

Decomposition and Aromatization of Ethanol on ZSM-Based Catalysts

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The adsorption, desorption, and reactions of ethanol have been investigated on pure and promoted ZSM-5 catalysts. FTIR spectroscopy indicated the formation of a strongly bonded ethoxy species on ZSM-5(80) at 300 K. TPD experiments following the adsorption of ethanol on both ZSM-5 and Mo₂C/ZSM-5 have shown desorption profiles corresponding to unreacted ethanol and decomposition products (H₂O, H₂, CH₃CHO, C₄H₁₀O, and C₂H₄). The main reaction pathway of ethanol on pure ZSM-5 is the dehydration reaction yielding ethylene, small amounts of hydrocarbons, and aromatics. Deposition of different additives, such as Mo₂C, ZnO, and Ga₂O₃ on zeolite, greatly promoted the formation of benzene and toluene at 773–973 K, very likely by catalyzing the aromatization of ethylene formed in the dehydration process of ethanol. Separate studies of the reaction of ethylene revealed that the previous additives markedly enhanced the selectivity and the yield of aromatics on ZSM-5.

1. Introduction

Levy and Boudart^{1,2} proposed first that the expensive Pt metal catalysts could be replaced by much cheaper metal carbides. This idea has been confirmed by several studies using mainly Mo₂C and W₂C.^{3,4} As it turned out recently, Mo₂C can not only replace Pt metals, but it exhibits a unique catalytic property, which is not possessed by Pt catalysts. Whereas methane decomposes to hydrogen and carbon on supported metals, it is converted to benzene on Mo₂C/ZSM-5 at 973 K with 70–80% selectivity at 10–15% conversion.^{5–14} This research was initiated by Chinese workers, who found that MoO₃/ZSM-5 can aromatize methane at 973 K with a high selectivity.¹⁵ The subsequent paper disclosed the reduction of MoO₃, the deposition of a large amount of carbon during the reaction, and the long induction period of the formation of benzene.¹⁶ A possible reason for the advantageous behavior of Mo₂C is that it acts as a mild activator toward methane: accordingly, the hydrocarbon fragments formed in the activation process have a certain lifetime to recombine into ethylene, the aromatization of which proceeds readily on the acidic sites of the zeolites.¹⁶ This favorable behavior of Mo₂C was later utilized in the aromatization of several higher alkanes.^{17–19}

Ethanol obtained from biomass fermentation is another raw material, which can be the source of H₂ or can be converted into more valuable hydrocarbon compounds. Previous studies revealed that the dehydration of ethanol occurs readily over zeolites of high Brønsted acidity.^{20–30} At higher temperatures, formation hydrocarbons and even aromatics have been observed.^{23–30} In the present work, we performed an extensive study on the aromatization of ethanol on a promoted ZSM-5 catalyst.

2. Experimental Procedures

2.1. Methods. Catalytic reactions were carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting

of a quartz tube (8 mm i.d.) connected to a capillary tube.^{7,19} The flow rate was, in general, 40 mL/min, but the reaction was also studied at different space velocities. The carrier gas was Ar, which was bubbled through ethanol at room temperature: its content was ~9.0%. Generally, 0.3 g of loosely compressed catalyst sample was used. In the case of the study of ethylene, we applied the same experimental procedures. The ethylene content of the carrier gas was ~10.0%. Reaction products were analyzed with two gas chromatographs: a HP 5890 equipped with PORAPAQ Q+S packed column (reaction of ethanol) and a HP 4890 equipped with PORAPAQ Q+S and 30 m long HP-PLOT Al₂O₃ column (reaction of ethylene).

FTIR spectra of adsorbed gases were recorded with a Biorad (Digilab. Div. FTS ISS) instrument with a wavenumber accuracy of ± 4 cm⁻¹. All the spectra presented are difference spectra. Temperature programmed desorption (TPD) curves were taken by a quadrupole mass spectrometer. The adsorption of ethanol (10% in helium carrier gas) was flown through the catalyst for 15 min at 300–304 K. The catalyst was then purged with pure He to remove any weakly adsorbed ethanol and lines for 90 min. The gas flow was introduced to the UHV system via a quartz capillary tube, which contained a leak UHV valve. A constant operating pressure of 8×10^{-6} Torr was maintained in the system during all TPD runs. The TPD experiment was performed using 40 mL/min He flow and a heating rate of 10 K/min from 300 to 873 K. Temperature programmed reaction (TPR) measurements were carried out with the used catalysts. The solid samples were cooled in flowing argon and then heated in a H₂ stream with a rate of 5 K/min, and the hydrocarbons formed were determined by gas chromatography.

2.2. Materials. Mo₂C-containing catalysts were the same as was used in the previous study.¹⁹ Unsupported Mo₂C was prepared by the carburization of MoO₃ (products of ALFA AESAR) by C₂H₆/H₂.³¹ The oxide was heated under a 10% v/v C₂H₆/H₂ gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min. Afterward, the sample was cooled to room temperature under argon. The carbide was passivated in flowing 1% O₂/He at 300 K. The surface area of Mo₂C is 20

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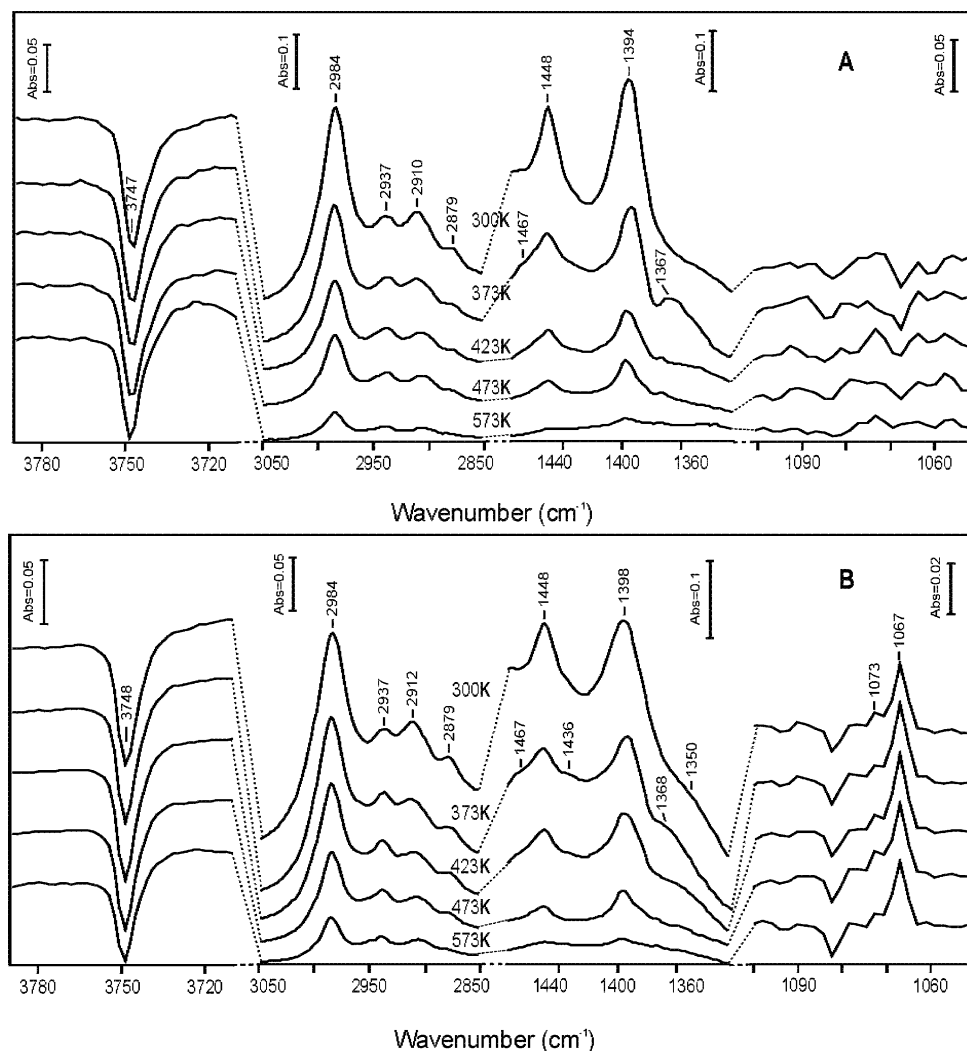


