CONVERSION OF METHANOL TO LOWER OLEFINS - APPLICATION STUDIES

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ABSTRACT

The conversion of methanol to lower olefins over various ZSM5 zeolite catalysts was studied in two-stage fixed bed reactor system. The catalysts containing ZSM5 zeolite with different SiO_2/Al_2O_3 ratios (73 and 183) modified with phosphorus and magnesium were used. Some effects of temperature, space velocity, and water to methanol ratio on the selectivity for C_2-C_4 olefins and product yields were determined. Catalyst deactivation due to coke formation was investigated. The activity loss from coking can be regained by oxidative regeneration. An aging test of over 34.5 hours on stream was performed during which 26.5 g of methanol/g of zeolite catalyst (SiO_2/Al_2O_3 ratio in ZSM5 is 183) was processed, yielding 17.5 g of C_2-C_4 olefins, among of them 5.3 g of propylene was found.

INTRODUCTION

The lower olefins, especially ethylene and propylene, are major raw materials for manufacture of many industrial organic chemicals. The synthesis of lower olefins from methanol, instead of from petroleum naphta, opens a new way to produce hydrocarbons from either natural gas or coal. The discovery that methanol can be converted selectively to hydrocarbons with ZSM5 type zeolite developed by Mobil Oil Corp. was first reported in the middle 1970's. By controlling zeolite structural and methanol conversion process parameters it is possible to enhance the yield of lower olefins. The results of the previous studies [1-4] have showed that to enhance the lower olefins yield the methanol conversion reaction must be run as follows: operate at short contact time, decrease the acidity of the zeolite, and increase the products shape-selectivity by reducing the apparent pore size of zeolite.

This paper describes the results of a process variable study

of the methanol to lower olefins conversion in a fixed bed reactor over various H-ZSM5 zeolite catalysts with different SiO_2/Al_2O_3 ratios. Some effects of temperature, space velocity, time on stream and water to methanol ratio on product yield were determined. The results from an aging test of four zeolite catalysts are described.

EXPERIMENTAL

Catalyst used. ZSM-5 Zeolite (ULTRAZET - designated by the Institute of Industrial Chemistry, Warszawa) in two ranges of SiO_2/Al_2O_3 ratio (73 and 183) was prepared according to the previously described procedure [5] . The zeolite was converted into the hydrogen form by stirring with the solution of hydrochloric acid (0.5 N, 353 K) for six hours. The method of modification of HZSM-5 involved a treatment of the zeolite with trimethyl phosphite as described in Mobil patent [6] . For the catalytic activity tests the zeolites were mixed with magnesium and/or aluminium oxide and tableted (5 x 5 mm tablets were formed) using polyvinyl alcohol (MW=100000) as the binder (binder content - 8 wt %). γ-Alumina (Pechiney-Saint-Gobain Activated Alumina, France) was used as the dehydration catalyst in the first step of the process. Catalyst's composition and characteristics are shown in Table 1.

Table 1

Catalyst's composition and characteristics

No	ZSM-5			Al_2O_3	MgO	Tablets ϕ/h [mm/mm]	Compression strength (after reaction) [kg/cm^2]
	[wt %]	SiO_2/Al_2O_3	P [wt %]	[wt %]	[wt %]		
A	50	73	2.3	50	0	5/5	37
B	50	73	2.3	40	10	5/5	30
C	50	183	0.7	40	10	5/4	45
D	50	183	0.0	40	10	5/4	70

Apparatus and procedure. The experimental studies on process variables were carried out in two-step fixed bed type apparatus with a continuous flow system at atmospheric pressure. Using two reactor system the first reactor contains alumina that promotes only a methanol dehydration reaction to dimethyl ether. Dehydration catalyst in the first reactor can be operated for long period without any significant loss in activity and therefore was

not studied in details.

