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Aromatization of dimethyl and diethyl ethers on Mo_2C-promoted ZSM-5 catalysts

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ABSTRACT

The adsorption and reaction pathways of dimethyl and diethyl ethers have been investigated on pure and Mo_2C-containing ZSM-5. The catalysts have been characterized by XPS and surface acidity measurements. FTIR spectroscopic measurements indicated that a fraction of both ethers dissociates on pure and Mo_2C-promoted zeolites already at 180–200 K resulting in the formation of methoxy from dimethyl ether, and ethoxy from diethyl ether. TPD experiments following the adsorption at 300 K showed desorption profiles corresponding to starting compounds and their decomposition products (methane, ethene and propene). ZSM-5 effectively catalyzed the reaction of dimethyl and diethyl ether above 473 K to yield various olefins and aromatics. From dimethyl ether xylene and from diethyl ether toluene were the main aromatic compounds. Adding Mo_2C to the zeolites greatly promoted the formation of aromatics very likely by catalyzing the aromatization of olefins formed in the reaction of ethers on zeolites.

1. Introduction

An attractive example at the synergistic phenomenon is that whereas neither Mo_2C nor ZSM-5 alone can produce benzene from methane, the combination of Mo_2C with ZSM-5 provides an unique and effective catalyst for the aromatization of methane [1–7]. Furthermore, while ZSM-5 alone catalyzes only the aromatization reactions of C_2–C_9 alkanes with low selectivity and yield [8–12], the deposition of Mo_2C on this zeolite greatly enhances the extent of the formation of aromatics [13–21]. Recently, it was found that Mo_2C also exhibits a marked promoting effect on the aromatization of ethanol [22,23] and methanol [24].

In the present work an account is given on the reaction of dimethyl ether (DME) and diethyl ether (DEE) on pure and Mo_2C-containing ZSM-5. The study of the reaction of DME was motivated by several reasons. DME is a key compound in the conversion of methanol to gasoline (MTG process) [25–33], and it is also a reaction intermediate in the aromatization of methanol [24]. In addition, DME as an alternative fuel can replace diesel oil, as the burning of DME produces much less pollutant [34–36]. The oxidation of DME has been also studied [37–39]. In a comparative study on its combustion on alumina-supported Pt metals Rh/Al_2O_3 exhibited the highest specific activity [37]. In spite of the growing interest towards the catalytic reactions of DME, its aromatization on ZSM-5-based catalysts was relatively neglected. Most of the studies dealt with the synthesis of light olefins, hydrolysis and steam reforming on ZSM-5 [40–45]. Even less attention was devoted to the aromatization of DEE. Abdel–Ghaffar found that at lower temperatures ethylene and ethanol are being formed in the reaction of DEE on ZSM-5, but the production of aromatics was not reported [46]. At higher temperatures additional reactions, such as addition of C_2 units, followed by isomerization, cracking and aromatization are expected.

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 [23, 24]. The flow rate was 40 ml/min (NTP). The carrier gas was Ar. The DME or DEE content was 8–10%. Generally 0.3 g of very loosely compressed catalyst sample was used. Reaction products were analyzed gas chromatographically using a Hewlett–Packard 5890 gas chromatograph with PORAPAK Q + PORAPAK S columns. The conversion of ethers 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 mole fraction of product i, and n_i is the number of carbon atoms in each molecule of gaseous products. FTIR spectra of adsorbed gases were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wavenumber accuracy of ±4 cm^{-1}. All the spectra presented are difference spectra. Thermal desorption measurements (TPD) were carried out in the catalytic reactor. The

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catalysts were treated with DME/Ar or DEE/Ar mixture containing 10% ethers at 313 K for 30 min, and flushed with Ar for 30 min. The TPD was carried out in Ar flow (20 ml/min) with a temperature ramp of 5 K/min from 313 K to 1063 K. Desorbing products were analyzed by gas chromatography. Samples were taken in every 5 min.

The XPS measurements were performed in a Kratos XSAM 800 instrument at a base pressure of 10^{-8} Torr using Mg$K\alpha$ primary radiation (14 kV, 10 mA). To compensate for possible charging effects, binding energies (BE) were normalized to the Fermi-level for the Mo_2C. The amount of coke deposited on the catalyst during the reaction was determined by temperature-programmed reaction (TPR). The catalyst was cooled down in flowing argon, then heated in H_2 stream with a rate of 5 K/min and the hydrocarbons formed were measured.

