Selective methanol conversion to BTX

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the reducing conditions ($S < 1$), and removes strongly chemisorbed CO and propylene from the catalyst surface, and (3) increases the amount of NO chemisorption. The role of La_2O_3 on Pd–La catalyst is as an abundant H_2 supplier and an excellent NO reserver through the three-way catalyst reactions. We attribute these findings to the strong interaction between Pd and La_2O_3 on α-Al_2O_3.

Acknowledgment

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Selective Methanol Conversion to BTX

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Methanol conversion to hydrocarbons may be engineered to increase the amount of aromatics, becoming an alternative source of BTX. The high exothermicity of the reaction calls for a fluidized-bed reactor. But industrial fluidized bed reactors exhibit large dynamic fluctuations, strongly screening the catalyst performances. Therefore, among a class of potentially suitable catalysts, two candidates, A and B, were chosen to be tested on a fixed bed reactor with respect to the BTX yield and the sensitivity to the operating conditions. Both catalysts are of ZSM-5 type, but they have different Si:Al ratios. The BTX amount is comparable with the literature-available data. The curvature radius of the response surface, used as a measure of the sensitivity, shows catalyst B to be more stable with respect to the operating conditions. Moreover, the low durene content may be taken as an advantage in the subsequent separation of aromatics.

Introduction

The common raw materials for the synthesis of BTX are the liquid fractions from hydrocarbon cracking and reforming. The total crude oil available by the year 2000, about 2500 million tons with an average naphtha yield of 18%, will have to satisfy the needs of both the chemical industry, taking into account a 5% increase, 300 million tons, and of reforming to get high-octane motor gasoline, which is foreseen at 650 million tons. In other words, some 100 million tons of naphtha equivalent have to be found elsewhere—gas oil, gas coal, or new sources (Taylor, 1979). Synthesis of liquid fuels based on the conversion of coal- or methane-derived CO + H_2 through the methanol-to-gasoline route emphasizes the shift to an alternative resource. The catalytic conversion of methanol to hydrocarbons has been investigated intensively in recent years, both economically (Harney and Mills, 1980) and scientifically, an extensive review being presented by Liu et al. (1983).

Now, it seems that there is some agreement concerning the first carbon–carbon bond formation through carbene

intermediate (Chang and Silvestri, 1977). The carbon chain proceeds through oligomerization and methylation, their relative contributions being investigated recently by Espinoza (1984). The catalyst structure and composition and the process engineering may induce a wide range of highly selective syntheses of paraffins, olefins, or aromatics, as shown in Table I. To our knowledge, the only industrial unit is a fixed-bed one operating in New Zealand (Fox, 1982). The other data collected in Table I are from laboratory or pilot-scale reactors. The fixed-bed reactors are widely used, but in order to better control the temperature fluidized-bed reactors have been tested, too. The catalysts used differ both in composition and structure, being designed as highly selective for different hydrocarbons. Considering the operating conditions, the temperature is moderate, between 300 and 500 °C, and the pressure is generally the atmospheric one, with some exceptions. Due to the catalyst used, the hydrocarbons distribution is very different: in some cases the process is selective in olefins, in other cases in aromatics. The aromatics are mostly methyl-substituted. Benzene was detected in a small amount only (Liederman et al., 1978). Toluene and xylenes are paramount (Védrine et al., 1980). The higher alkylbenzenes are present in smaller quantities. According to Chang and Silvestri (1977), it is because of their lower