Figure 1. FTIR spectra of ZSM-5(80) (A) and 2% Mo₂C/ZSM-5(80) (B) following ethanol adsorption (1.5 Torr) at 300 K and after subsequent heating under continuous degassing.

m²/g. According to XRD analysis, Mo₂C prepared in this was in the β form. Supported Mo₂C catalysts have been made in similar ways by the carburization of MoO₃-containing supports with a C₂H₆/H₂ gas mixture. The MoO₃/support samples were prepared by impregnating the support with a basic solution of ammonium heptamolybdate to yield 2 wt % MoO₃. The same impregnation methods were used for the preparation of ZnO-, Ga₂O₃-, and Re-promoted ZSM-5. In these cases, the starting compounds were Zn(NO₃)₂, Ga(NO₃)₃, and (NH₄)₂ReO₄. The suspension was dried and calcined at 863 K for 5 h. The following materials were used as supports: ZSM-5 (Zeolyst Intern. Ltd.) with a SiO₂/Al₂O₃ ratio of 80 and 280 and a BET area of 425 and 400 m²/g, respectively. To remove the excess carbon deposited on Mo₂C during the preparation, the catalyst was reduced before the catalytic measurements in situ at 873 K in a H₂ stream for 60 min. The gases used were of commercial purity (Linde). All the catalyst samples were characterized previously by XPS. The binding energy for Mo(3d_{5/2}) showed some slight variations with different samples, but it fell in the range of 227.7–228.2 eV and for C(1s) was 283.8 eV. These values are consistent with those attributed to Mo₂C.^{7, 32,33}

3. Results and Discussion

3.1. FTIR and TPD Measurements. Figure 1 shows the IR spectra of ZSM-5(80) following the adsorption of ethanol at

300 K for 10 min and after subsequently heating the sample to higher temperatures under continuous evacuation. This heat treatment caused a gradual attenuation of absorption bands without any significant shift or appearance of new spectra features. The bands observed at 300 K are collected in Table 1, which also contains the characteristic IR features of various compounds detected following the surface reaction of the adsorbed ethanol.^{34–43} We obtained practically the same results for the Mo₂C/ZSM-5(80) catalyst.

TPD spectra for various products are presented in Figure 2. In the case of pure ZSM-5(80), we found the formation of the following compounds: ethanol (T_p = 353 and 455 K), acetaldehyde (T_p = 354, 455, and 512 K), H₂O (T_p = 354, 470, and 523 K), C₂H₄ (T_p = 353 and 516 K), and H₂ (T_p = 352, 456, and 516 K). A small amount of diethyl ether (T_p ~ 462 K), not shown in Figure 2, was also detected in the desorbing products. Calculations showed that the chemicals desorbed in the same peaks as ethanol were its fragments. When 2% Mo₂C and other promoters were deposited on ZSM-5(80), only slight variations were experienced in the peak temperatures and in the amount of desorbed compounds. A new feature is that a small quantity of toluene (T_p = 585–625 K) also desorbed from the promoted zeolite. Other aromatics were not detected, which is very likely due to the desorption of most of the ethanol at lower temperatures.

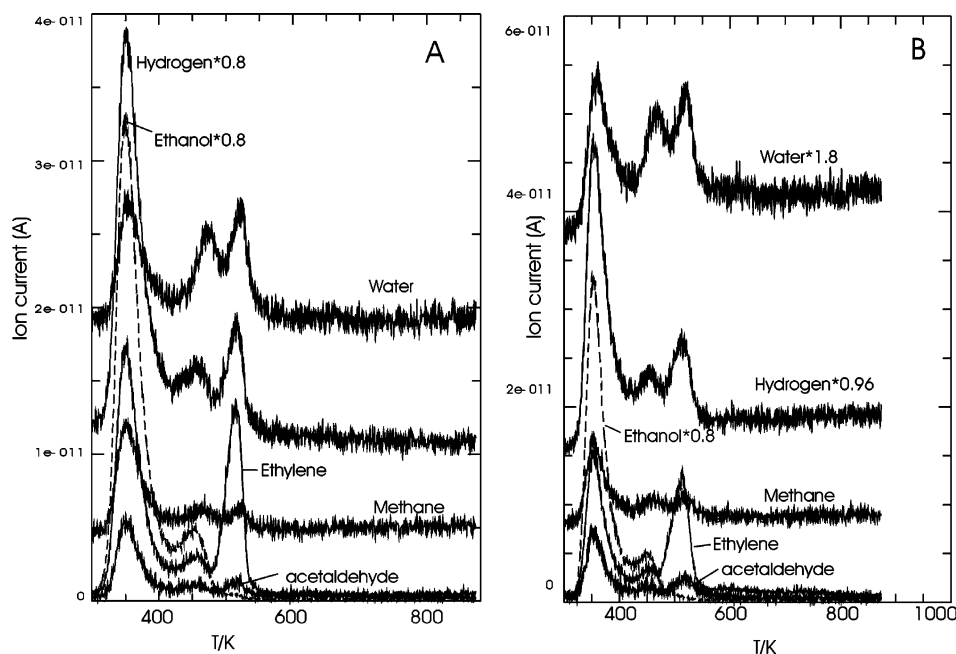
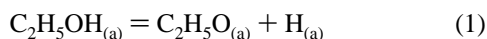


Figure 2. TPD spectra obtained following ethanol adsorption at 300 K on ZSM-5(80) (A) and 2% Mo₂C/ZSM-5(80) (B).