The studies concerning only the second step of the process have been performed. The special stainless steel tubular reactor (50cm long and 0.5cm in diameter) was developed for these purposes. Three separate electrical heating sections were constructed. The upper part of the reactor was used as a preheater for the gaseous products from the first reactor and for water additionally allowed into the conversion reactor. Six thermocouples connected to a multichannel recorder provided facilities for the controlling of temperature of the gaseous substrates at the inlet to the reactor and to record a profile of the temperature in the catalyst bed. 90 g of HZSM-5 zeolite catalyst was placed on support grid and then calcined at 833 K in a flow of argon/oxygen for six hours. A blend of methanol and water (80/20 w/w) was delivered to the first reactor by a metering pump at a constant feed rate. The hot vapours leaving the first reactor containing a near equilibrium mixture of dimethyl ether, methanol and water were combined with water vapour and fed into the second reactor. Product analysis was provided in a Chrom 4 Chromatograph as described in the details elsewhere [4].

RESULTS

The effects of temperature, space velocity (WHSV), and water to methanol ratio were determined. These parameters were examined over a range of 688-748 K, 0.66-25.0 h^{-1} and 0.25-2.96 g/g, respectively. Representative data are shown in Table 2. Fig. 1 shows the change of activity of the catalyst (A) with the reaction temperature. Changes in aromatics and olefins yield with time on stream on studied catalysts are shown in Fig. 2 - 5. The dependence of C_2-C_4 olefin yield and selectivity in methanol conversion reaction on the water to methanol ratio ilustrates Fig.6.

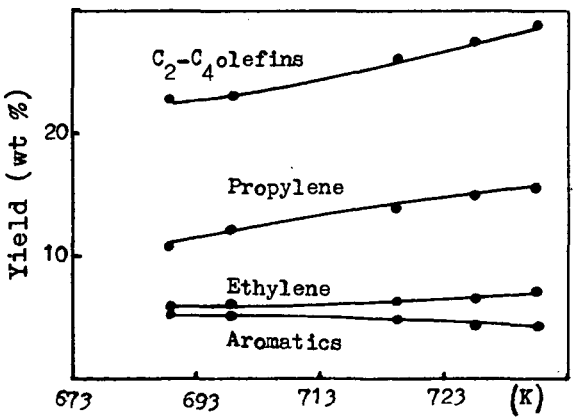

Fig. 1. Effect of temperature on methanol conversion. Catalyst A. WHSV=1.2 h^{-1} H_2O/CH_3OH=2.3

Table 2

Operating conditions and distribution of hydrocarbons in the conversion of methanol