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Table I. Methanol to Hydrocarbons Conversion Engineering: Comparative Analysis

ref	reactor	catalyst	temp, °C	LHSV (MWHSV), h⁻¹	convn, %	productivity, kg/(kg·h) (kg/(L·h))	hydrocarbons distribution,[a] wt %			
							$C_2 + C_2'$	$C_3 + C_3'$	$C_4 + C_4'$	aromatics
Chang and Silvestri (1977)	fixed bed	zeolite	371	108	47.5	20[b] (12)	0.1 + 12.4	2.5 + 26.7	7.8 + 15.8	6.6
Liederman et al. (1978)	fluid bed	zeolite	371	0.77[b] (1)	98.18	0.432 (0.25)[b]	0.1 + 6.54	2.37 + 7.9	11.7 + 6.24	26.91
Derouane et al. (1978)	fixed bed	HZSM-5	350	2.48	100	1.41[b] (0.85)	3.4[c]	16.4[c]	24.3[c]	29.2[c]
Chang et al. (1978)	fixed bed, 353 psig	ZSM-5	371	0.9[b] (1.5)	97	0.5 (0.3)[b]		30.2		45.5
Lee et al. (1978)	fluidized bed, 25 psig	ZSM-5	420	(1.0)	99.8	0.435 (0.25)[b]	5.6	5.9 + 5.0	16.2 + 7.3	20.0
Anderson et al. (1979)	fixed bed	ZSM-5	400		100		2.9 + 0.0[e]	10.3 + 0[e]	8.4 + 0.0[e]	78.4[e]
Chang et al. (1979)	fixed bed, 50 atm	ZSM-5	370	1.2	90	0.61[b] (0.37)	0.8	6.0	12.4	34.8
Dejaifve et al. (1980)	fixed bed	HZSM-5	372	7.9[b] (10.27)	81.2[c]	3.9 (2.34)[b]	18.1[c]	32.1[c]	27.4[c]	9.5[c]
Anthony and Singh (1980)	Berty autoclave	chabazite	418	0.33	50	0.12[b] (0.07)	5 + 8	8 + 5		
Kaeding and Butter (1980)	fixed bed	ZSM-5	500	0.77[b] (1)	100	0.44 (0.26)[b]	1.2 + 6.8	14.9 + 7.3	19.3 + 6.4	24.5
Kasai et al. (1981)	fixed bed	pyrazinium salts $H_3PW_{12}O_{40}$	285		23.1	0.001 (0.0006)[b]	0.4 + 61[c]	1.4 + 13.1[c]	1.9 + 3.5[c]	
Dettmeier et al. (1982)	fixed bed	H-chabazite	350–430	0.65–5.2[b] (0.5–4)	70	0.25 (0.15)[b]	10 + 40[d]	0 + 38	0 + 6	
Fox (1982)	fixed bed (2 stages)	ZSM-5	400–420		100		1.09	7.65	15.19	39.68
Liu et al. (1983)	fluid bed	modified AW 500	430	0.3[b] (0.4)	100	0.16 (0.1)	2.4 + 30.2	17.6 + 32.5	4.05 + 6.3	
Mihail et al. (1983)	fixed bed	modified zeolite	340–410	1.3	97	0.68 (0.40)	0.46 + 16.1	6.9 + 11.96	10.3 + 5.98	20.2

[a] C_n, C_n': paraffins and olefins, respectively, with n carbon atoms. [b] The catalyst was supposed to have the density 0.6 g/cm³. [c] In carbon atoms. [d] C_1–C_4 paraffins. [e] mol % composition.

diffusivities due to steric constraints of the catalyst pores, while Liederman et al. (1978) expect their catalytic cracking. Aromatics remain fairly constant with respect to the temperature (Chang and Silvestri, 1977; Liederman et al., 1978; Chang et al., 1978) except at temperatures above 400 °C (Chang and Silvestri, 1977; Chang et al., 1978). An enhanced selectivity in methylbenzenes may be obtained by increasing the pressure (Chang et al., 1978; Chang et al., 1979) or by adding water to the feed (van den Berg et al., 1980). A major problem is the presence of durene, which can be up to 20% of the aromatics (Chang et al., 1978; Fox, 1982) and must be separated.