2.2. Materials

Mo_2C-containing catalysts prepared in the same way as described in our previous papers [23,24]. 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 suspension was dried and calcined at 863 K for 5 h. The following materials were used as support ZSM-5 with SiO_2/Al_2O_3 ratio at 80 and 280, BET area: 425 and 400 m^2/g. 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. Afterwards the sample was cooled down to room temperature under argon. The carbide so formed was passivated in flowing 1% O_2/He at 300 K, or used at once in the catalytic reactor. In order to remove the excess carbon deposited on the Mo_2C during the preparation, and the Mo–O species produced during passivation, the Mo_2C-containing catalyst has been reduced before the catalytic measurements in situ at 873 K in H_2 stream for 60 min. DME was the product of Gerling Holz Comp. with 99% purity. Other gases used were of commercial purity (Linde).

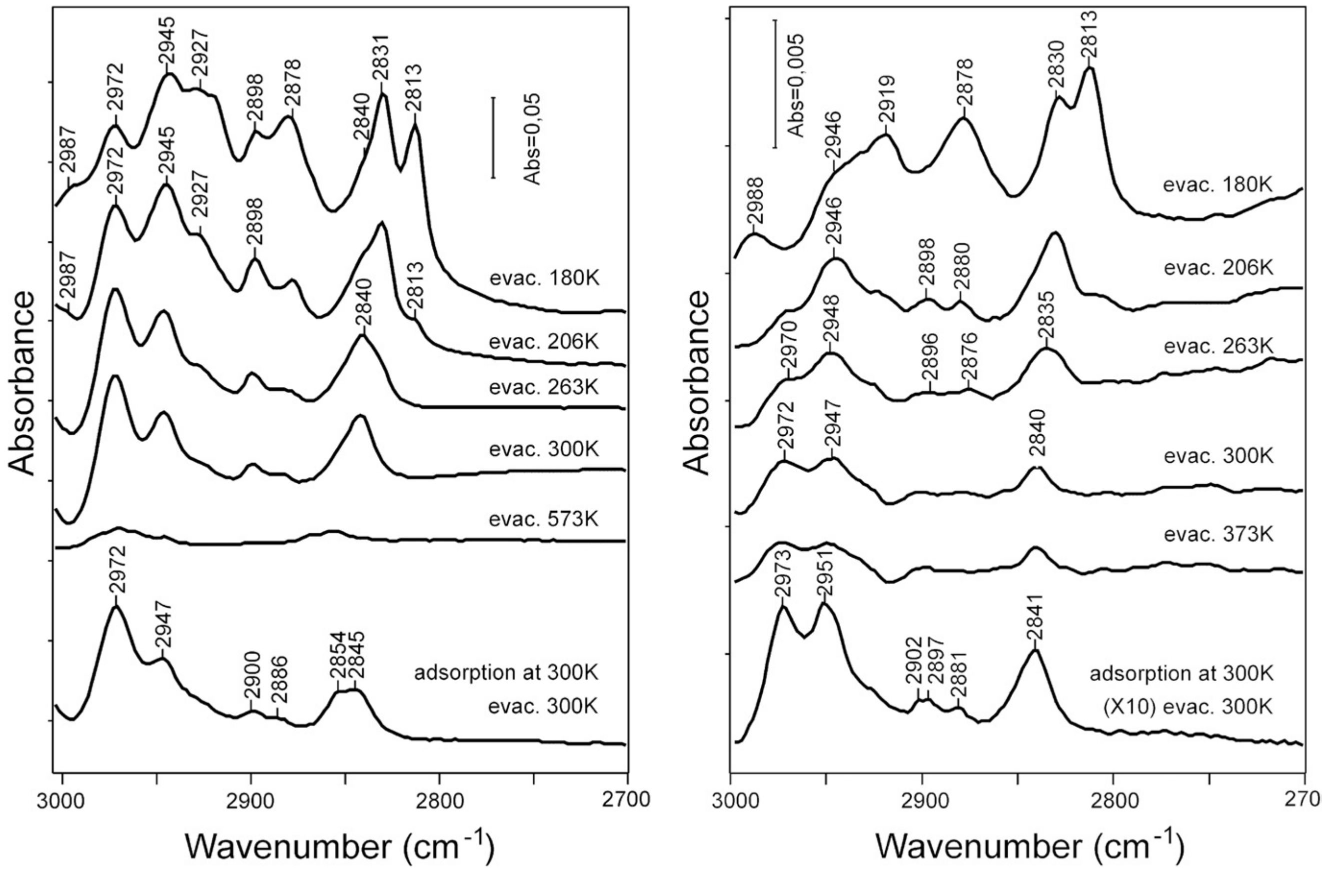
All of the catalysts used in this study have been characterized by XPS measurements. The binding energy for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) showed some slight variation with different samples, but dropped to 227.8–228.2 and 230.7–231.1 eV, respectively; that for C(1s) dropped to 283.8 eV. These values are consistent with those attributed to Mo_2C [47,48]. In terms of the acidity of the catalysts, we refer to our previous work, which used the same samples [49]. 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.