Catalyst No	A	A	A	B	B	B	C	C	C	C	C	C	C	D	D	D	D
Temperature K	703	736	740	740	743	738	748	746	750	748	750	748	746	743	743	745	747
Space velocity gCH_3OH/g cat.h	1.15	1.34	1.41	1.38	1.38	1.37	0.8	0.79	0.79	0.66	0.8	0.8	0.8	2.3	2.28	2.5	2.44
Water/Methanol g/g	2.45	2.19	2.14	2.30	2.30	2.30	0.25	0.97	1.52	1.74	1.80	2.28	2.96	2.15	2.21	2.12	2.16
Conversion %	92.68	97.23	94.29	95.41	96.28	90.74	99.68	98.74	97.92	98.23	97.60	97.18	92.78	94.23	94.05	95.15	95.20
Selectivity %																	
Hydrocarbons	42.41	43.54	43.17	43.45	43.37	42.30	43.74	43.62	43.62	43.65	43.61	43.59	43.07	43.12	43.14	43.47	43.00
Dimethyl Ether	2.15	0.34	0.95	0.49	0.63	2.37	0.00	0.22	0.22	0.17	0.22	0.27	1.12	1.04	1.00	0.39	0.58
Water	55.41	56.12	55.88	56.06	56.00	55.92	56.25	56.17	56.16	56.18	56.18	56.14	55.81	55.84	55.86	56.07	56.48
Hydrocarbons wt %																	
Ethylene	13.24	15.49	15.26	16.57	17.53	14.37	10.90	10.29	10.26	10.59	9.70	9.62	8.71	8.82	8.69	7.33	7.93
Propylene	30.47	35.56	36.58	36.57	35.52	36.48	31.36	40.16	44.08	44.89	43.97	46.80	46.38	47.37	46.69	44.07	48.52
Butenes	13.76	16.81	15.53	15.84	15.11	15.29	22.16	21.86	21.25	21.08	21.66	20.57	20.14	21.00	21.68	20.97	21.12
Methane	0.85	0.88	1.84	0.91	1.34	1.84	2.22	1.82	1.40	1.69	1.13	1.13	1.16	0.97	0.95	0.74	0.84
Ethane + Propane	2.70	2.73	2.19	3.71	4.02	1.57	3.58	2.37	2.05	1.97	1.79	1.51	1.26	0.97	0.96	1.21	1.31
Butanes	9.70	6.34	4.91	5.34	5.10	4.05	4.52	2.82	2.33	2.34	2.73	2.17	2.03	2.91	2.67	2.41	2.35
C_5+ aliphatics	14.83	12.37	12.44	13.18	12.55	16.69	16.61	15.09	14.58	13.46	15.53	14.70	17.38	14.95	14.86	19.03	13.90
C_6+ aromatics	14.53	9.72	11.16	7.79	8.93	9.72	9.16	5.68	4.05	3.88	3.50	3.31	2.83	2.73	3.40	4.24	3.83
C_2-C_4 olefin selectivity %	57.48	67.87	67.36	68.98	68.15	66.13	63.92	72.31	75.59	76.58	75.32	76.89	75.24	78.18	77.06	72.37	77.62
C_2-C_4 olefin Yield %	22.61	28.73	27.42	28.59	28.45	25.39	27.88	31.14	32.28	32.83	32.06	32.61	30.06	31.76	31.27	29.93	32.07
Propylene yield %	12.00	15.10	14.90	15.20	14.84	14.00	13.70	17.30	18.80	19.25	18.70	19.80	18.50	19.20	18.90	18.20	19.90

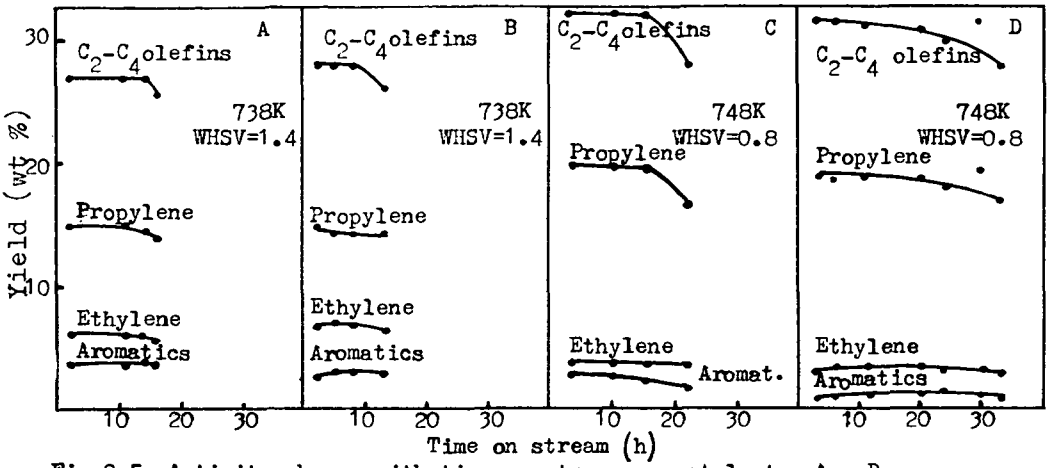

Fig.2-5. Activity change with time on stream on catalysts A - D.