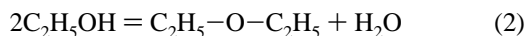
TABLE 1: Characteristic Absorption Bands Following Ethanol Adsorption on Various Solids at 300 K

mode	CeO ₂ ³⁴	SiO ₂ ³⁵	ZSM-5 (80)	Mo ₂ C/ZSM-5 (80)	SiO ₂ ³⁸	di-σ-C ₂ H ₄ + Mo ₂ C/Mo(110) ⁴⁰
			this paper			
			ethanol		acetaldehyde	ethylene
$\nu_{as}CH_3$	2960	2982	2937, 2984	2937, 2984	2988	
$\nu_{as}(CH_2)$						3010
ν_sCH_3		2932	2937	2937		
ν_aCH_3					2914	
ν_sCH_2	2836		2910	2912		2935
CH ₂ -scissor						1395
δCH_2	1473	1496, 1484				
$\delta_{as}CH_2$			1478			
$\delta_{as}CH_3$		1452	1448	1448, 1436	1448	
δ_sCH_3	1383	1378	1394*	1398		
δCH					1388	
δ_aCH_3					1356	
CH ₂ -wag(s)						1180
νCC						1035
νCO	1107, 1057			1067	1724	
CH ₂ -twist(s)						905
CH ₂ -rock						635
ν_sMC						380

Infrared spectroscopic studies disclosed that ethanol strongly interacts with pure ZSM-5(80). The negative feature in the OH frequency range indicates an interaction of ethanol with the OH groups of the sample. The absorption bands detected (Table 1) suggest that most of the adsorbed ethanol dissociates on ZSM-5(80) at 300 K



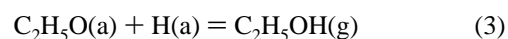
to give ethoxy species. In addition, the coupling of two adsorbed ethanols may also occur,



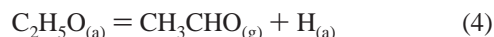
yielding diethyl ether. Heating the adsorbed layer caused no significant spectral changes, indicating the transformation of adsorbed ethoxy species into other surface compounds. According to FTIR spectroscopic measurements, adding Mo₂C to ZSM-5 influenced only little these features, suggesting that mainly the species adsorbed on ZSM-5 determine the charac-

teristics of IR spectra. One important difference is the appearance of the peaks at 1073 and 1067 cm⁻¹ due to a C–O bond, which were very weak or not observable on pure ZSM-5. Note that we could not detect absorption bands of ethylene, suggesting that its desorption immediately occurs upon formation. Analyzing the spectra obtained on other promoted ZSM-5(80) led us to the same conclusion. It appears that the small amount (2%) of additive cannot influence appreciably the adsorptive properties of ZSM-5(80) of large surface areas.

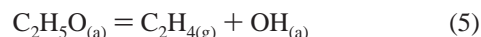
This behavior was also reflected in the result of TPD measurements. From undoped ZSM-5(80), the desorption of ethanol, ethylene, acetaldehyde, water, and hydrogen was observed. We assume that the desorption of ethanol is mostly the result of the associative reaction of adsorbed ethoxy and hydrogen



A fraction of the ethoxy species is transformed into acetaldehyde,



which desorbed with a $T_p = 512$ K. Another one is converted into ethylene,



which desorbs with $T_p = 516$ K.

3.2. Catalytic Reaction of Ethanol. 3.2.1. Effects of ZSM-5-Containing Catalysts. The reaction of ethanol on pure ZSM-5(80) occurred at very low temperatures, 373–423 K (conversion is 2.5–10%). The initial products were diethyl ether and water. From 473 K, the formation of the diethyl ether diminished to a low level and completely ceased above 573 K. At the same time, ethylene and water became the major products, and their formation continuously increased with the temperature (Figure 3). The selectivity of ethylene increased to ~55% at 773 K and to ~73% at 873 K. The formation of propylene also occurred above 473 K. It reached its maximum selectivity, 18–20%, at

673 K and then decreased. Aromatics, toluene, benzene, xylene, and C_9 , were also produced from 523 K. Their total selectivity remained at low levels in the temperature range of 573–873 K: the highest value measured was 12–13%. The conversion of ethanol approached 95–98% even at 523 K. Similar measurements have been performed with ZSM-5(280). This zeolite was somewhat less active at lower temperatures than ZSM-5(80), but almost total conversion was attained at and above 573 K. At 373–473 K, diethyl ether was again the major product (Figure 3). At and above 523 K, the formation of ethylene became dominant, and it was almost the sole product above 573 K with a selectivity of 90–95%. Aromatics evolved with low selectivity, less than 2–2.5%. As the number of Brønsted sites is much lower on ZSM-5(280) as compared to those present on ZSM-5(80), the lower dehydration activity of ZSM-5(280) supports the idea that the acidic centers of zeolite play an important role in the dehydration of ethanol. As will be discussed later, the lower acidity is also responsible for the

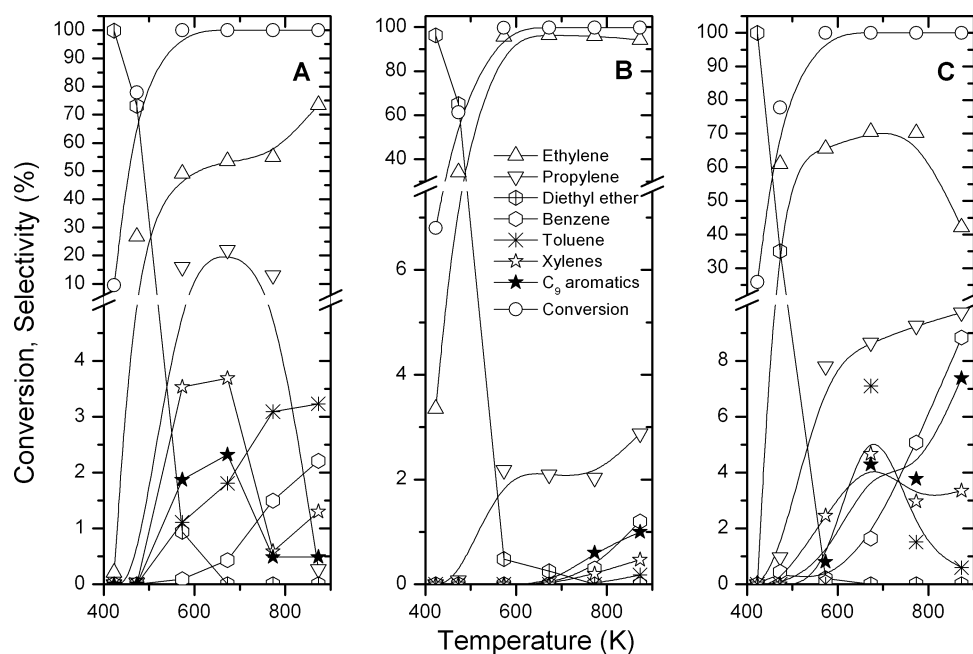


Figure 3. Reaction of ethanol on ZSM-5(80) (A), ZSM-5(280) (B), and 2% $\text{Mo}_2\text{C}/\text{ZSM-5(80)}$ (C).