Scope of This Paper

The methanol conversion to aromatics, in particular to BTX, is engineered, for obvious reasons (Lee et al., 1978), in fluidized catalytic reactors. It is well-known that fluidized reactors exhibit local relatively large fluctuations in the heterogeneous structure of the bed (Peeler and Whitehead, 1982), which influence both conversion and selectivity. Yutani et al. (1983) observed that insignificant differences in the holes of a jet distributor, due to machining or errosion, affect the jetting/bubbling behavior. In order to do a rapid discriminatory analysis of the catalysts performances, we had to eliminate these fluctuations using a fixed-bed reactor. After selecting two suitable catalysts among a larger number of potential active zeolites, our aim was to identify a region of stable operating conditions with respect to the amount of BTX that could be reached.

Experimental Section

Catalysts. The experiments have been done with two catalysts of ZSM-5 type. Catalyst A has been obtained following Argauer and Landolt (1972). After filtration and drying, it has been calcined 4 h at 550 °C and treated with a 10% ammonia nitrate solution in order to have a 0.2% sodium content. The H form has been obtained through calcination at 600 °C for 4 h. The zeolite has been included in a kaolin-based matrix and extruded as cylinders 2–3 mm in length and 1.5 mm in diameter. It has been dried and calcined again at 550 °C for 4 h. Eventually the catalyst has been modified through ionic exchange with a 10% aluminum nitrate solution. Catalyst B has been obtained under similar conditions, but the base zeolite has been prepared following a proper method. Its main features concern the amorphous silica–aluminum precipitation, the composition of the mixture undergoing crystallization, and the organic agent used in this operation. We emphasize that this zeolite has the crystallographic structure of ZSM-5, but another Si:Al ratio, and the kaolin-based matrix, which included the zeolite, has been substituted with active alumina.

Measurement of Catalysts Properties. The physical properties of the two catalysts are nearly the same, with the difference that in the second case the mechanical resistance is improved. The BET surface area by N_2 adsorption has been determined as 240 m²/g. The density is 0.67 g/cm³. The X-ray spectra are presented in Figure 1. The X-ray diffraction analysis has been done with Cu $K\alpha$ radiation by using a DRON-3 diffractometer. For both
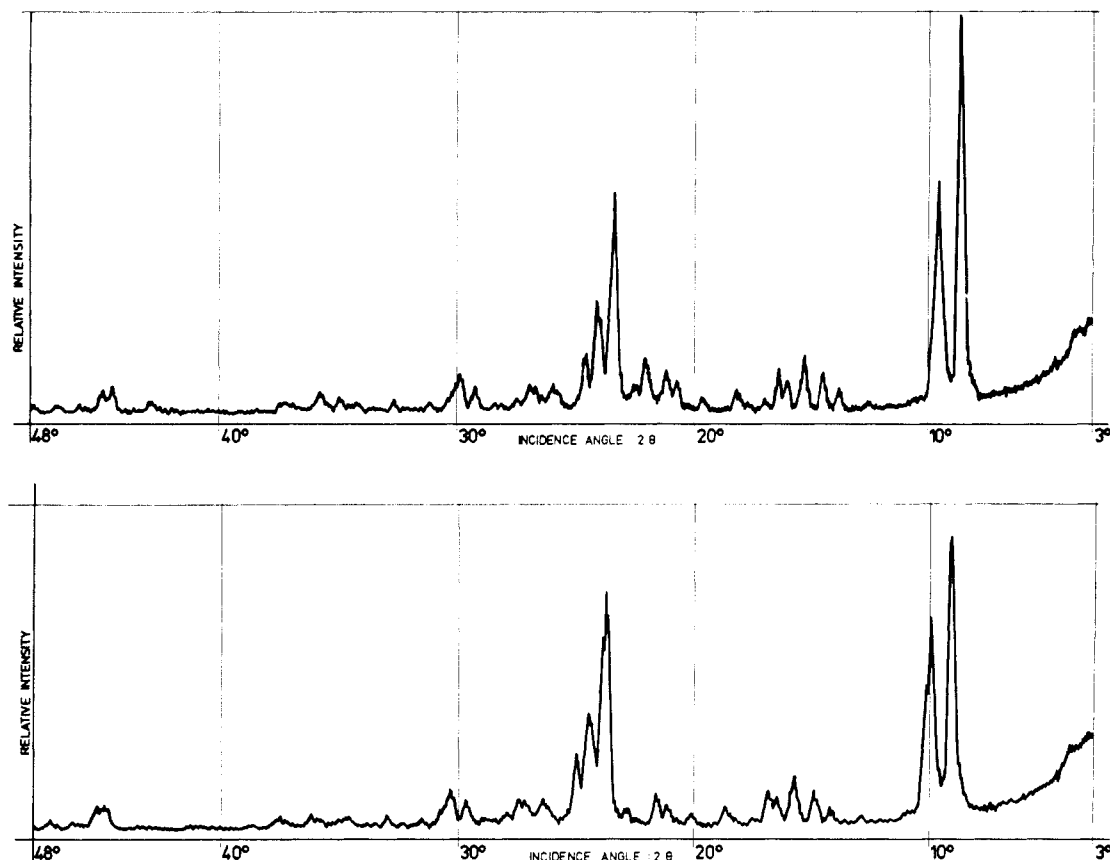
Figure 1. X-ray spectra for the catalysts.

