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Dimethyl Ether as a Source of Reactive Species for Alkylation of Benzene

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Abstract The co-reaction of dimethyl ether and benzene has been investigated on pure and promoted-ZSM-5 catalysts at 473–773 K. It was found that the addition of benzene to dimethyl ether markedly increased the formation of toluene, xylene and C_9 aromatics on ZSM-5 at and above 623 K. This feature is attributed to the reaction of benzene with the reactive hydrocarbon species formed in the decomposition of dimethyl ether on the acidic sites of ZSM-5 zeolite. The extent of the enhancement was further increased by ZnO and Mo_2C promoters.

Keywords Co-reaction of dimethyl ether and benzene · Alkylation of benzene · ZSM-5 catalyst · Decomposition of dimethyl ether

1 Introduction

The preparation of mono and dialkyl benzenes is a very important process for hydrocarbon industry, therefore a large amount of work has been devoted to this subject [1–5]. The most widely used alkylation agents are methanol [6–10], ethanol [11–13], ethane [14], propene [15], but dimethyl ether [16] has been also applied. In our recent study on the aromatization of methanol on ZSM-5 zeolite we found that adding Mo_2C to ZSM-5 greatly promoted the formation of various aromatics, such as xylene, C_9, toluene and benzene in decreasing selectivity [17]. An interesting observation was that when we added benzene to methanol the rate of the formation of methylated products dramatically increased, particularly on Mo_2C-containing zeolite. Mo_2C/ZSM-5 was previously found to be an effective catalyst for the aromatization of various C_1–C_8 alkanes [18–26]. An important difference is that in the latter cases benzene was the main aromatic compound, C_7–C_9 aromatics were produced only as minor products.

In the continuation of our research program in this area, recently we examined the aromatization of dimethyl and diethyl ether on promoted-ZSM-5 [27]. The reaction of both ethers occurred with higher yields on Mo_2C-containing ZSM-5 zeolite. The main aromatic compounds were toluene, xylene and C_9 compounds, which assumedly formed in the methylation of benzene in the secondary reactions. In the present work we examine the effect of pre-added benzene on the product distribution of dimethyl ether on pure and promoted ZSM-5. We want to ascertain the reaction pathways of the production of above C_7–C_9 aromatics: are they exclusively formed in the reaction of benzene with olefins generated by the decomposition of DME, or the reactive species developed in the dissociation or reaction of DME are responsible for the rapid alkylation process.

2 Experimental

2.1 Methods

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube [17]. The flow rate was 40 mL/min. The carrier gas was Ar. The DME content was 8–10%. In the study of DME + benzene reaction, same amount of benzene was added to the carrier gas. Generally 0.3 g of loosely

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compressed catalyst sample was used. Reaction products were analyzed gas chromatographically using an Agilent 4890 D gas chromatograph with PORAPAK Q + S column and EQUITY-1 FUSED SILICA Capillary Column (30 m × 0.53 m × 3.0 μm film thickness). Samples for analysis were taken in the 30th min of reaction at different temperatures. The conversion of DME was calculated taking into account its amount consumed. The selectivity for reaction products, S; was defined as

$$S_i = \frac{x_i n_i}{\sum_i x_i n_i}$$

where x_i is the mol fraction of product i, and n_i is the number of carbon atoms in each molecule of gaseous products. Thermal desorption measurements (TPD) were carried out in the catalytic reactor. The catalysts were treated with DME/Ar or DME + benzene/Ar mixture containing 10% DME or 10% DME and 10% benzene at 323 K for 30 min, and flushed with Ar for 30 min. The TPD was carried out in Ar flow (20 mL/min) with ramp at 5 K/min from 323 to 1,023 K. Desorbing products were analyzed by gas chromatography. FTIR spectra of adsorbed gases were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wavenumber accuracy of ±4 cm^{-1}.

