonium ion exchange of NaM zeolite at 353 K for different times, each time for one hour, followed by calcinations at 773 K for 5 hours. Proper amount of alkali (Li, K, Cs), alkaline earth (Mg, Ca, Sr), and transition metals (Cu, Mo, Mn, Ag, etc.) oxides were introduced into NaM zeolite by impregantion of the respective metal nitrate solutions at 353 K, followed by calcinations at 973 K for several hours.

Characterization. The acidic and basic properties of Mordenite zeolites with or without metal modification were analyzed using NH_3-TPD and CO_2-TPD, respectively. Before the TPD experiments, all samples had been treated at 773K in N_2 for several hours. The adsorption of NH_3 or CO_2 was saturated at room temperature, followed by purging with N_2 at 333 K for at least one hour. TPD was then carried out at a heating rate of 12 K/min. The reduction of transition metal oxides was characterized by conventional TPR. All temperature-programmed studies were carried out using a TCD detector, and the TPD or TPR peak signals were recorded and calculated quantitatively.

Catalysis. Catalytic pyrolysis of n-hexane was performed in a continuous flow micro-reactor. N-hexane flew continuously through the catalyst together with steam, with the steam/hydrocarbon weight ratio to be 0.9 and the space velocity (WHSV) to be 3.6 h^{-1}. The reactor temperature was 808K for bare zeolite catalysts and 890K for metal oxide modified NaM catalysts. The reaction products after TOS of 1 h were analyzed by on-line gas chromatography with a TCD detector and Porapak Q column. Results were reported as conversions calculated as the weight percent of n-hexane reacted, molecular selectivity and yields, especially to ethylene.

Results and Discussion

The curves of ammonia thermal desorption for NaM and three NaHM zeolites (figures not shown) exhibit mainly two peaks: low-temperature peak with T_{max} at 497 K, typically representative of weak Lewis acid centers or cationic sites, and high-temperature peak with T_{max} at 813 K, corresponding to strong Brönsted acid centers. It is found that, the higher temperature peak increases with the proton content in the NaHM zeolites, while the same peak can hardly be found in the case of NaM zeolite. **Figure 1** shows the catalytic pyrolysis results over the zeolites as a function of acidic amount, which was calculated from the amount of the NH_3-TPD peak at higher temperature. There is a clear trend that, with the increase of zeolite acidity, the activity increases while both the selectivity of ethylene and the ratio of $(C_1+C_2)/C_3$ decrease. This is due to the well-known cracking reaction on acidic catalysts, possibly via carbenium ion mechanism: the strong Brönsted acidic sites of NaHM zeolites protonate n-hexane to form carbenium ions, followed by β-scission to form smaller molecules. According to this mechanism, C_3 hydrocarbon and alkane would be the predominant cracking products rather than ethylene. Meanwhile, secondary undesirable reaction such as aromatization might occur between the olefin products and the carbenium ion intermediates, and coke formation becomes severe with the increase of strong acidity.

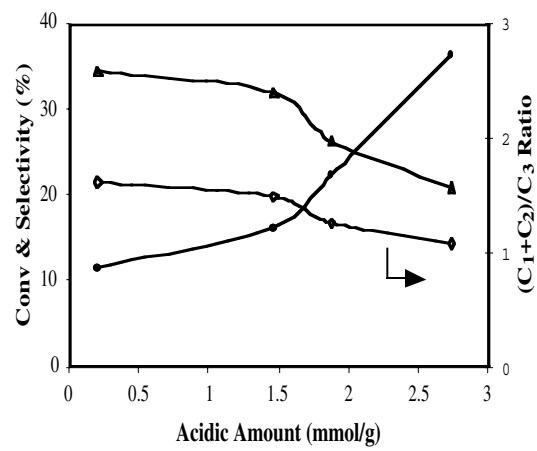

Figure 1. Catalytic pyrolysis (808 K) results of n-hexane over Mordenite zeolites with different acidic amount.
●: Conversion of n-hexane; ▲: Yield of ethylene
✧: $(C_1+C_2)/C_3$ Ratio.

In order to increase the ethylene selectivity, non-acidic NaM zeolite was selected, and basic metal oxide such as alkali (Li, K, Cs) and alkaline earth (Mg, Ca, Sr) were incorporated.

Figure 2 shows results of catalytic pyrolysis over metal supported NaM zeolite catalyst as a function of base amount, which was calculated from the peak amount of the CO_2-TPD (pictures not shown). It is interesting to find that with the increasing basic sites introduced, both the activity and the yield to ethylene increase. This is because the catalytic cracking over non-acidic or basic catalysts with steam conditions follows a free radical mechanism, where the selectivity to alkene, especially ethylene, increases when compared with the carbenium ion mechanism on acidic catalysts.