TABLE 2: Main Results Obtained in Reaction of Ethanol on Various Catalysts

catalyst	T (K)	selectivity (%)									
		CO	methane	ethylene	ethane	propylene	benzene	toluene	xylene	C_9^+	Σ aromatics
ZSM-5(80)	773	0.48	0.42	53.14	0.74	19.80	1.86	4.91	4.71	1.62	13.10
	873	0.37	0.82	73.53	1.02	12.94	2.21	3.23	1.30	0.49	7.23
ZSM-5(280)	773	0.72	0.11	89.54	0.23	3.61	0.22	1.26	1.65	0.50	3.62
	873	0.51	0.27	93.21	0.36	3.06	0.41	0.58	0.18	0.00	1.17
2% $\text{Mo}_2\text{C}/\text{ZSM-5(80)}$	773	0.88	0.51	60.31	2.10	8.42	4.26	9.19	7.73	2.47	23.65
	873	3.09	8.16	42.23	1.69	9.73	8.83	7.38	3.35	0.59	20.15
2% $\text{Mo}_2\text{C}/\text{ZSM-5(280)}$	773	1.28	0.27	85.80	0.96	3.69	0.85	2.08	1.96	0.47	5.36
	873	0.90	0.51	91.26	0.81	1.87	1.25	0.96	0.62	0.08	2.91
2% $\text{Re}/\text{ZSM-5(80)}$	773	6.03	0.92	58.03	3.02	12.03	1.91	5.22	4.76	1.68	13.57
	873	31.46	4.38	59.38	8.29	4.09	3.52	2.80	0.98	0.00	7.30
2% $\text{Ga}_2\text{O}_3/\text{ZSM-5(80)}$	773	1.10	0.92	48.33	3.44	6.54	9.34	14.66	9.11	1.80	35.00
	873	6.59	3.26	36.86	4.97	3.23	22.44	16.07	4.04	0.69	43.25
2% $\text{ZnO}/\text{ZSM-5(80)}$	773	0.86	4.17	56.67	1.49	6.99	5.78	9.16	4.90	1.73	21.57
	873	2.04	6.59	66.56	1.60	3.78	6.10	4.20	0.95	0.28	11.54
ZSM-5(80) + 2% $\text{Mo}_2\text{C}/\text{ZSM-5(80)}$	773	0.58	0.60	44.91	1.28	17.05	3.77	9.81	8.51	2.72	24.81
	873	0.79	1.35	67.58	1.34	10.71	6.38	6.14	2.25	0.35	15.11
ZSM-5(80) + 2% $\text{Ga}_2\text{O}_3/\text{ZSM-5(80)}$	773	0.77	1.54	29.33	2.76	10.94	11.00	17.93	12.65	3.28	44.85
	873	5.67	3.69	33.03	4.37	4.42	20.47	18.57	5.95	1.66	46.66
ZSM-5(80) + 2% $\text{ZnO}/\text{ZSM-5(80)}$	773	0.64	3.17	33.28	1.29	14.26	10.15	14.61	9.58	1.96	36.29
	873	1.89	3.89	58.74	1.22	10.93	8.42	7.42	2.24	0.56	18.64

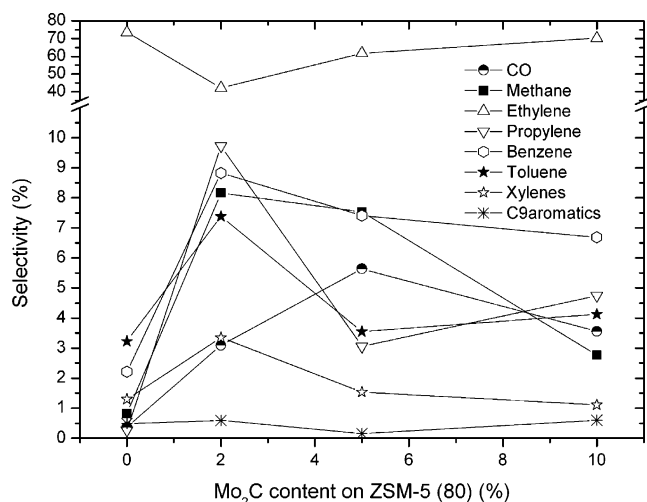


Figure 4. Effects of Mo_2C content of ZSM-5(80) on the selectivities of various products formed in the reaction of ethanol at 873 K.

low selectivity of the formation of aromatics on ZSM-5(280) as compared to that measured on ZSM-5(80).

More attractive results were obtained when Mo_2C was combined with zeolites. In the case of ZSM-5(80), 2% Mo_2C left the conversion of ethanol practically unchanged. The formation of diethyl ether dropped to a low level even at 473 K (Figure 3), but the selectivities for all aromatics increased by 60–80%. The optimum temperature of the formation of these compounds appeared to be 873 K. At higher temperatures, the capability of the catalyst to produce aromatics gradually decayed. Raising the loading of Mo_2C led to the decay of the formation of C_6 – C_9 aromatics. Deposition of Mo_2C on ZSM-5(280) exerted a similar favorable influence on the selectivity of aromatics. Some characteristic data for the effect of Mo_2C content of ZSM-5(80) are plotted in Figure 4.

The selectivity of aromatics was somewhat improved by depositing 2% ZnO on ZSM-5(80) as compared to pure zeolite, but the highest selectivity value, ~35–43%, was attained on 2% $\text{Ga}_2\text{O}_3/\text{ZSM-5(80)}$ (Figure 5). At 773 K, benzene, toluene, and xylene formed with almost equal selectivities; at 873 K, benzene was the dominant aromatic compound. At 973 K, however, the formation of all aromatics was reduced very likely due to the deposition of some kind of coke. As the dehydration