2.2 Materials

The following materials were used as support ZSM-5 with $SiO_2/A1_2O_3$ ratio at 30, 80 and 280, BET area: 400, 425 and 400 m^2/g. For the preparation of Mo_2C-containing catalysts the starting materials were pure MoO_3 or MoO_3/support samples. The latter were prepared by impregnating the supports with a basic solution of ammonium heptamolybdate to yield the desired % of MoO_3. The same impregnation method, using the incipient wetness procedure, was applied for the preparation of ZnO-, and Ga_2O_3-promoted ZSM-5. In these cases the starting compounds were $Zn(NO_3)_2$ and $Ga(NO_3)_3$. The suspensions were dried and calcined at 863 K for 5 h. MoO_3 samples were heated under 10% v/v C_2H_6/H_2 gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min [21, 22]. Afterwards the sample was cooled down to room temperature under argon. In order to remove the excess carbon deposited on the Mo_2C during the preparation, the Mo_2C-containing catalyst has been reduced before the catalytic measurements in situ at 873 K in H_2 stream for 60 min.

All of the catalysts used in this study have been characterized by XPS measurements. The binding energy for $Mo(3d_{5/2})$ and $Mo(3d_{3/2})$ showed some slight variation with different samples, but dropped to 227.8–228.2 and 230.7–231.1 eV, respectively; that for C(1s) dropped to 283.8 eV. These values are consistent with those attributed to Mo_2C [28, 29]. In terms of the acidity of the catalysts, we refer to our previous work, which used the same samples [30]. We found that during the preparation of Mo/ZSM-5 catalyst, Mo compounds reacted with OH groups of ZSM-5. As a result, the Brönsted sites decreased markedly in number, but were not completely eliminated. The greater the carbide content, the greater the decrease. At the same time, the Lewis acidity was somewhat enhanced by Mo_2C deposition. DME was the product of Gerling Halz Corp. (99%), and the benzene was the product of Carlo Erba (99.5%). Other gases used were of commercial purity (Linde).

3 Results and Discussion

3.1 TPD and FTIR Measurements

The primary aim of TPD and FTIR measurements is to ascertain the effect of benzene on the adsorption and desorption of DME. Following the adsorption of DME at 313 K on ZSM-5(80) we observed a large peak for DME at 373 K and a smaller one at 523 K. In addition, much less amounts of propene, ethylene, *n*-butane and butenes desorbed in the temperature range of 500–650 K with slightly different peak temperatures (Fig. 1a). A continuous desorption of H_2 and CO was also experienced. Adding benzene to DME markedly diminished the adsorption of DME suggesting that a significant fraction of adsorption sites are occupied by benzene. The desorption features of other products remained practically unaltered (Fig. 1b). The desorption of benzene occurred below 450 K. The fact that the peak temperatures for DME and its decomposition products were not affected by benzene may indicate that there are no interaction between DME and benzene in the adsorbed layer. This is confirmed by FTIR spectroscopic studies, which showed only the absorption bands belonging to undissociated DME, methoxy and methyl species [27, 31, 32], which were not affected by benzene. On ZSM-5(280) we measured much less amounts of DME, alkenes and *n*-butane desorbed. The presence of benzene further decreased the uptake of DME and their decomposition products.

3.2 Catalytic Studies

The reaction of DME has been first studied on ZSM-5(80) zeolite in the temperature range 473–823 K. Note that benzene alone underwent a slight decomposition on zeolites in this temperature range: it was only ~2% at 673 K, ~6% at 773 K and 8–10% at 823 K. The decomposition of DME on ZSM-5(80) attained a total conversion at ~573 K. Addition of benzene to DME influenced only little the conversion of DME based on its consumption, but influenced the product distribution. Figure 2 shows