Table II. Experimental Data, Catalyst A

expt	temp, °C	LHSV, h^{-1}	feed compsn, MeOH, wt %	BTX, wt %
1	345	0.77	100	9.32
2	375	0.88	100	11.91
3	375	1.31	100	11.76
4	405	1.70	100	11.65
5	405	1.14	100	11.69
6	405	0.80	100	10.99
7	425	1.23	100	9.85
8	425	1.80	100	11.13
9	345	0.77	60	3.47
10	405	0.85	60	6.08
11	345	1.75	60	2.46
12	405	1.75	60	6.89
13	345	0.80	50	3.75
14	375	1.25	50	5.30
15	405	1.80	50	3.91
16	345	0.80	90	5.12
17	405	0.82	90	8.19
18	345	1.68	90	6.18
19	405	1.71	90	7.26
20	375	1.14	75	6.62
21	325	1.20	75	5.86
22	425	1.20	75	7.31
23	425	0.99	75	7.74
24	375	0.51	75	3.50
25	375	2.04	75	5.76
26	375	1.22	75	8.41
27	375	1.25	75	8.71

Table III. Experimental Data, Catalyst B

expt no.	temp, °C	LHSV, h^{-1}	feed compsn, MeOH, wt %	BTX, wt %
1	340	0.575	100	12.40
2	340	1.76	100	11.34
3	375	0.485	100	10.77
4	375	0.645	100	12.67
5	375	1.09	100	12.80
6	375	1.26	100	10.35
7	375	1.243	100	12.60
8	375	1.249	100	11.79
9	375	2.07	100	11.41
10	410	0.6	100	12.66
11	410	1.65	100	11.46
12	425	1.214	100	11.90
13	325	1.115	100	11.57

catalysts the diffraction maxima correspond with those of ZSM-5 zeolite. For catalyst B we observe a maxima splitting trend at $2\theta = 8.9°$ and $23.1°$, while catalyst A does not exhibit such a trend. This difference between the two catalysts may be attributed to the different SiO_2/Al_2O_3 ratios. It is well-known that with an increasing SiO_2/Al_2O_3 ratio there is a modification trend from the orthorhombic to the monoclinic structure (Wu et al., 1979). The monoclinic structure is characterized by the appearance

of the maxima splitting, as it is in the case of catalyst B.

Apparatus and Reaction Method. The reactor used was a glass tube of 20 mm i.d. filled with catalyst diluted with inert material at a 1:1 ratio. Liquid methanol, fed with a dosimetric pump, has been vaporized in a preheating inert-material-filled zone. The fractions of the resulting products have been subjected to chromatographic analysis. Further experimental details have been already published (Mihail et al., 1983). The operating conditions and the BTX amount for the two catalysts are presented in Tables II and III. The detailed analyses of the aromatics for catalyst A are presented in Table IV. The reported temperature is that measured at the spot location.