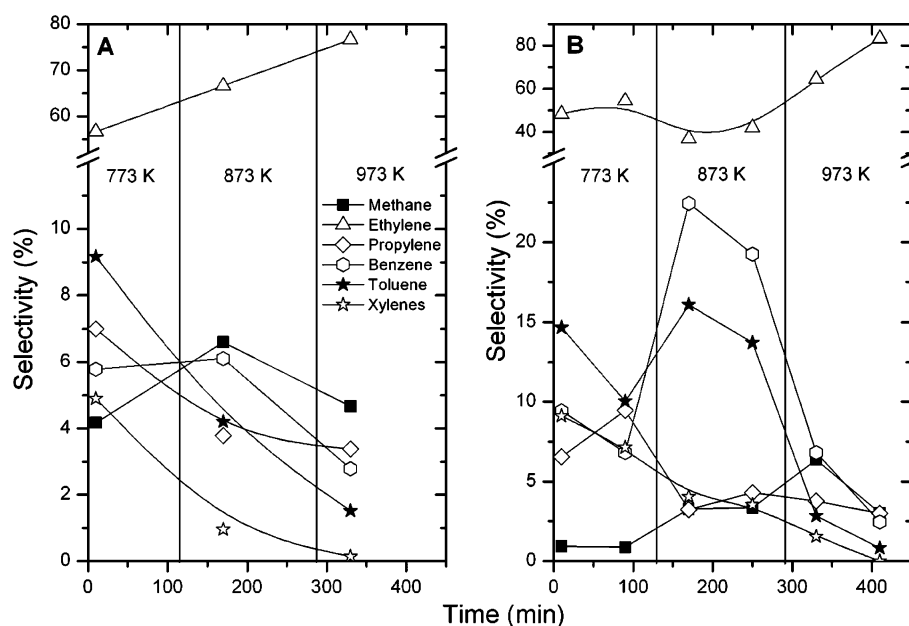


Figure 5. Reaction of ethanol over 2% ZnO/ZSM-5(80) (A) and 2% $\text{Ga}_2\text{O}_3/\text{ZSM-5(80)}$ (B) catalysts at different temperatures.

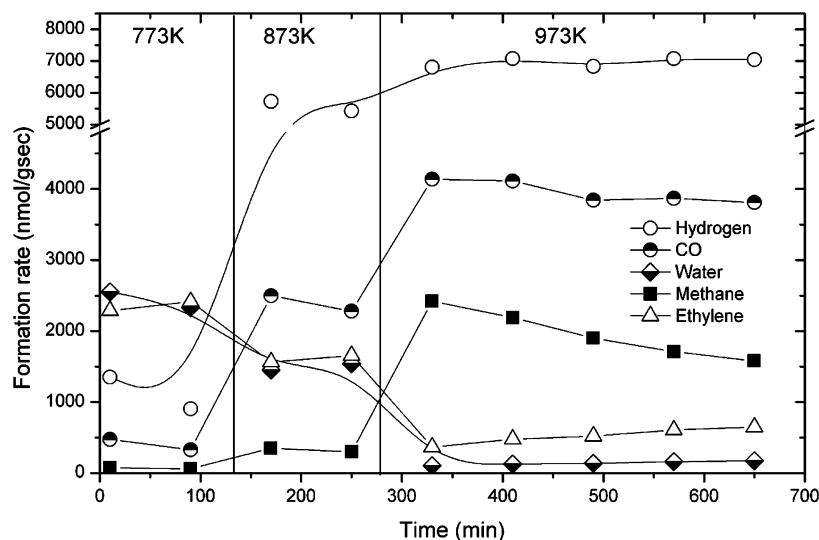


Figure 6. Reaction of ethanol over 2% Re/ZSM-5(80) catalysts at different temperatures.

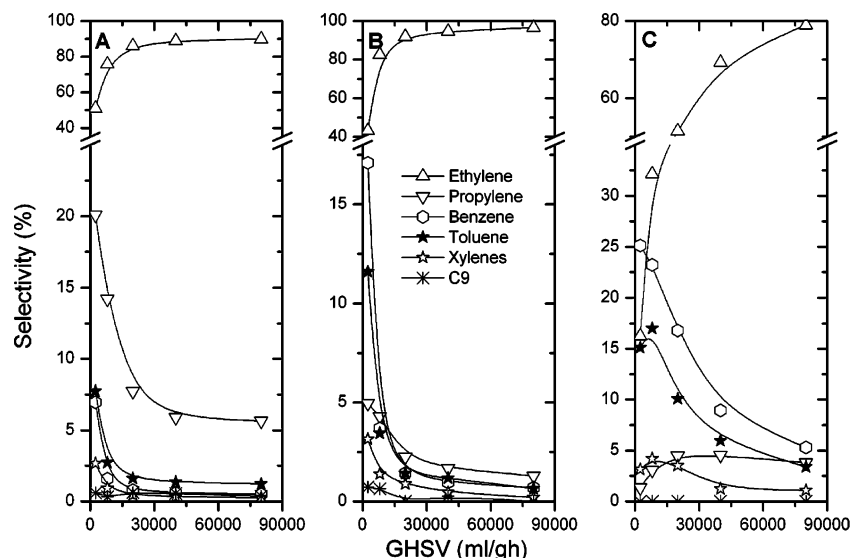


Figure 7. Effects of space velocity on the reaction of ethanol over ZSM-5(80) (A), 2% Mo₂C/ZSM-5(80) (B), and 2% Ga₂O₃/ZSM-5(80) (C) at 873 K.

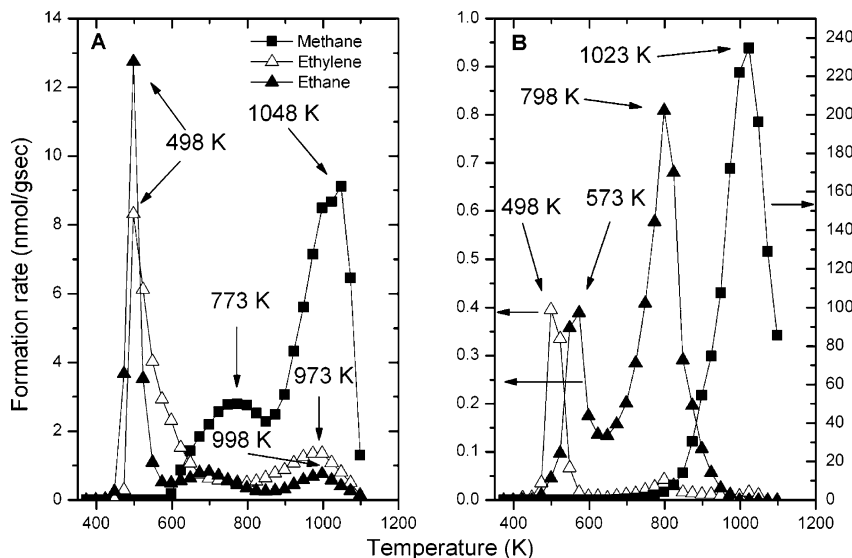


Figure 8. Formation of hydrocarbons in the TPR measurements following ethanol reaction at 823 K for 180 min over ZSM-5(80) (A) and 2% Mo₂C/ZSM-5(80) (B).

of ethanol occurred (e.g., the formation of ethylene proceeds easily even on pure ZSM-5), the favorable effect of all previous promoters can be obviously attributed to their ability to catalyze the aromatization of ethylene (see section 3.4). Important data are collected in Table 2.