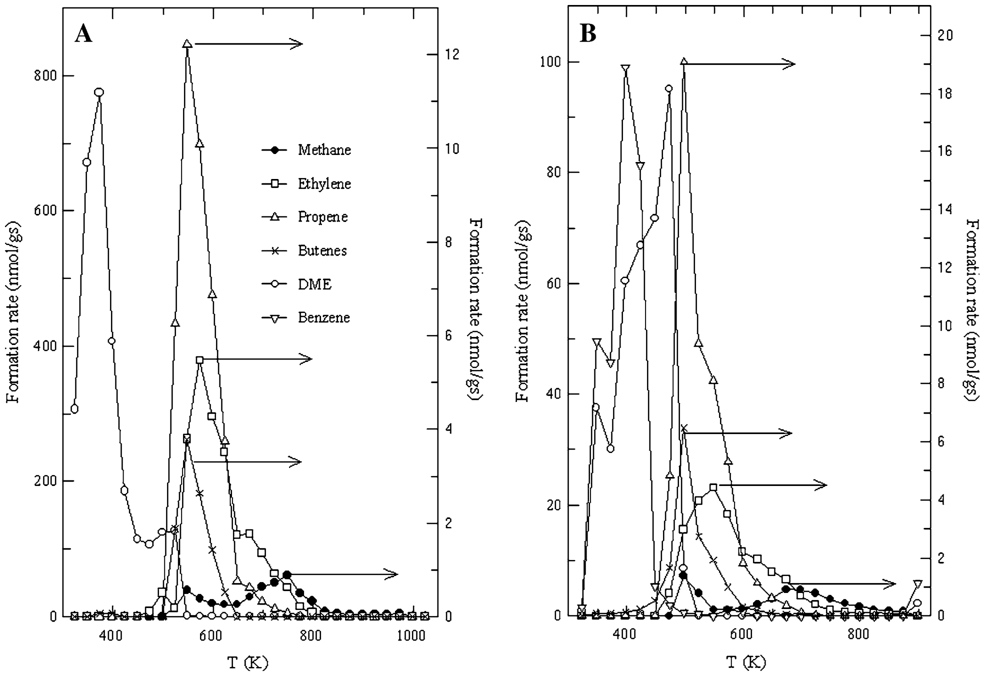

Fig. 1 TPD spectra following the adsorption of DME **a** and DME + benzene **b** on ZSM-5(80) at ~313 K. After adsorption (~30 min), the samples were treated with Argon for 30 min before heating

the formation of various products in the reaction of DME + benzene reacting mixture (1:1) on pure ZSM-5(80) as a function of temperature. For comparison we also plotted the results obtained in the absence of benzene. It appears that the addition of benzene to DME dramatically enhanced the rates of formation of xylene, toluene and C_{9+} aromatics at all temperatures. Detailed analysis of the aromatics revealed the formation 1,2 diethyl benzene as well as 1,3,5 trimethyl benzene. Data are presented in Table 1. The production of ethene and propene is practically unaltered up to about 723 and 673 K, respectively (Fig. 2). Above these temperatures, however, their amounts are diminished in the presence of benzene. The formation of butene was also lower in the whole temperature range. At the same time we measured a significant consumption of benzene during the reaction, which increased with the temperature to reach the highest value ~80% at 673 K. This result clearly indicates that benzene enter reaction with DME, or alternatively with compounds formed in its decomposition.

These characteristics were observed for ZSM-5(30) of higher Brönsted acidity. In contrast, we experienced a much less reactivity with ZSM-5(280) of markedly lower Brönsted acidity [30]. In the absence of benzene the complete decomposition of DME occurred at ~673 K and the total selectivity of aromatics was only ~6.5% at 673–773 K. The presence of benzene markedly inhibited the extent of the decomposition of DME, which was about 20% at 773 K, and approached 100% only at 823 K. In spite of this behavior, the rates of formation of all aromatics were appreciably enhanced even at 773 K, and dramatically at 823 K. To demonstrate the effect of the composition of ZSM-5 on the alkylation of benzene the rates of formation of various aromatics measured at 723 and 823 K are plotted in Fig. 3.

In order to determine the stability of the catalyst experiments have been carried on ZSM-5(80) in time on stream at 623 K. As shown in Fig. 4, no decline in the conversion of DME occurred in 15 h, but some scatterings in the rates of formation of the products were experienced. This scattering is very likely due to the fluctuation in the evaporation of benzene. In order to determine the amount of carbonaceous deposit in the course of the co-reaction at 673 K for 3 h, we performed TPR measurements. We detected the formation of methane ($Tp = 798$ and 973 K) and less amounts of ethene ($T_p = 773$ and 948 K), ethane ($T_p = 773$ and 973 K), propene ($T_p = 730$ K) and butene ($T_p = 700$ K). The sum of the hydrocarbons, expressed in surface carbon is 2.7 mgC/gcat.

The co-reaction of DME + benzene was also examined on Mo_2C-, ZnO-, and Ga_2O_3-promoted ZSM-5(80). In previous study we found that Mo_2C on this zeolite influenced only little the conversion of DME measured for pure ZSM-5, but enhanced the formation of xylene and C_{9+} aromatics [27]. We observed now a similar promoting effect particularly for ZnO-, and Mo_2C-containing samples. In the case of DME + benzene mixture the highest rate increase in the C_7–C_{9+} aromatics was measured for 2% ZnO/ZSM-5(80) catalyst. Data are collected in Table 2.