Statistical Modeling of the Process

The first step to establish the optimal operating conditions is the design of an experimental program in order to obtain the experimental data. The independent variables are the temperature in °C, the linear hourly space velocity (LHSV) in h^{-1}, and the percent content of methanol in the feed (water-diluted methanol), designed as x_1,
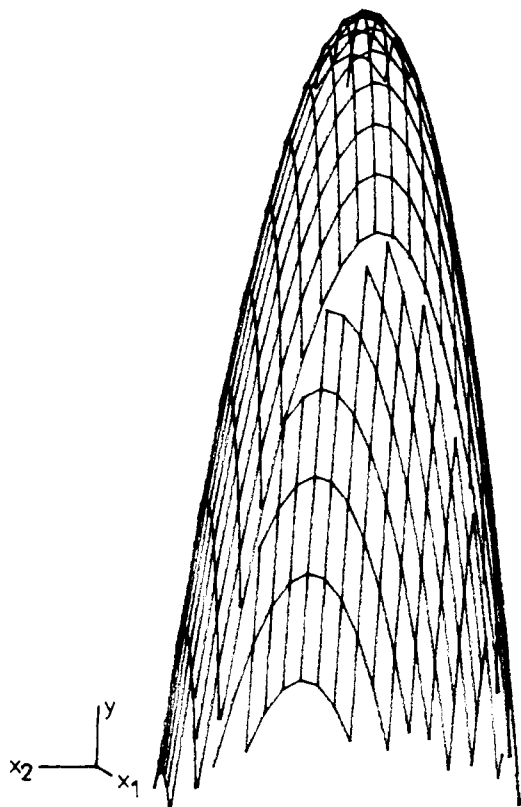
Figure 2. Response surface for catalyst A (pure methanol as feed).

Figure 3. Response surface for catalyst B (pure methanol as feed).

Figure 4. Aromatics and BTX performances for catalyst A: (1) T = 405 °C and 100% methanol as feed; (2) T = 375 °C and 75% methanol as feed; (Δ) aromatics; (□) BTX.

x_2, and x_3, respectively. The dependent variable y is the amount of BTX (wt %) resulting from reaction. For catalyst A, the experimental program was of central-composite type for all three parameters involved above. Because the case of pure methanol as feed seemed very favorable, a second experimental program of the same type, but only for the first two parameters, was performed. As a whole, this double experimental program covered a large area, with special emphasis for the cases of 100% methanol in the feed. Keeping in mind the major importance of the pure methanol as feed, the experimental program performed for catalyst B was designed for the first two independent variables only. The standard error of the replicates, in BTX, was 0.39. For both catalysts, the statistical models were second-order polynomial regressions. For catalyst A it reads

$$y = -129.623 + 0.666937x_1 + 15.8973x_2 - 0.236192x_3 - 0.000845254x_1^2 - 6.06295x_2^2 + 0.00243022x_3^2$$

with the standard error of the estimate of 1.11. The model maximum values are x_1 = 394.5 °C, x_2 = 1.31 h^{-1}, x_3 = 100%, and y = 13% BTX. Its mapping for pure methanol as feed is presented in Figure 2.

For catalyst B, the statistical model reads

$$y = -33.4035 + 0.225239x_1 + 6.35407x_2 - 0.000284875x_1^2 - 1.787x_2^2 - 0.00751751x_1x_2$$

with the standard error of the estimate of 1.13. The model maximum values are x_1 = 381.2 °C, x_2 = 0.975 h^{-1}, and y = 12.8% BTX. Its mapping is presented in Figure 3. As a whole, referring to the standard error of the estimate, the models seem to agree quite well with the experimental data.