In contrast to the previous promoters, adding 2% Re to ZSM-5 led to the alteration of the product distribution at higher temperatures. The formation of ethylene gradually decayed, and more H₂ and CO appeared in the products. This change was reflected in the rate of formation of water, which was 2552 nmol/gs at 773 K and decreased to 1450 nmol/gs at 873 K and to ~130 nmol/gs at 973 K. A dramatic decay occurred in the formation of ethylene at 973 K, when a significant amount of methane was produced (Figure 6). Accordingly, the presence of the Re metal dramatically altered the reaction pathway at high temperature and the reaction between ethylene and water



to yield CO, H₂, and CH₄ comes into prominence. Similar results were obtained when various Pt metals were deposited on ZSM-5. It should be noted that the Re differs from the Pt metals, as

Re on ZSM-5 could catalyze the aromatization of methane, although its efficiency was less than that of Mo₂C/ZSM-5.^{45,46} It appears that the presence of water could markedly change the catalytic behavior of Re.

Figure 7 shows the effect of space velocity on the selectivity of various products on pure and promoted ZSM-5(80) at 873 K. The general feature is that the selectivity of aromatic compounds is the highest at the lowest flow rate. Their selectivity gradually decreased with the rise of space velocity together with that of other products. An exception is ethylene, the dominant product of the reaction, the selectivity of which increased with the flow rate of the ethanol + argon gas mixture. The results strongly suggest that the aromatics are produced in secondary processes. Note that the formation of diethyl ether and acetaldehyde has not been identified on either sample. An important finding is that the selectivity of the total aromatics was always much higher on promoted ZSM-5(80) as compared to pure zeolite.

3.2.2. TPR Measurements for Used Catalysts. As a significant deactivation of all catalysts has been experienced at higher temperatures, it seemed worthwhile to determine the amount and reactivity of coke deposited on the catalysts. Following the reaction for 3 h at 873 K, the samples were cooled to 373 K in

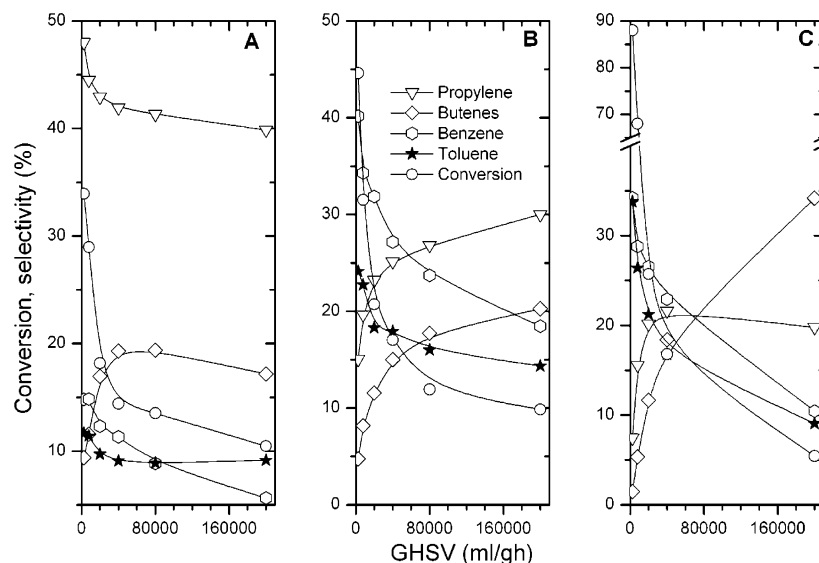


Figure 9. Effects of space velocity on the reaction of ethylene over ZSM-5(80) (A), 2% Mo₂C/ZSM-5(80) (B), and 2% Ga₂O₃/ZSM-5(80) (C) at 873 K.

TABLE 3: Characteristic Data for Reaction of Ethylene on Different Catalysts^a

T (K)	catalyst	selectivity (%)														
		water %	conv %	methane	ethane	prop ane	propene	butene	pentane	pentene	benzene	toluene	m,p-xylene	o-xylene	aromatics	yield of aromatics
773	H/ZSM-5(80)	0	46.68	0.9	1.6	5.0	47.2	19.7	2.7	6.0	2.3	7.0	4.5	1.4	15.2	7.1
873	H/ZSM-5(80)	0	24.84	3.6	3.1	2.4	44.5	11.6	0.5	2.2	14.9	11.4	2.6	0.8	29.7	7.4
773	2% Mo ₂ C/ZSM-5(80)	0	36.86	0.7	1.6	1.7	42.4	17.8	2.3	8.3	3.4	8.8	5.6	1.6	19.3	7.1
873	2% Mo ₂ C/ZSM-5(80)	0	41.01	4.4	2.0	1.8	26.3	8.6	0.5	1.2	28.3	19.4	3.6	1.1	52.4	21.5
773	2% Mo ₂ C/ZSM-5(80)	3	30.22	0.5	3.5	1.6	40.6	16.7	2.2	8.0	3.1	8.9	7.2	2.0	21.2	6.4
873	2% Mo ₂ C/ZSM-5(80)	3	20.18	2.3	5.1	0.4	31.7	9.8	0.6	1.7	19.6	18.5	6.0	1.8	45.9	9.3
773	2% Mo ₂ C/ZSM-5(80)	14	30.7	0.4	2.4	1.9	41.5	16.5	2.4	7.7	2.8	8.3	8.0	1.9	21.0	6.4
873	2% Mo ₂ C/ZSM-5(80)	14	17.1	2.0	4.4	0.3	33.1	10.5	0.6	1.4	19.1	18.1	5.9	1.7	44.8	7.7
773	2% Re/ZSM-5(80)	0	51.6	0.9	2.3	4.2	40.7	17.9	2.5	6.5	2.9	8.4	4.7	1.5	17.5	9.0
873	2% Re/ZSM-5(80)	0	39.4	3.1	10.9	1.2	23.8	7.0	2.5	6.5	27.8	17.7	3.5	1.1	50.1	19.7
773	2% Zn/ZSM-5(80)	0	81.7	3.6	18.0	1.7	5.5	1.9	0.3	0.4	15.3	31.5	15.1	4.3	66.2	54.1
873	2% Zn/ZSM-5(80)	0	74.5	3.9	22.1	0.4	3.1	1.0	0.5	0.0	37.8	25.7	3.6	1.2	68.3	50.9
773	2% Zn/ZSM-5(80)	3	49.1	4.4	3.1	0.8	17.6	6.0	1.1	2.5	15.0	26.9	12.9	3.7	58.5	28.7
873	2% Zn/ZSM-5(80)	3	65.6	14.2	17.8	0.6	4.3	1.3	0.4	0.1	30.5	23.8	2.8	0.9	58.0	38.0
773	2% Ga/ZSM-5(80)	0	73.5	1.9	2.6	3.2	13.3	4.4	1.4	1.2	14.2	28.6	17.2	4.6	64.6	47.5
873	2% Ga/ZSM-5(80)	0	69.1	3.2	4.4	2.4	8.2	1.7	0.2	0.2	39.3	31.4	5.8	1.8	78.3	54.1
773	2% Ga/ZSM-5(80)	3	48.8	1.8	5.1	1.8	18.2	6.1	2.1	2.5	12.5	25.2	12.1	3.6	53.4	26.1
873	2% Ga/ZSM-5(80)	3	52.8	4.9	8.5	1.0	8.8	2.1	0.4	0.2	35.4	28.1	4.2	1.3	69.0	36.4
773	2% Ga/ZSM-5(80)	14	56.6	1.8	5.7	2.7	18.3	5.7	2.5	2.1	12.6	23.5	11.5	3.4	51.0	28.9
873	2% Ga/ZSM-5(80)	14	62.2	3.1	9.5	1.4	7.0	1.3	0.3	0.1	36.7	28.4	4.2	1.4	70.7	44.0