Since the decomposition of DME produces significant amounts of olefins, the obvious explanation for the

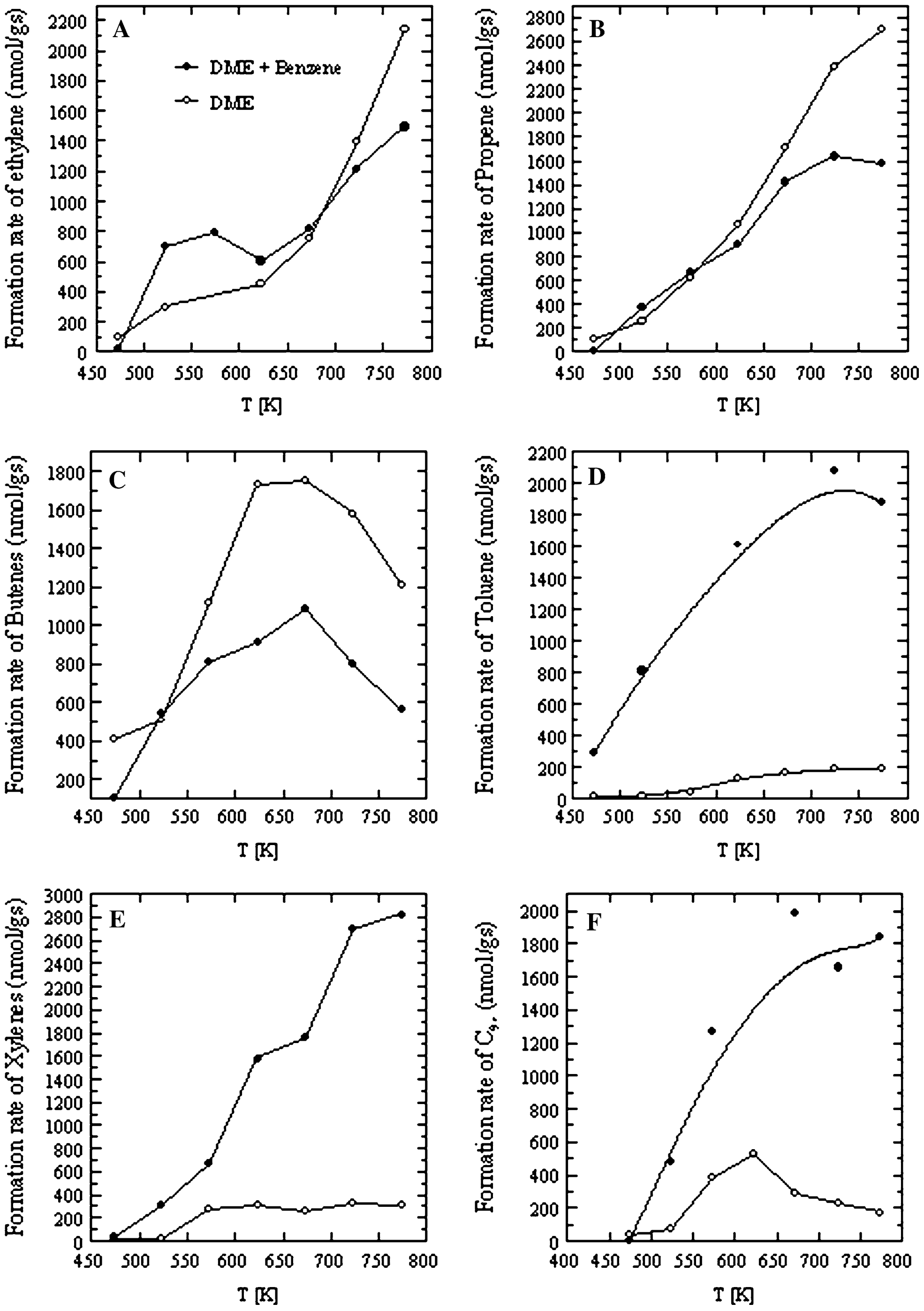

Fig. 2 Rates of formation of various products in the reaction of DME and DME + benzene on ZSM-5(80) as a function of temperature

enhancement of the formation of C_7–C_{9+} aromatics is that olefins are reacting with benzene to yield these compounds. The subsequent experiments, however, did not support fully this idea. As shown in Table 1, adding ethene to benzene increased drastically the rate of formation of ethyl and diethyl benzenes, but exerted no or little influence on the formation of other aromatics. Very small changes were found in product distribution on the addition of propene, butene and butane. The influence of ethane was also tested, but the result was negative.