3. Results

3.1. Dimethyl ether

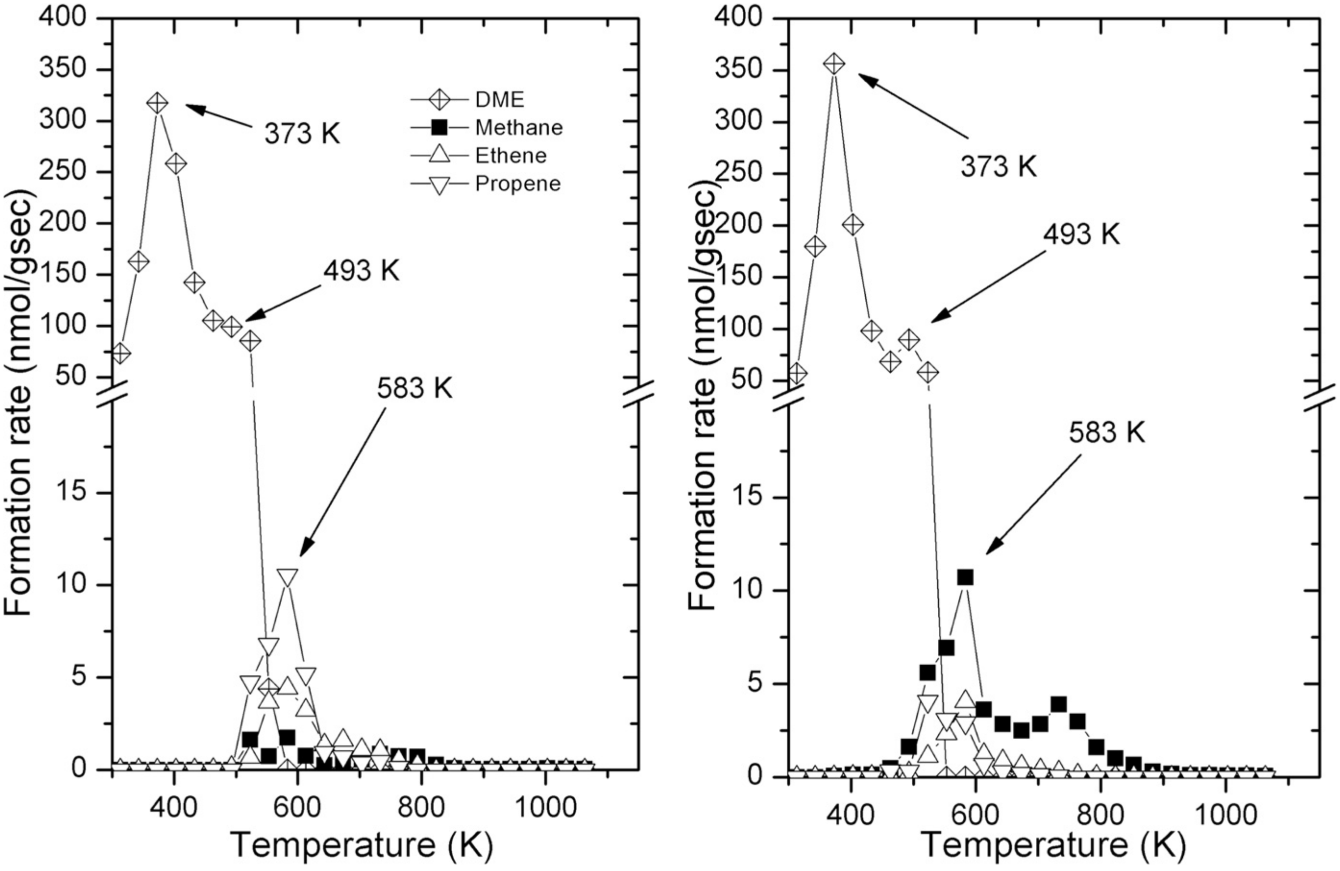
3.1.1. FTIR and TPD measurements

Fig. 1A shows the IR spectrum of ZSM-5(80) after adsorption of DME at ∼180 K for 15 min. and subsequent degassing at different temperatures. At 180–206 K vibrational modes are observed at 2997, 2972, 2945, 2927, 2898, 2878, 2840, 2831 and 2813 cm^{-1}. In the low frequency region weak absorption bands appeared at 1475,



(A) (B)

Fig. 1. FTIR spectra of ZSM-5(80) (A) and 2% Mo_2C/ZSM-5 (B) following the adsorption of dimethyl ether (1.5 Torr) at 180–190 K, and after heating the samples to different temperatures during continuous degassing.



(A) (B)

Fig. 2. TPD spectra following dimethyl ether adsorption on pure ZSM-5(80) (A) and 5% Mo_2C/ZSM-5(80) (B) at 300 K.

Table 1
Characteristic absorption bands of adsorbed dimethyl ether and its primary dissociation products

Vibrational mode	$DME_{(g)}$ [51]	$DME_{(a)}$ alumina [51]	$CH_3O_{(a)}$ alumina [51]	$CH_3O_{(a)}$ silica [52]	$(CH_3)_2O$/Rh(111) [53]	$CH_{3(a)}$ Mo_2C/Mo(100) [50]
$\upsilon_a(CH_3)$	2996	2984	2960	2954	2950	2930
	2925	2922				
$\upsilon_s(CH_3)$	2817	2821	2849	2858		
$2\delta(CH_3)$	2887	2890				
$\delta(CH_3)$	1470	1477	1475		1465	1370
	1456	1459	1420			
$\gamma(CH_3)$	1244	1252	1081		1175	
	1179	1116				
$\upsilon_{as}(CO)$	1102	1092	1055			
$\delta_s(CH_3)$						1180
$\delta_s(CO)$					885	
$\delta(COC)$					450	