Results and Discussions

From the experimental results presented in Figure 4 we may reach conclusions about the performances of catalyst A with respect to BTX. For pure methanol as feed, it has
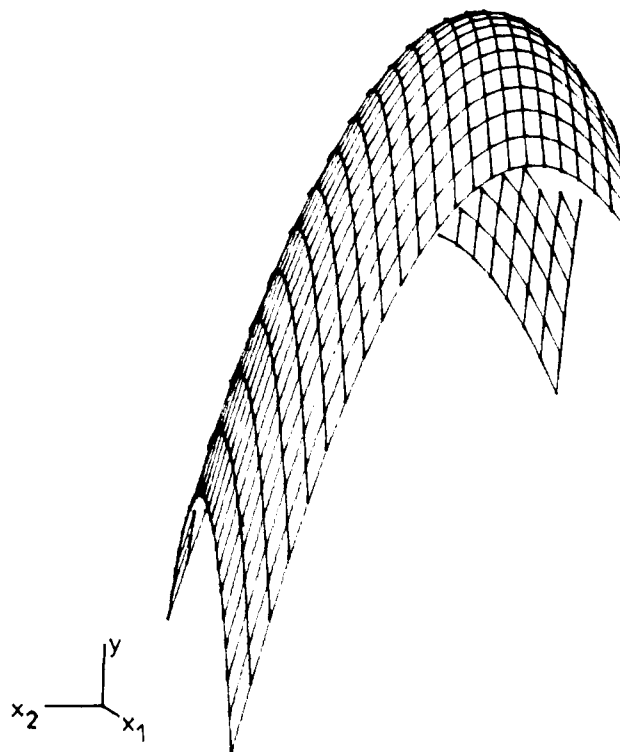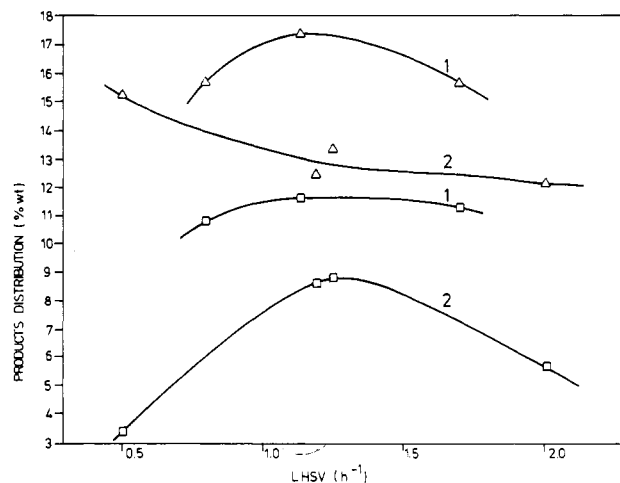
a reduced sensitivity, but outside the selected region, that is, for water-diluted methanol as feed, the BTX amount varies significantly. There is no similar region with respect to the aromatics. From Figure 5 we observe the reduced sensitivity of catalyst B with respect to BTX, while the aromatics depend strongly on the operating conditions. The hydrocarbons and BTX productivities seem acceptable when compared with the reported data for Table I, being 0.59 kg of hydrocarbons/(kg of catalyst·h) and 0.14 kg of BTX/(kg of catalyst·h), respectively. The selectivity in BTX is affected by the feed composition, but it is difficult to obtain a statistical model with an acceptable confidence degree; generally, it is lower when we add steam, when compared with pure methanol as feed.