All these results suggest that the marked enhancement in the formation rates of toluene, xylene and C_{9+} aromatics cannot be merely attributed to the reaction of benzene with these olefins. In the interpretation of this finding we have to take into account the reaction pathway of DME. The conversion of DME to olefins (DTO process) is closely related to the methanol to olefins (MTO process) [16, 33–41]. The key step in both cases is the formation of C–C bond. Several mechanisms have been proposed. According to Oláh and Molnár [37] it is now generally accepted that

Table 1 Effects of DME and various alkenes on the alkylation of benzene over ZSM-5(80)

	Formation rate (nmol/gs)											
	Toluene		Xylene		Ethyl-benzene		Di-ethyl-benzene		1,3,5 tri-methylbenzene		Other C_{9+}aromatics	
	A	B	A	B	A	B	A	B	A	B	A	B
DME (alone)	165	243	257	355	0	0	289	212	208	79	321	139
DME + benzene	1,613	1,879	1,579	2,826	388	79	104	23	668	998	1,069	750
DME + ethylene	7	335	92	105	5,111	750	2,262	92	45	78	3,803	485
DME + propene	39	542	264	241	466	626	397	81	23	46	1,441	998
DME + 1-butene	49	379	188	206	184	556	3	3	24	52	1,956	630
DME + ethane	24	18	1	1	0	0	0	0	0	0	7	17