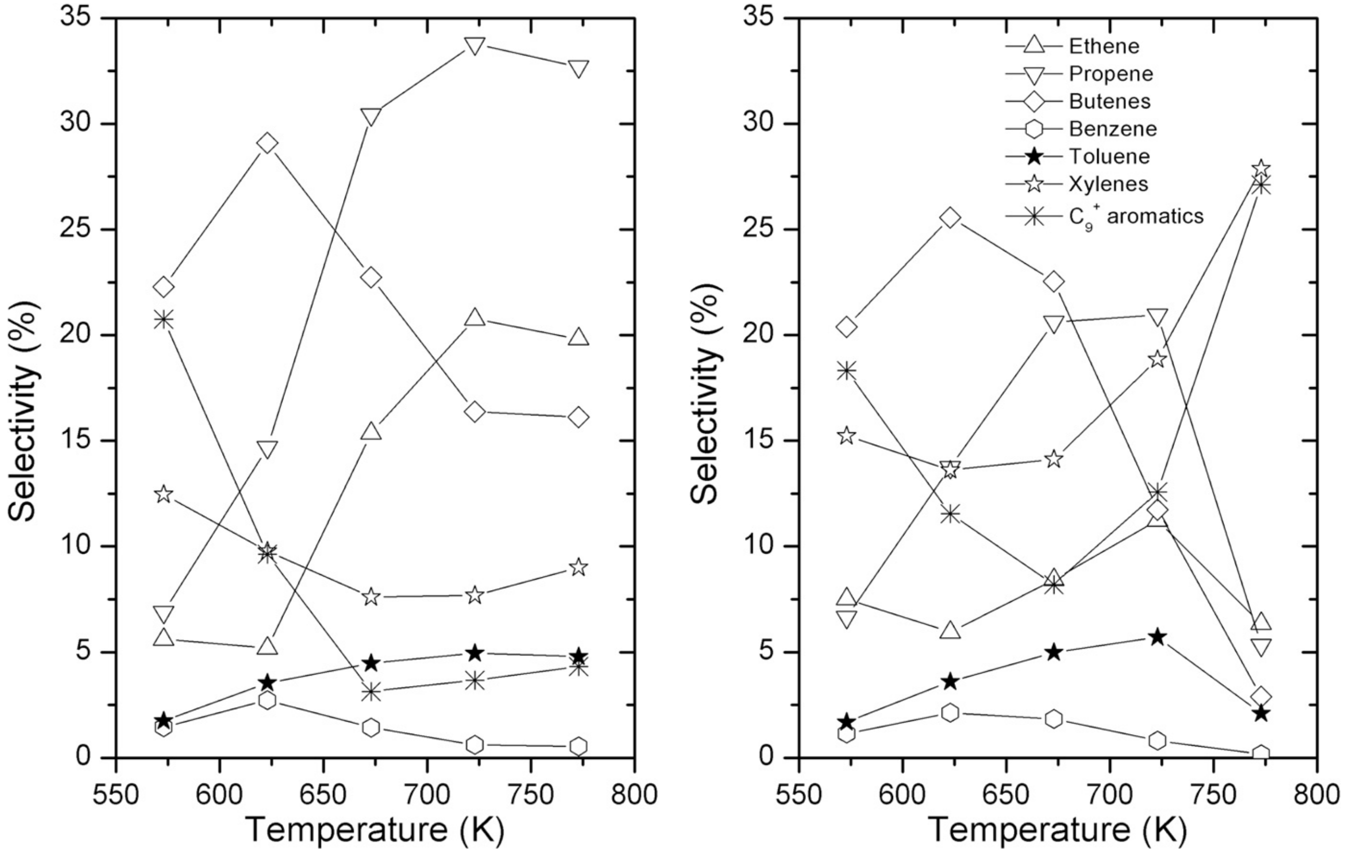
1457 and 1428 cm^{-1} (not shown). Upon heating the sample under continuous degassing the intensities of the bands at 2927, 2898, 2878, 1457 and 1428 cm^{-1} gradually decreased. At room temperature an IR spectrum with major vibrational modes at 2972, 2945, 2840 and 1457 cm^{-1} is observed. The bands at 2898, 2878 and 2813 cm^{-1} became very weak or not detectable. When the adsorption was performed at 300 K we observed the same spectral features. Very similar spectra were obtained for 5% Mo_2C/ZSM-5(80), but with much less intense bands (Fig. 1B). They exhibited somewhat less stability than on the pure zeolite. In Table 1 the characteristic vibrations of DME and its possible dissociation products are collected.

TPD spectra for various products after adsorption of DME on pure and 5% Mo_2C/ZSM-5(80) at 313 K are displayed in Fig. 2. From pure ZSM-5 the major desorbing product is DME ($T_p =$ 373 and 493 K). The desorption of a much smaller amounts of ethene ($T_p \sim 583$ K), and propene ($T_p \sim 583$ K) were also observed. From Mo_2C containing ZSM-5 we found the same products with slightly different peak temperatures. A slight continuous desorption of hydrogen and CO was also observed from both samples. An interesting feature of TPD curves is that methane was also released particularly from Mo_2C-containing catalyst. This is formed very likely in a surface reaction of carbonaceous species.

3.1.2. Catalytic reaction of DME

The reaction of DME on pure Mo_2C started at 500–523 K and the highest value, 15–17%, was achieved already at 673 K. Above this temperature a rapid deactivation of the Mo_2C occurred. The major products were methane, CO and CO_2 with selectivity of 50, 30 and 15%, respectively. Other carbon-containing compounds were detected only in traces.