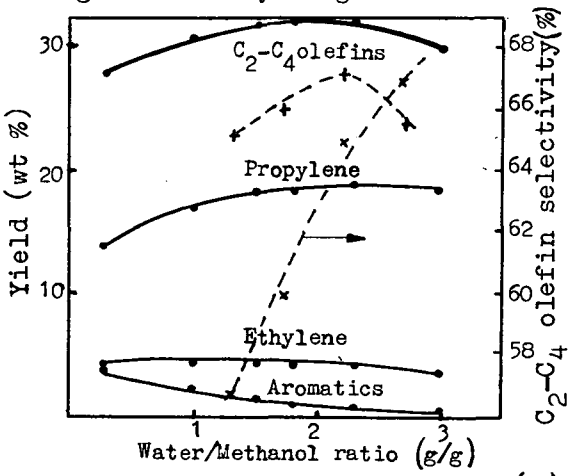

Fig. 6. Effect of water/methanol ratio on methanol conversion. Catalyst A and C.
---- A - 738K; WHSV=1.4 h^{-1}
——— C - 748K; WHSV=0.8 h^{-1}

The performance of the catalyst (D) throughout the 13 successful cycles in the long aging test is shown in Table 3, where the outlet concentrations of products formed from methanol are plotted as function of time on stream in each cycle.

Table 3

Product distribution in long-term aging test. Temp. 733 K; WHSV=1.2; diluent gas - He. I^x - temp. 743 K; WHSV=0.8; H_2O/CH_3OH = 2.7.

Cycle No	1		6			8			10		12		I^x
Time on stream in cycle, h	1	24	1	6	25	5	24	29	1	19	1	22	30
Composition, wt %													
ethylene	7.1	6.2	8.9	9.0	6.9	10.6	6.6	6.7	8.0	7.2	8.5	7.2	8.5
propylene	45.3	42.0	43.9	41.4	38.7	45.5	42.3	40.4	48.0	40.0	46.8	39.5	51.7
butenes	29.4	32.0	29.2	27.0	26.1	28.1	22.2	21.2	27.5	22.2	27.3	21.2	22.2
methane	1.1	1.3	2.4	3.8	8.5	1.7	8.3	10.6	1.5	8.7	1.5	10.1	0.9
ethane/propane	1.3	1.8	1.5	1.4	1.5	0.8	0.2	0.2	0.9	1.0	1.2	0.9	1.4
butanes	2.1	2.7	2.7	3.2	3.5	1.5	0.9	0.8	1.7	1.2	2.0	0.9	2.5
C_5+aliphatics	13.8	18.0	11.4	14.0	20.3	10.7	14.8	12.1	12.3	14.8	12.6	14.0	11.1
dimethyl ether	-	4.0	-	-	10.0	-	4.8	8.0	-	4.9	0.1	5.9	1.3

DISCUSSION

The results from the process variable study previously published [2 - 4] provided basis to select operating conditions for above described experiments. It was found that reaction temperature should be higher than 733 K, and WHSV not be higher than 2.0 h^{-1} and water to methanol ratio at the range 2.0-2.2. Higher space velocity required that the reaction temperature should be so high as 773 K to maintain the conversion level above 90 %. The increasing the temperature above 773 K gave the higher olefin selectivity but simultaneously the amount of methane was increased above 4 %. For these reason WHSV = 1.4 h^{-1} was chosen in further studies.

The next process parameter controlling the formation of olefin which was optimized was water to methanol ratio. The charge stock used in the study was a blend of methanol and water (20 %). This composition simulated the product from the commercial methanol plant. By co-feeding of water to the effluent from the dehydration reactor the contact time of the reactants was shortened resulting in an improvement through the prevention of coke deposition. The relation shown in Fig. 6 allowed one to make a conclusion that the olefin selectivity and yield increases parallely to water/methanol ratio. The optimization of this process parameter is limited because simultaneously with the enhacement of selectivity - conversion and yield of the process are decreased. The maximum C_2-C_4 olefin yield (greater than 28 wt %) and conversion more than 95 % were achieved for water/methanol ratio equals 2.2 over catalysts (A) and (B). The modification of the zeolite with magnesium oxide (B) resulted in the shortening of lifetime of the catalyst (from 17.5 to 13.5 hrs) and the insignificant increasing of the olefins yield.