A = 623 K; B = 773 K

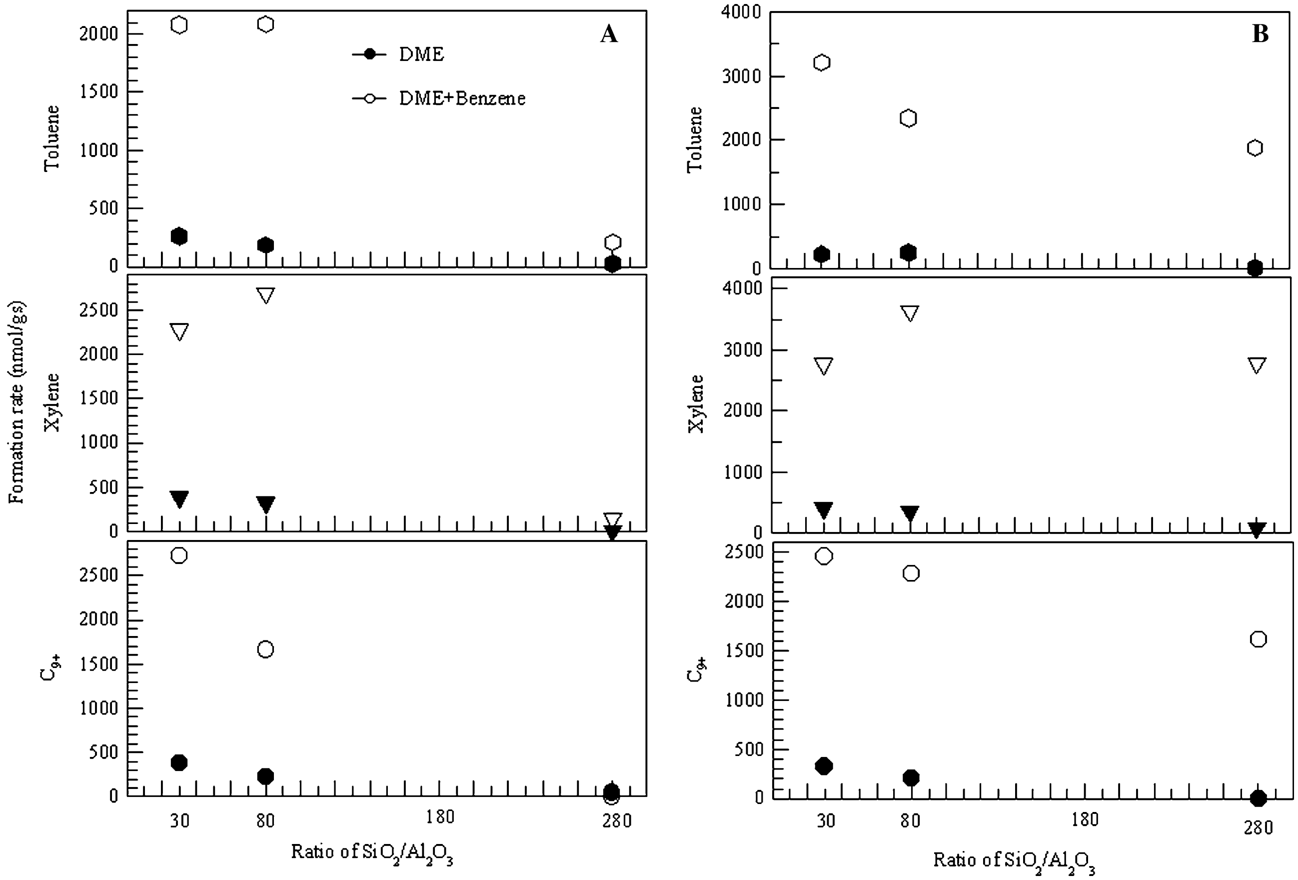

Fig. 3 Effects of the composition of ZSM-5 on the rates of formation of various aromatics from DME and DME + benzene (1:1) at 723 K **a** and 823 K **b**

methanol undergoes preliminary Brönsted acid catalyzed dehydration step, and DME, or equilibrium mixture of DME and methanol, acts as the precursor to hydrocarbon formation. As regards the details of this complex process and the reaction intermediates different views have been expressed. The formation of free carbene radicals [34], trimethyloxonium and ylide intermediates [37], carbocations [35] and surface methoxy species has been suggested [38]. FTIR spectroscopic studies on the interaction of DME with various solids confirmed that in the activation of DME by the acidic sites of oxides and ZSM-5 zeolites adsorbed methoxy and methyl species

$$(CH_3)_2O = CH_3O_{(a)} + CH_{3(a)} \tag{1}$$

are formed [27, 31, 32], the reaction of which may lead to the formation of C–C bond. Besides, the hydrocarbon-pool mechanism has also gained increasing acceptance [16, 39]. It proceeds via repeated methylations and dealkylations of

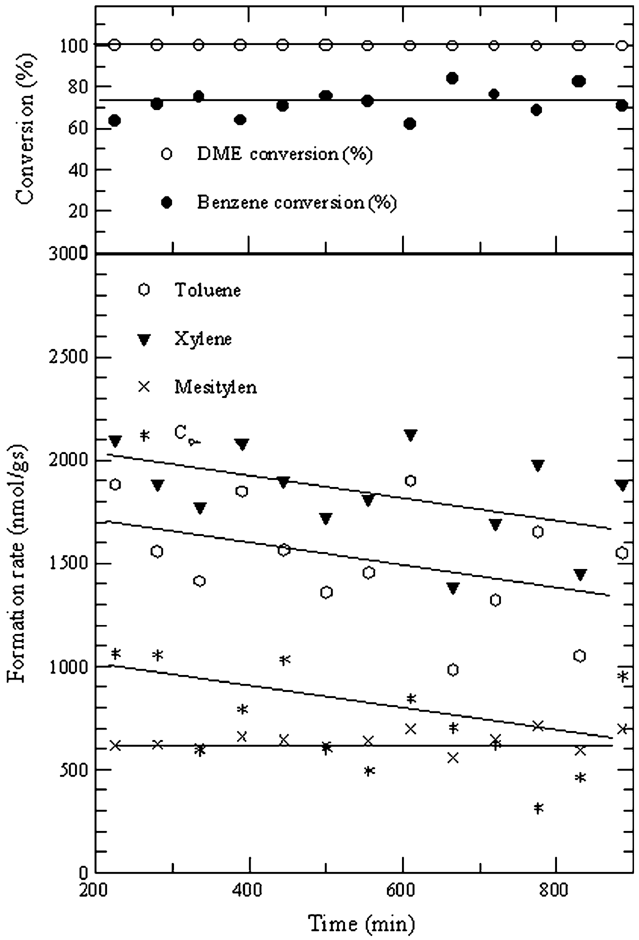

Fig. 4 Rates of formation of various products in the reaction of DME + benzene on ZSM-5(80) in time on stream at 673 K