Unpromoted ZSM-5 was found to be an effective catalyst for the reaction of DME. Independently on the composition, reaction of DME was observed above 473 K (Fig. 3A). The conversion was 10% at 473 K, which grew to 95–97% at 573 K. An interesting feature of the reaction on pure ZSM-5 is the formation of methanol in few % at low temperature, 473–523 K. The aromatization of the DME was observed already at 573 K, when benzene, toluene, xylene and C_9 aromatics were produced. Raising the temperature was disadvantageous for their production particularly for that of C_9 aromatics, but favored the formation of C_2–C_3 olefins. The selectivity of C_4 olefins also decreased at higher temperatures. Selectivity data obtained for ZSM-5(80) as a function of reaction temperature are displayed in Fig. 3A. Aromatics were produced with somewhat lower selectiv-



(A) (B)

Fig. 3. Selectivities of the products formed in the reaction of dimethyl ether over ZSM-5(80) (A) and 5% Mo_2C/ZSM-5(80) (B) at different temperatures.

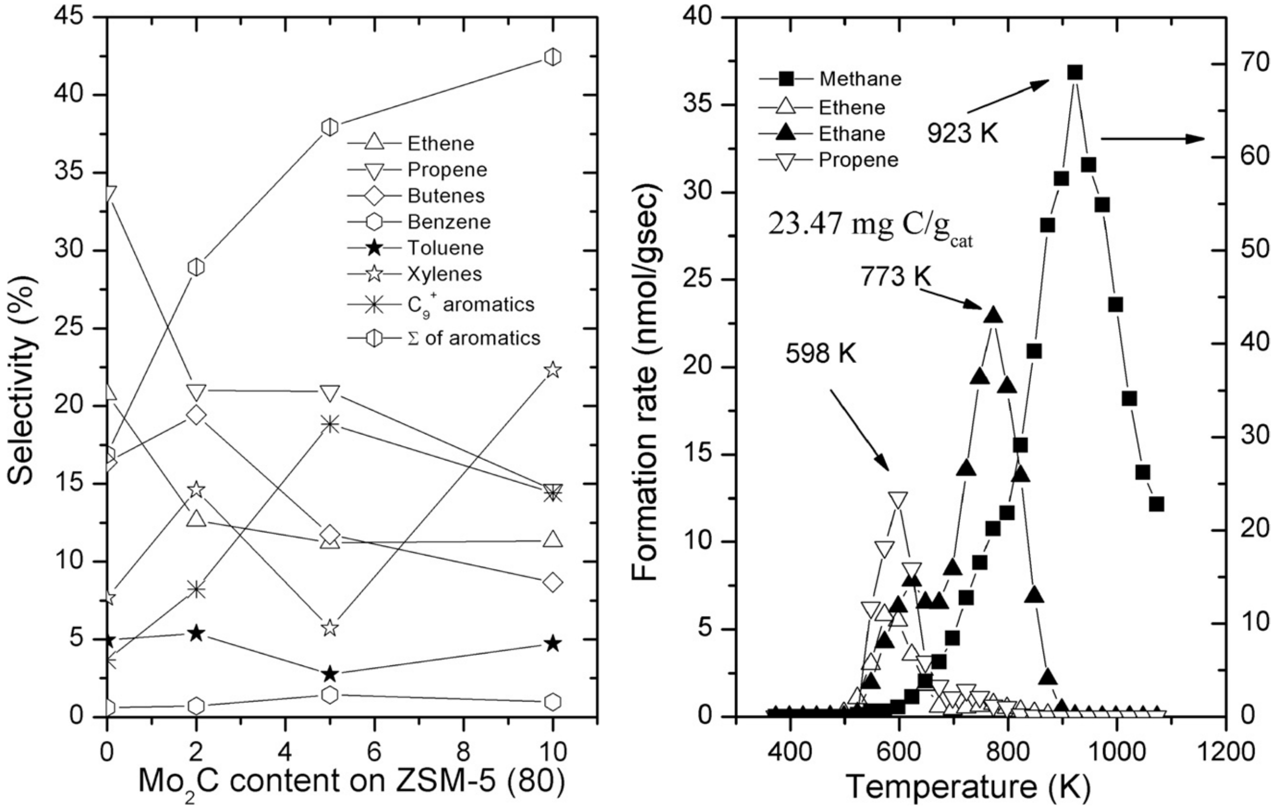
Table 2
Main results obtained in the reaction of dimethyl ether on ZSM-5-based catalysts