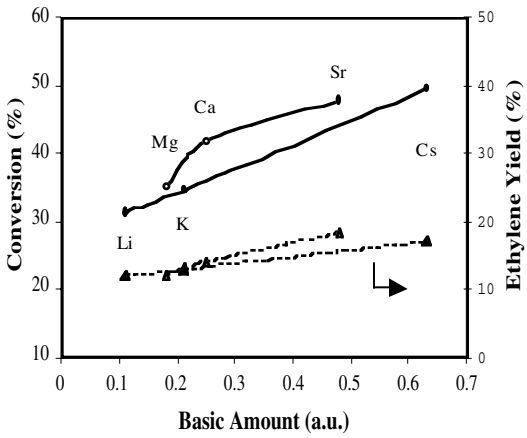

Figure 2. Catalytic pyrolysis (890 K) results of n-hexane over alkali and alkaline earth metal oxide supported Mordenite zeolites with different basic amount.
●: Conversion of n-hexane; ▲: Yield of ethylene.

TPR profiles of different transition metal oxide supported on NaM zeolites (pictures not shown) differ from one another because of the difference in both the electronic state and the reducibility of each metal oxide. For example, the reduction of CuO/NaM starts at about 500 K, while MoO_3/NaM can only be reduced at temperature higher than 870 K. It's therefore our intention to compare the catalytic cracking results of these catalysts as a function of their reducibility.

Figure 3 shows the results of the catalytic pyrolysis over transition metal (Ag, Cu, Mn, Mo) oxides supported NaM zeolite as a function of the starting temperature of respective TPR peaks. It can be found that, the metal oxides that are easier to be reduced (except MnO) show approximately higher catalytic acitivity and yields to alkenes including ethylene. It has been reported that, catalytic cracking over non-reducible transition metal oxide catalysts such as Cr_2O_3/Al_2O_3 under aerobic conditions, *i.e.*, oxidative catalytic cracking, follows a free radical mechanism, where activated oxygen species abstract hydrogen from hydrocarbons to form radicals[3]. Accordingly, high yields of ethylene would be expected[3]. The present work does not involve O_2 during the catalytic pyrolysis. However, lattice oxygen in reducible transition metal oxide supported catalysts may exhibit the similar free-radical oxidative catalytic cracking of n-hexane. The easier the metal oxide to be reduced, the higher extent of this oxidative effect might have.

We also found that, if the transition metal oxide was reduced to metal, the catalytic activity decreased greatly. For example, the conversion of n-hexane over PbO_2/NaM and VO_3/NaM catalysts are 57.2% and 37.0%, respectively. But for Pb/NaM and V/NaM, they are only 10.8% and 3.6%, respectively. This shows again the importance for the existence of oxidative cracking.

Table 1 shows the catalytic pyrolysis over the same transition metal oxide supported catalysts with or without steam. It can be seen that, in the presence of steam, the catalytic activity and ethylene selectivity decrease greatly. This indicates that steam plays an important role in keeping the transition metal oxides at higher oxidation state and therefore exhibiting the oxidative catalytic pyrolysis for n-hexane.

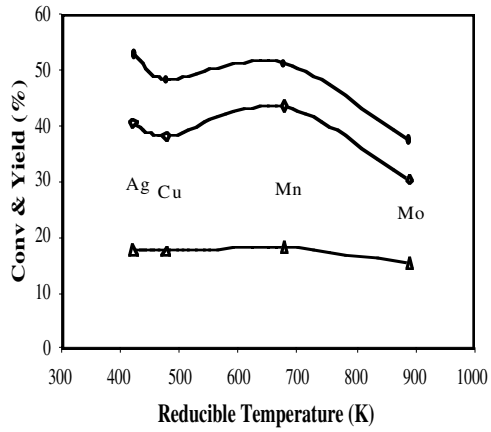

Figure 3. Catalytic pyrolysis (890 K) results of n-hexane over alkali and alkaline earth metal oxide supported Mordenite zeolites with different basic amount.
●: Conversion of n-hexane; ▲: Yield of ethylene.
✧: Total yields of alkenes.

Table 1. Results of catalytic pyrolysis of n-hexane over M_xO supported NaM in N_2 or H_2O (890 K, WHSV 3.6 h^{-1}, H_2O/henxae ratio 0.9, TOS 1h)

Cat.	Conversion (%)		X_{C2H4} (%)*		Y_{alkene} (%)*	
	a	b	a	b	a	b
Ag_2O/NaM	28.0	53.0	34.3	33.6	19.8	40.6
CuO/NaM	28.6	48.5	20.2	36.0	19.4	38.2
MnO/NaM	26.3	51.4	31.0	35.5	19.4	43.7
MoO/NaM	11.8	37.5	38.8	41.0	8.5	30.4

*X_{C2H4}: Selectivity to ethylene; Y_{alkene}: Yield of alkenes.
a: Reaction in N_2; b: Reaction in H_2O

Acknowledgement. We are grateful for the financial supports from National Natural Science Foundation of China, SINOPEC, and the Pennsylvania State University.

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