It is known [7] in the art that the catalytic activity and selectivity for the formation of lower olefins over ZSM-5 catalyst depend on such catalyst parameters as activity and SiO_2/Al_2O_3 ratio. The selectivity to C_2-C_4 olefins increases with diminishing of the strong Bronsted acid sites population, which are probably located at channel intersections [8] as it was observed by Balkrishnam [7]. In general, decreasing of the catalytic activity of the zeolite can be achieved by decreasing of the surface acidity (concentration of all acid sites) parallely with increasing SiO_2/Al_2O_3 ratio. It is also knows [9] that higher yield of olefins can be obtained over phosphorus-modified ZSM-5 zeolite. Therefore, the zeolite catalysts which

contain ZSM-5 with SiO_2/Al_2O_3 ratio equal to 183 and modified with phosphorus and magnesium were prepared. Modification of ZSM-5 zeolite by oxides of magnesium and/or aluminium was aimed to improve the catalyst selectivity towards lower olefins as well as at the preparation of a catalyst with the required mechanical strength. These two features are very important for the catalyst practical application in the industrial process of conversion of methanol to lower olefins. Those modifications of catalysts required us to optimize such a process parameter as the contact time (WHSV). The optimization of this parameter shows that WHSV should be at the level of 0.8 h^{-1} enabling the maintenance of conversion higher than 95 %. Previously [3] we observed the changes of olefin selectivity in dependence to a maximum gradient in the bed. It was noticed that the reducing of temperature gradient gives the increasing of the olefin selectivity. The temperature gradient strongly depends on WHSV and water/methanol ratio. In order to correct these parameters the influence of the dilution of methanol with water on methanol transformation was studied. On comparing C_2-C_4 olefin yields for the zeolite catalyst (A) and (C) (Fig. 6) it is shown that the maximum yield over the range of water/methanol = 1.8 - 2.2 is not so sharply marked for the catalyst (C) as for (A). In order to obtain the high olefin selectivity it is necessary to resolve the problem of such a dilution of substrate at which the conversion will be at the level enabling the recovery and recycling of the unconverted methanol and dimethyl ether to the process. An isolation of these compounds from a big amount of water is difficult technological problem. Therefore the parameters of the process must be checked in a pilot plant and than it will be possible to answer the question to which economical level the conversion can be lowered in order to obtain the best olefin selectivity. Like it was expected the C_2-C_4 olefin yield (Fig.2-5) was increased to more than 30 % using the zeolite catalysts with higher SiO_2/Al_2O_3 ratio. The yield of propylene was also high - about of 20 wt %. The direct comparision of the life-time of the studied catalysts with the various SiO_2/Al_2O_3 ratios was difficult because of the different WHSV used in the experiments. However, refering the life-time of catalyst to the amount of methanol processed on the catalyst it was possible to compare those catalysts.From the results presented in Table 4 it is noticed the prolonged life-time of catalyst (C) and (D) up to 22 and 35 hrs, respectively. It can be also concluded that the best catalyst is that one (D) containing HZSM-5

zeolite with SiO_2/Al_2O_3 = 183 modified with magnesium oxide. During 34.5 hours on stream 26.5 g of methanol/g of catalyst was processed forming 17.5 g of C_2 - C_4 olefins, among of them 5.3 g of propylene was found.

Table 4

Comparision of life-time of the catalysts per cycle

Catalyst No	Working time at conversion level above 90 % [hrs]	Methanol processed [g/g cat]	Propylene [g/g cat]
A	17.5	49	7.3
B	13.5	38	5.7
C	22.0	35	7.0
D	34.5	55	10.5

Considerable effort was devoted to the study of catalyst aging which is mainly due to coking. The deactivation is reversible and most of the catalytic activity can be restored by controled coke burning. A noteworthy feature of this process is that a catalyst ages in a band. This was evident from the change of the temperature profil through the catalyst bed. Coke formation which deactivates the catalyst during its time on stream and requires a periodical regeneration determines the cyclic behaviour of the process of methanol conversion to lower olefins.

The results of these studies have demonstrated the feasibility of converting methanol to lower olefins in a fixed bed reactor. These data can be used to develop the design basis for a fixed bed pilot plant.

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