Catalyst	Temp. (K)	Selectivity (%)									
		Ethylene	Propylene	C_4 aliph.	C_5 aliph.	C_6 aliph.	Benzene	Toluene	Xylenes	C_{9+} arom.	∑aroma
ZSM-5(80)	723	20.8	33.8	16.4	3.5	0.9	0.6	5.0	7.7	3.7	16.9
	773	20.5	33.0	15.7	3.9	0.8	0.5	4.9	8.5	4.5	18.3
2% Mo_2C/ZSM-5(80)	723	12.7	21.0	3.6	7.8	2.8	0.7	5.4	14.6	8.2	28.9
	773	14.1	19.2	12.9	5.0	1.4	0.3	6.9	17.5	11.9	36.6
5% Mo_2C/ZSM-5(80)	723	11.2	21.0	11.7	5.1	1.4	0.8	5.7	18.9	12.6	37.9
	773	7.1	6.5	3.2	1.7	1.1	1.0	5.5	27.3	27.1	60.8
10% Mo_2C/ZSM-5(80)	723	11.3	14.6	8.7	4.2	2.3	1.0	4.7	22.3	14.4	42.5
	773	8.2	4.7	2.1	1.2	0.9	0.5	3.4	22.5	20.5	46.9
ZSM-5(280)	723	9.3	45.7	25.4	9.5	2.1	2.1	1.4	2.4	1.1	6.9
	773	14.5	49.3	21.7	6.6	0.4	1.1	1.8	2.5	0.5	5.9
2% Mo_2C/ZSM-5(280)	723	8.7	35.9	21.8	8.9	3.7	1.8	3.7	8.8	3.6	17.8
	773	11.4	35.7	17.3	7.2	2.0	1.2	5.9	10.3	3.1	20.4
5% Mo_2C/ZSM-5(280)	723	11.5	22.7	11.7	5.0	0.4	2.3	5.7	17.8	12.2	38.0
	773	8.2	8.2	3.7	2.2	0.1	0.2	5.0	25.3	24.9	55.5
10% Mo_2C/ZSM-5(280)	723	9.1	35.6	21.4	10.5	4.3	1.5	3.0	8.2	2.7	15.4
	773	11.9	31.6	15.5	7.9	2.5	1.0	4.9	11.3	4.0	21.2

ity on ZSM-5(280) compared to ZSM-5(80). Characteristic data for both zeolites are collected in Table 2.

Deposition of Mo_2C on zeolites influenced only little the conversion of DME obtained for pure ZSM-5, but affected the product distribution. The formation of aromatics, particularly that of xylenes and C_9, was clearly enhanced at the expense of olefins. In contrast to the unpromoted ZSM-5 the selectivity of xylenes and C_9 increased with the temperature. Addition of 2% Mo_2C to ZSM-5(80) raised total aromatic selectivity at 723 K from 16.9% to 28.9%. This value increased to 37.9% in case of 5% Mo_2C/ZSM-5(80) and reached value of 42.5% for 10% Mo_2C/ZSM-5(80).

Selectivity data for 5% Mo_2C/ZSM-5(80) are presented in Fig. 3B. The effect of Mo_2C content of ZSM-5 on the product distribution is shown in Fig. 4A.The reaction of DME has been followed on 5% Mo_2C/ZSM-5(80) in time on stream at 673 K. No decline in the conversion of DME and in the selectivity of various aromat-



(A) (B)

Fig. 4. Effects of Mo_2C content of ZSM-5(80) on the selectivities of various products formed at 723 K (A). Formation of hydrocarbons in the TPR measurements following dimethyl ether reaction on 5% Mo_2C/ZSM-5(80) at 673 K for 17 h (B).