In Table V we compare the hydrocarbons distribution of the two catalysts with the results of Chang et al. (1981). We note that we have small quantities of durene among the aromatics A_{11}, which is an advantage. Referring to the ethanol conversion to gasoline (Whitcraft et al., 1983), we note that in our case the xylenes are present in a larger

Table IV. Liquid Organic Products Analysis for Catalyst A[a]

expt	C_7H_{16}	C_6H_6	C_7H_8	C_8H_{10}		M	C_9H_{12}			$C_{10}H_{14}$			$C_{11}H_{16}$	$C_{12}H_{18}$
				xyl	o-xyl		PC	HM	AC9	D	ID	P		
1	0.86	0.29	2.12	5.44	1.47	1.65	2.60	0.33	1.39	0.02	0.11	0.11	0.16	0.16
2	2.82	0.66	3.26	6.01	1.98	2.07	1.49	0.44	1.10	0.08	0.16	0.23	0.46	0.63
3	2.28	0.56	3.16	6.40	1.64	2.14	1.29	0.42	0.43	0.06	0.10	0.12	0.23	0.34
4	0.46	0.29	3.22	6.53	1.61	1.35	1.04	0.29	0.33	0.05	0.06	0.13	0.22	0.25
5	0.66	0.59	3.40	5.56	2.14	1.60	1.49	0.30	0.55	0.07	0.11	0.27	0.15	0.45
6	1.34	0.55	3.61	5.31	1.52	0.89	1.02	0.10	0.33	0.03	0.06	0.08	0.21	0.25
7	2.75	0.62	2.94	4.71	1.58	1.20	1.19	0.24	0.39	0.72	0.06	0.12	0.26	0.24
8	3.11	0.56	3.04	5.83	1.70	1.72	1.37	0.32	0.52			0.19	0.26	0.30
9	0.01	0.00	0.09	2.75	0.63	1.11	1.58	0.22	0.68	0.09	0.05	0.15	0.11	0.29
10	0.03	0.05	0.66	4.27	1.15	0.79	1.29	0.14	0.34	0.06	0.04	0.10	0.19	0.24
11	0.29	0.00	0.00	2.10	0.31	0.84	0.88	0.31	0.53	0.07		0.12	0.08	0.16
12	0.03	0.00	0.54	5.16	1.19	1.18	1.00	0.22	0.32	0.10		0.09	0.16	0.19
13	0.08	0.00	0.23	2.92	0.60	0.98	1.28	0.28	0.42	0.11		0.09	0.07	0.17
14	0.14	0.00	0.60	3.86	0.84	1.07	1.08	0.17	0.36	0.06	0.03	0.08	0.01	0.14
15	0.03	0.00	0.32	2.94	0.65	0.82	0.81	0.15	0.25	0.07		0.10	0.11	0.18
16	0.42	0.00	0.64	3.79	0.69	1.08	1.32	0.36	0.54	0.12		0.09	0.06	0.13
17	0.17	0.00	1.38	5.45	1.36	1.02	2.49	0.13	0.31	0.10		0.08	0.13	0.20
18	0.23	0.00	0.45	5.02	0.71	1.80	1.40	0.53	0.59	0.13		0.14	0.11	0.20
19	0.23	0.00	0.70	5.69	0.87	2.37	1.73	0.70	0.69	0.32			0.10	0.21
20	0.01	0.00	0.18	5.10	1.34	2.20	1.72	0.48	0.53	0.23	0.01	0.23	0.28	0.40
21	0.32	0.00	0.66	4.58	0.62	0.51	1.52	0.64	0.90	0.12	0.01	0.13	0.05	0.12
22	0.03	0.00	0.86	5.00	1.45	1.14	1.23	0.21	0.31	0.11		0.11	0.16	0.20
23	0.01	0.00	1.03	5.16	1.55	1.07	1.36	0.16	0.33	0.11		0.16	0.16	0.19
24	0.00	0.00	0.27	2.46	0.78	1.73	3.58	0.60	1.89	0.30	0.32	0.57	1.05	1.51
25	0.05	0.00	0.24	4.66	0.86	2.43	1.87	0.59	0.67				0.12	0.19
26	0.24	0.00	1.18	6.15	1.08	1.67	1.22	0.33	0.53	0.00	0.00	0.10	0.08	0.16
27	0.26	0.00	1.37	6.22	1.12	1.93	1.44	0.47	0.33	0.12		0.13	0.09	0.18