organic reaction centers trapped inside the zeolite voids. Based on these findings we assume that the above reactive intermediates, mainly allylic and other C_xH_y fragments, enter reaction the benzene molecule activated on the Brönsted sites of the zeolite yielding various alkyl compounds. The finding that in the reacting mixture of DME + benzene an ehancement occurred in the formation of methylated benzene, and not in that of ethyl and diethyl benzene, may suggest that the CH_3O species formed in the dissociation of DME (Eq. 1) is the important methylating agent.

As concerns the influence of promoters, ZnO increases the formation of toluene and xylenes, the other two, Mo_2C and Ga_2O_3 enhance mainly the formation of C_{9+} aromatics. This promoting effect can be attributed to the increased rate of the activation of DME and to the higher concentration of the reactive species. Mo_2C prepared on Mo(100) single crystal exhibited a high reactivity towards DME under UHV conditions [42]. The extensive lowering of the work function of Mo_2C/Mo(100) following the adsorption of DME indicated a strong interaction consisting of an electron donation from the oxygen lone pair of DME to the carbide surface. As a result one of the C–O bonds is cleaved yielding $CH_3O_{(a)}$ and $CH_{3(a)}$ fragments (Eq. 1), as the primary products. HREEL spectroscopic measurements provided spectroscopic evidences for the formation of these species. Another possible role of the Mo_2C and ZnO is to activate the light olefins formed in the early reaction of DME on ZSM-5. Previous works disclosed Mo_2C can promote effectively the aromatization of olefins by providing active dehydrogenation centers for them resulting in

Table 2 Effects of various additives on the formation of aromatics in the reaction of DME on ZSM-5(80) in the absence and presence of benzene

Catalyst	Reacting gas	Formation rate (nmol/gs)																	
		Toluene			Xylene			Ethyl-benzene			Di-ethyl-benzene			1,3,5 tri-methylbenzene			Other C_{9+}aromatics		
		A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
ZSM-5(80)	DME	165	13	243	257	267	355	0	0	0	289	0	212	208	114	79	321	220	139
	DME + benzene	1,613	1,393	1,879	1,579	1,762	2,826	388	263	79	104	45	23	668	790	998	1,069	896	750
ZSM-5(280)	DME	5.7	30	15	124	204	93	3	14	8	4	5	1	–	–	–	5	6	1
	DME + benzene	3	16	1,517	0	0	291	0	0	0	0	0	0	0	0	56	24	25	53
5% Mo_2C/ZSM-5(80)	DME	122	193	241	357	448	457	0	28	19	11	6	2	–	–	–	437	309	278
	DME + benzene	1,366	1,332	1,805	1,454	1,805	2,690	375	298	92	61	44	13	–	–	–	2,286	2,031	2,201
2% ZnO/ZSM-5(80)	DME	16.5	159	–	281	441	–	4	0	–	0	0	0	162	228	–	293	322	–
	DME + benzene	2,514	2,993	4,309	1,999	2,894	3,242	3	3	0	182	52	1	–	–	–	1,774	4,636	2,791
2% Ga_2O_3/ZSM-5(80)	DME	131	227	–	352	416	–	0	0	–	0	0	–	200	163	–	455	246	–
	DME + benzene	1,655	1,309	2,471	1,521	1,650	3,152	501	275	105	–	–	–	–	–	–	752	748	765

A = 623 K; B = 673 K; C = 773 K

different C_xH_y products, which are converted into aromatics on the acidic sites of the zeolite [17, 18].

4 Conclusions

(i) Adding benzene to dimethyl ether markedly enhances the formation of toluene, xylene, and C_{9+} aromatics on ZSM-5 zeolites.
(ii) The extent of the enhancement was the largest over ZSM-5 of high Brönsted acidity.
(iii) Further increase occurred on ZnO-, Mo_2C-promoted ZSM-5(80).
(iv) From the comparison of the effect of DME with that of various alkenes and alkanes it was inferred that CH_3O species and/or C_xH_y hydrocarbon fragments formed in the activation and decomposition of DME are responsible for the enhanced alkylation of benzene.

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