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Dehydroaromatization of Methane with a Small Amount of Ethane for Higher Yield of Benzene

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Abstract: The dehydroaromatization of methane was investigated with addition of a few ethane. A high benzene yield was achieved at a higher space velocity. The addition of CO_2 could improve the stability.

Keywords: Aromatization, benzene, methane, space velocity, TPO.

In recent years, the methane dehydroaromatization (MDA) has attracted more attention rather than the methane oxidative coupling (MOC)[1-6], in the interest of researching the effective approaches for the chemical conversion of natural gas. Some works concerned the zeolite support effects or effects of transitional metal promoters like Fe, Co and Cu have been reported[7]. The catalyst structure determination and characterization of the active sites using like XRD, NMR, temperature programmed oxidation (TPO), TG-DTA were also reported[4,6,8].

In order to improve the activity and get higher aromatic yield, several approaches have been taken[2, 3]. In our previous work, a significant promotion of benzene formation has been achieved with addition of a small amount of ethane into the methane feed[3]. This work concerned addition of a small amount of ethane in the reaction of dehydroaromatization of methane at higher space velocities. The carbon deposition during the reaction was investigated by TPO tests and N_2 adsorption analysis.

Results and Discussion

The zeolite ZSM-5 supported Mo catalysts were prepared by impregnation, the impregnated samples were dried at 105 ^{o}C for 2 h and calcined at 500 ^{o}C for 6 h, the sample size was controlled to 20-40 mesh. The MDA reaction tests were operated in a quartz tubular flow micro-reactor. The catalyst sample was pretreated in He and then tested in the reaction feed, and the reaction products were analyzed by two on-line gas chromatographs. The catalysts after reaction were measured by TPO and N_2 adsorption tests. The MDA was performed at 725 ^{o}C and 3 atms, the methane

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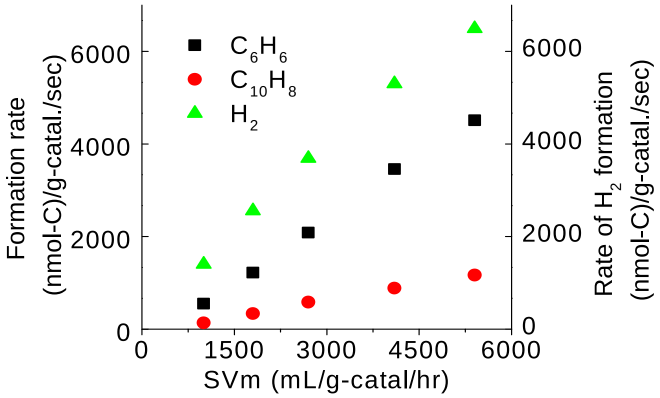
conversion was 7.8% at a space velocity of 2700 mL/g-catal./hr, the benzene yield was 1140 nmol-C/g-catal./sec (The unit is based on carbon balance. For example, there are six atoms of carbon in one molecule benzene C_6H_6, or two atoms of carbon in 1 molecule ethane C_2H_6). An addition of small amount of ethane could improve the formation rate of benzene and aromatic yield. The effects of space velocity on catalytic performance were investigated using a co-feed of CH_4+6.3%C_2H_6, and the methane space velocity was adjusted from 1000 mL/g/hr to 5400 mL/g/hr, the effective results were shown in **Figure 1**. The benzene formation rate was only 550 nmol-C/g-catal./sec at SVm = 1000 mL/g/hr, it increased linearly with the rise of space velocity and reached a value of 4510 nmol-C/g-catal./sec at SVm = 5400 mL/g/hr. The formation rate of naphthalene followed the similar trend of enhancement with the increase of space velocity, so did the formation rate of hydrogen.

Figure 1 Influence of space velocity SVm on the catalyst performance



T=725 °C, P= 3atm, Catalyst=6%Mo/HZSM-5, CH_4+6.3 (V)%C_2H_6

Table 1 Texture properties of Mo/HZSM-5 catalyst in MDA reaction with different feed

No.	Reaction feed and condition[a]	BET surface area (m^2/g)	Volume of N_2 adsorbed (cm^3/g)
1	Fresh catalyst	332	77.1
2	CH_4 only	198	45.6
3	CH_4+6.3%C_2H_6	102	23.5
4	CH_4+2.6%CO_2	304	70.1

a: T=725 °C, P=3 atm, catalyst weight=300 mg, t=7 hr, methane SV in the different feeds = 2700mL/g-catal./hr

The catalytic performances were stable for the space velocity of 1000, 1800, 2700 mL/g/hr during the seven hours tests. When 2.6 (V)% CO_2 was added, the stability could be enhanced for higher space velocity even at 4100 or 5400 mL/g/hr. The effect tests of reaction temperature and system pressure were also operated.

The used catalysts were characterized using TPO measurements and N_2 adsorption tests (**Table 1, Table 2**). The results indicated that at high space velocity there were the bottle neck phenomena of coke deposition on the catalyst performance and stability, the addition of CO_2 could inhibit the coke deposition and improve the stability.

Table 2 TPO results of Mo/HZSM-5 catalyst in MDA reaction at different SV

No.	SVm^a of co-feed (mL/g/hr)	Peak number	O_2 peak(s)		Peak area (a.u)	
			Ti (^{o}C)	Hi (a.u)	O_2	CO_2
1	2700	2	531	626	45.3k	81.2k
			633	446		
2	4100	2	516	574	64.6k	96.9k
			648	1031		
3	5400	2	524	604	65.3k	104.9k
			681	1368		

a: T=725 ^{o}C, P=3 atm, catalyst weight=300 mg, t=7 hr

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