[a] The following symbols or abbreviations are used: C_7H_{16}, heptane; C_6H_6, benzene; C_7H_8, toluene; xyl, m-xylene + p-xylene; o-xyl, o-xylene; M, mesitylene; PC, pseudocumene; P, prehnitene; ID, isodurene; D, durene; other C_9 aromatics; AC9, hemimethylene; HM, pseudocumene; $C_{11}H_{16}$, pentamethylbenzene; $C_{12}H_{18}$, hexamethylbenzene.
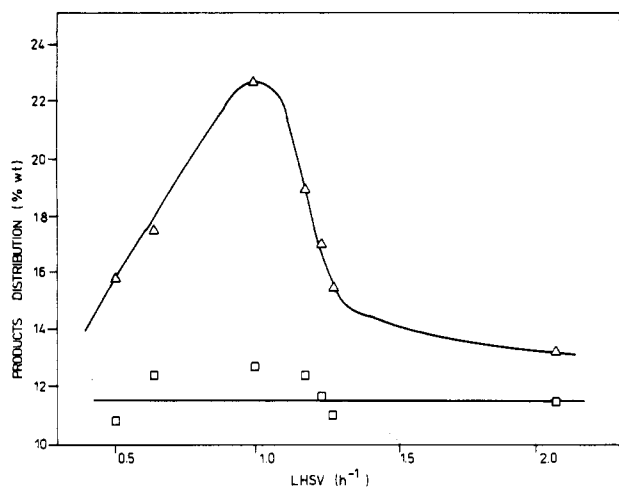
Figure 5. Aromatics and BTX performances for catalyst B, $T = 375$ °C and 100% methanol as feed: ($\triangle$) aromatics; ($\square$) BTX.

Table V. Hydrocarbons Distribution, wt %

product	catalyst A	catalyst B	ZSM-5 catalyst, Chang et al. (1981)
CH_4	2.24	0.63	1.00
C_2H_6	0.93	0.30	0.60
C_2H_4	1.58	5.02	0.50
C_3H_8	21.69	9.68	16.20
C_3H_6	2.52	6.52	1.00
C_4	22.54	18.73	25.50
C_5, C_6^+	9.64	16.30	14.00
C_6H_6	1.37	0.00	1.70
C_7H_8	7.77	6.58	10.50
A_8	17.70	22.88	18.00
A_9	9.05	11.14	7.5
A_{10}	1.45	1.00	3.3
A_{11}	0.36	0.85	0.2
A_{12}	1.16	0.17	0.2

amount and the predominant paraffins are C_3–C_5 instead of C_5–C_8. Comparison with the products distribution from cracking and reforming shows that there is no special problem concerning the separation of products resulting from the methanol conversion.

For catalyst A we may observe that the region between 380 and 415 °C and LHSV = 1.1 h^{-1} and 1.6 h^{-1} with pure methanol as feed is a region with the amount of BTX above 11%. For catalyst B, the corresponding region covers virtually the whole range investigated, that is, the region between 325 and 425 °C and LHSV = 0.5 h^{-1} and 1.75 h^{-1}. To give a better insight into the spatial configuration of the response surfaces, we have computed the curvature radia (Braemer and Kerbrat, 1976) predicted by the two models at the optimum point. The ratio of their total curvature is $K_A/K_B = 10.34$ and of their mean curvature is $H_A/H_B = 3.39$. For catalyst B, the area in the

LHSV–temperature plane for which the BTX amount exceeds 11% is 2.79 times larger than for catalyst A. It seems that catalyst B presents a plateau region with the BTX amount above 11%. This reduced sensitivity with respect to the operating conditions could be an advantage of technical nature for large industrial plants.

Conclusions

We have developed a catalyst for BTX synthesis that because of its relatively stable performance may dampen the usual industrial fluctuating conditions encountered in a fluid bed. We do not conclude that the reduced sensitivity with respect to the operating conditions is due solely to the crystalline structure, this subject being left for further research. Moreover, this catalyst produces hydrocarbons with a low durene content.

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