^a Data were taken after 60 min on-stream with a specified temperature.

Ar flow and then heated from 373 to 1073 K in a 20 mL/min H₂ stream at a heating ramp of 5 K/min. Some TPR curves are displayed in Figure 8. From ZSM-5(80), the evolution of ethane and ethylene started at 450 K, and T_{\max} occurred at 498 K. The formation of methane began at 600 K and gave two peaks, the smaller one at 773 K and the larger one at 1048 K. High-temperature peaks for ethylene and ethane were also observed at 973 and 998 K, respectively. The amount of coke calculated from the TPR curves is 0.81 mg of C/g_{cat}. Coke deposited on 2% Mo₂C/ZSM-5 showed completely different properties. Low-temperature peaks of ethylene and ethane appeared at 498 and 573 K, respectively. An additional ethane peak was also observed with $T_{\max} = 798$ K. The amount of coke corresponding to these peaks is smaller with 1 order of magnitude as compared to values found in the case of pure H-ZSM-5(80). Formation of methane started at 800 K and resulted only in one peak with $T_p = 1023$ K. The total amount of carbon deposited on 2% Mo₂C/ZSM-5 was calculated to be 4.71 mg of C/g_{cat}. Note that similar TPR measurements with untreated and unused 2% Mo₂C/ZSM-5(80) resulted in 1.63 mg of C/g_{cat}.

3.2.3. Effects of Pure and Silica-Supported Mo₂C. Some experiments also have been performed with pure Mo₂C and 10%

Mo₂C/SiO₂ catalysts. The reason was that whereas the first one catalyzed alone the aromatization of C₆–C₈ alkanes,^{19,43,44} the second one exhibited aromatization even in the case of methane.¹⁶ Mo₂C prepared by the C₂H₆/H₂ gas mixture exhibited a high activity toward ethanol. Its decomposition was observed even at 423 K, when the conversion was ~10%. The main products at 473–573 K were water and diethyl ether. With the rise of the temperature, the selectivity of diethyl ether decreased from ~80% (473 K) to ~2% (673–873 K). In contrast, the formation of hydrogen, water, and ethylene became dominant: the selectivity of the latter was ~50 at 773 K and 83% at 873 K. Interestingly, acetaldehyde was also formed in this temperature range with a selectivity of 20–10%. Other compounds appearing were ethane, methane, propylene, and butenes. Aromatics were not identified. The conversion of ethanol increased when Mo₂C was deposited on silica. Almost 75–85% conversion was attained at 773 K. The major products formed were ethylene with a selectivity of 30–45% and acetaldehyde, $S = 37$ –25%. While the selectivity of ethylene increased with the temperature, that of acetaldehyde dramatically decreased. Other products were CO, methane, and ethane. Aromatics and diethyl ether appeared only in minor amounts; their total selectivity remained below

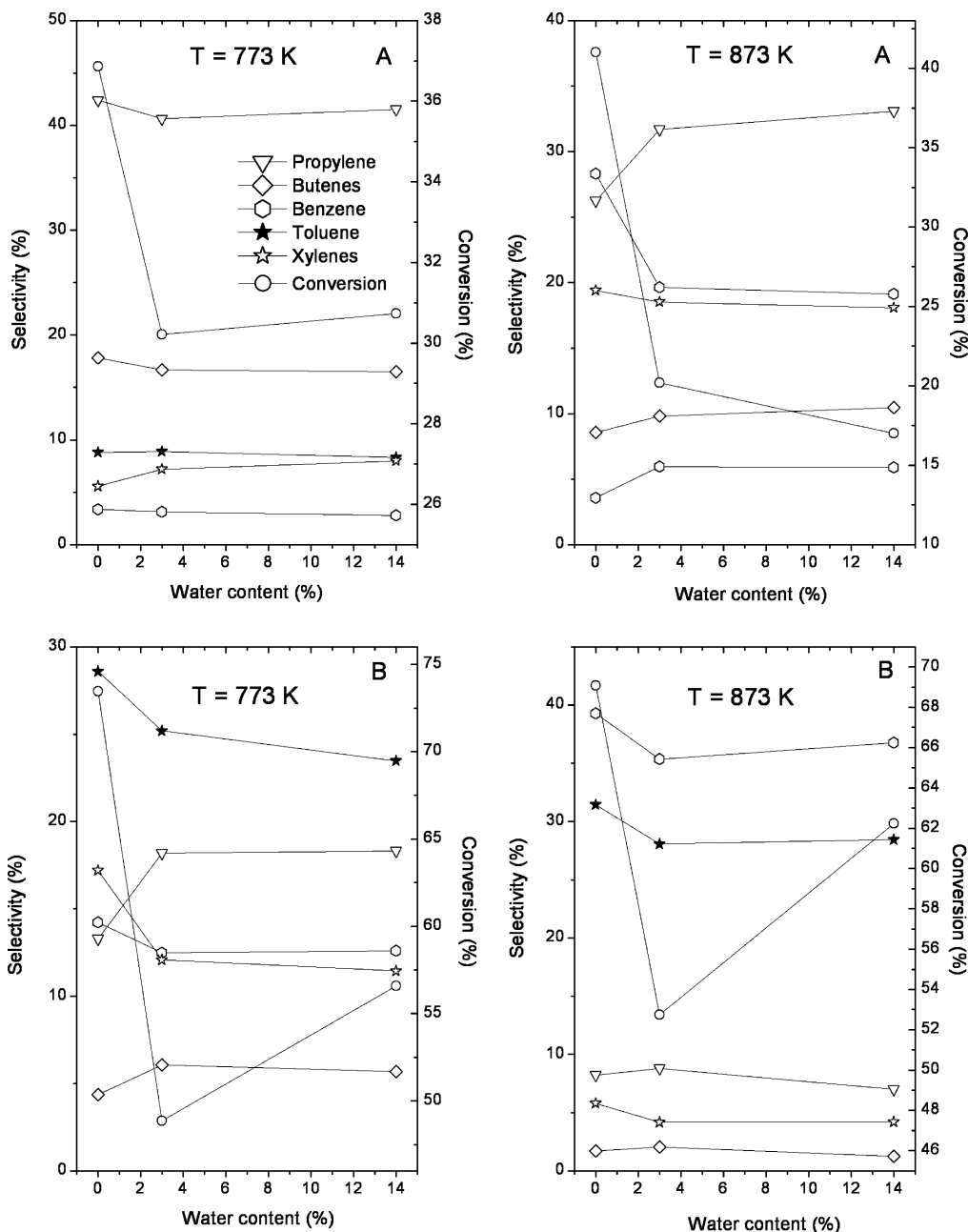


Figure 10. Effects of water on the conversion of ethylene and on the selectivity of some compounds at different temperatures. 2% Mo₂C/ZSM-5(80) (A) and 2% Ga₂O₃/ZSM-5(80) (B).

1.0–1.5%. Similar features were observed when the Mo₂C content was lowered to 1%.

3.3. Catalytic Reactions of Ethylene. As a large amount of ethylene was found in the products, in separate experiments, we examined its reaction on the catalyst samples used in this work. The following procedure was applied. The reaction was started at 773 K where it was held for 110 min on-stream, after that, the temperature was raised to 873 K and maintained for another 110 min. Afterward, the reaction was followed 973 K for 200 min. A general feature valid for all catalyst samples is the occurrence of a slow deactivation at 773 K and a much faster one at 873–973 K. Ethylene is aromatized readily on ZSM-5(80) yielding benzene, toluene, and xylene with decreasing selectivities. Whereas their total selectivity was relatively low, ~15%, on pure ZSM-5(80) at 773 K, it increased to 29.7% at 873 K and to 56% at 973 K. Other main products were propylene and 1-butene. Deposition of 2% Mo₂C on this zeolite

modified the conversion values and influenced the product distribution as well. The aforementioned selectivity values increased to 29, 59, and 77%, respectively. The enhanced formation of aromatics occurred at the expense of alkanes and alkenes. Mo₂C/ZSM-5(80) was found to be a rather stable catalyst at 773–873 K, but it deactivated rapidly at 973 K. The advantageous effect of 2% Re additive to ZSM-5 appeared at 873 K, when the total selectivity of aromatics increased from 29.7 to 50%. This value was even larger at 973 K, when the catalyst gradually lost its activity and aromatizing property. Highest conversion and aromatic selectivities were measured on ZnO- and Ga₂O₃-promoted zeolite. On the latter sample, the rate of deactivation was also the lowest. Important data are collected in Table 3.

For some catalysts, we determined the effect of the space velocity. A general feature is that the selectivities of the aromatics decreased, while those of other major products, propy-

lene, butene, and pentene, increased with a rise of the flow rate. Results obtained for pure and doped ZSM-5(80) are shown in Figure 9.

In the explanation of the aromatization of ethylene, we should take into account that on acidic zeolite, such as ZSM-5, lower alkenes oligomerize through a carbenium-ion mechanism over protonic sites followed by isomerization and decomposition to produce a variety of lower alkanes.⁴⁷ According to the assumption of Poutsma,⁴⁸ aromatics are formed from alkenes by the successive deprotonation and hydride transfer to carbenium ions. As was proposed before adding ZnO and Ga₂O₃ to zeolite, a new route for the activation of ethylene opens.^{47–52} They act as dehydrogenation centers resulting in different products, allylic and other C₃H_y species, which are converted into aromatics. It is very likely that Mo₂C promotes the aromatization of ethylene in a similar way. Data obtained from the variation of the residence time clearly suggest that the formation of aromatics from ethylene also occurs in secondary processes.

As in the dehydration of ethanol, equal amounts of water and ethylene were formed; in the subsequent measurements, we examined the effects of water on the aromatization of ethylene. Some results are shown in Figure 10. In the case of pure ZSM-5(80), the addition of water to ethylene influenced only little the course of the reaction. The situation was different for 2% Mo₂C/ZSM-5(80); when it was due to the marked decay in the conversion, the yield of aromatics became considerably lower. The possible reason is that water interacts with Mo₂C, converting its surface layer into oxy carbide, which reduces its dehydrogenation activity toward ethylene. In the study of the reaction of Mo₂C with water vapor, we observed the evolution of hydrogen from 673 to 700 K, when the Mo–O species was detected by XPS measurements. Water exerted relatively less deterioration on the catalytic performance of ZnO- and Ga₂O₃-promoted ZSM-5(80). Characteristic data concerning the effect of water are also presented in Table 3.

3.4. Use of Two Bed Reactors. As ZSM-5(80) is an effective catalyst for the dehydration of ethanol and the presence of various promoters can markedly promote the aromatization of ethylene, we examined whether we could enhance the formation of aromatics by using two beds of catalyst. This approach was found to be very effective in the case of the aromatization of ethane over the Re/ZSM-5 catalyst.⁵³ In the first bed we put pure ZSM-5(80) and in the second bed promoted ZSM-5(80) samples were placed, which effectively converted ethylene into aromatics. The two beds were separated by glass wool that was 1.5–2.0 mm thick. As was expected, the selectivity of all aromatics was enhanced as compared to pure ZSM-5(80). When Mo₂C/ZSM-5(80) was used in the second bed, the aromatic selectivity increased from 13 to 25% at 773 K and from 7 to 15% at 873 K. Putting ZnO/ZSM-5(80) in the second bed also resulted in an increase in the previous values from 13 to 36.5% at 773 K and from 7 to 19% at 873 K. The best results were obtained by a combination of ZSM-5(80) with 2% Ga₂O₃/ZSM-5(80). In this case, aromatic selectivity increased from 13 to 45% at 773 K and from 7 to 47% at 873 K. Results obtained are also given in Table 2.

Conclusion

(i) Ethanol adsorbs strongly on ZSM-5-based catalysts most likely in the form of an ethoxy species, which decomposes to several compounds at higher temperatures.

(ii) The dehydration of ethanol occurred readily on ZSM-5 yielding ethylene, water, and small amounts of aromatics.

(iii) Deposition of the various additives (Mo₂C, ZnO, and

Ga₂O₃) on ZSM-5 markedly promoted the formation of aromatics from ethanol.

(iv) This feature was attributed to their catalytic effect on the aromatization of ethylene formed in the dehydration of ethanol. The influence of water on the yield of aromatics varied with the nature of the promoters.

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