Table 3
Characteristic absorption bands of diethyl ether and its primary dissociation products

Vibrational mode	$(C_2H_5)_2O_{(gas)}$ [50]	$(C_2H_5)_2O_{(a)}$ monolayer Cu(111) [56]	$(C_2H_5)_2O_{(a)}$ multilayer Mo_2C/Mo(100) $T_a = 100$ K [50]	$C_2H_5O_{(a)}$ alumina [54]	$C_2HO_{5(a)}$ ZSM-5 [23]	$C_2H_{5(a)}$ Mo_2C/Mo(100) [55]	$C_2H_{4(a)}$ ZSM-5 present study
$\nu_a(CH_2)$	2953	2930 2961					
$\nu_a(CH_3)$	2981	2976	2986	2970	2937 2984	2963	2938
$\nu_s(CH_3)$				2900	2910	2938	2858
$\nu_s(CH_2) + \nu(CH_3) + 2^*\delta(CH_3)$	2872	2870	2895	2930 2870	2937	2860	
$\nu(CO)$				1450 1390			
$\delta(CH_2)$	1492						
$\delta_a(CH_3)$ in plane	1454				1478		1470
$\delta_a(CH_3)$ out of plane	1453	1442	1464		1448		
$\delta_s(CH_3) + \omega(CH_2)$	1381, 1371, 1354		1390				1230
$\tau(CH_2)$	1278	1280	1285		1394	1478	
$\rho(CH_2 + CH_3)$	1170	1170					
$\rho(CH_2) + \nu(CO) + \nu(CC)$ + bends	1144	1157		1170			
$\omega(CH_2)$							
$\nu(CO)$, ν_a("COC")	1130	1112	1150				
$\rho(CH_3)$, $\nu(CC)$	1047	1044					955
$\nu(CC + CO) + \rho(CH_3)$	923		940				
$\tau(CH_2)$							
$\nu(CC)$, $\nu_s(CCO)$, $\rho(CH_3)$	848		835				
$\rho(CH_3 + CH_2)$	823	823					
$\rho(CH_2)$							
$\delta(CCO)$	419		449				
$\nu_s(MC)$							

ics occurred in 7 h. Positive effect of Mo_2C was also observed in case of ZSM-5(280). While over pure sample total aromatic selectivity amounted to ∼7% at 723 K, this value raised to 18% over 2% Mo_2C/ZSM-5(280) and 38% over 5% Mo_2C/ZSM-5(280). At higher Mo_2C loading (10%) the total aromatic fell to ∼15% (Table 3).

In one case after catalytic run at 673 K for 17 h we carried out temperature-programmed reaction (TPR) with H_2. The results plotted in Fig. 4B, show the formation ethylene, propylene ($T_p = 598$ K) ethane ($T_p = 773$ K) and a much larger amount of methane ($T_p = 923$ K). The sum of the hydrocarbons, expressed in surface carbon is 23.47 mg_C/g_{cat}. The carbon content of DME passed through the catalyst in 17 h is 8.32 g_C/g_{cat}. It means that only its 0.28% underwent total decomposition to surface carbon. This means that the carbon deposition cannot influence appreciably the selectivities of various compounds.

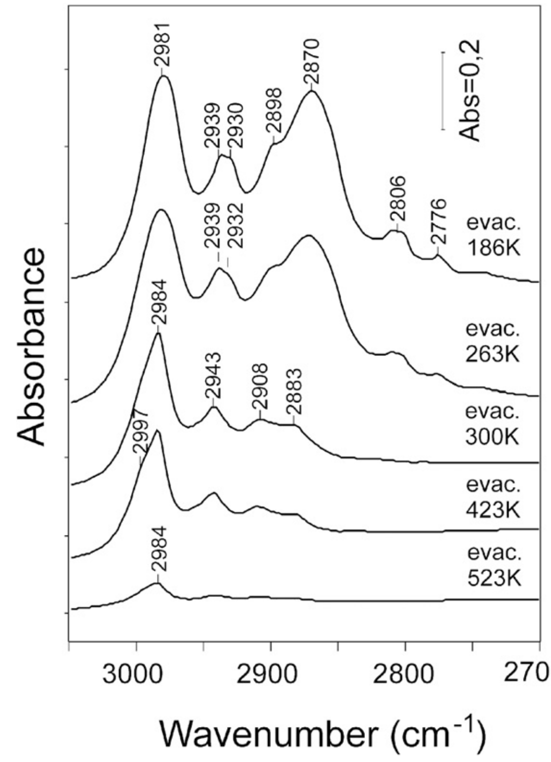


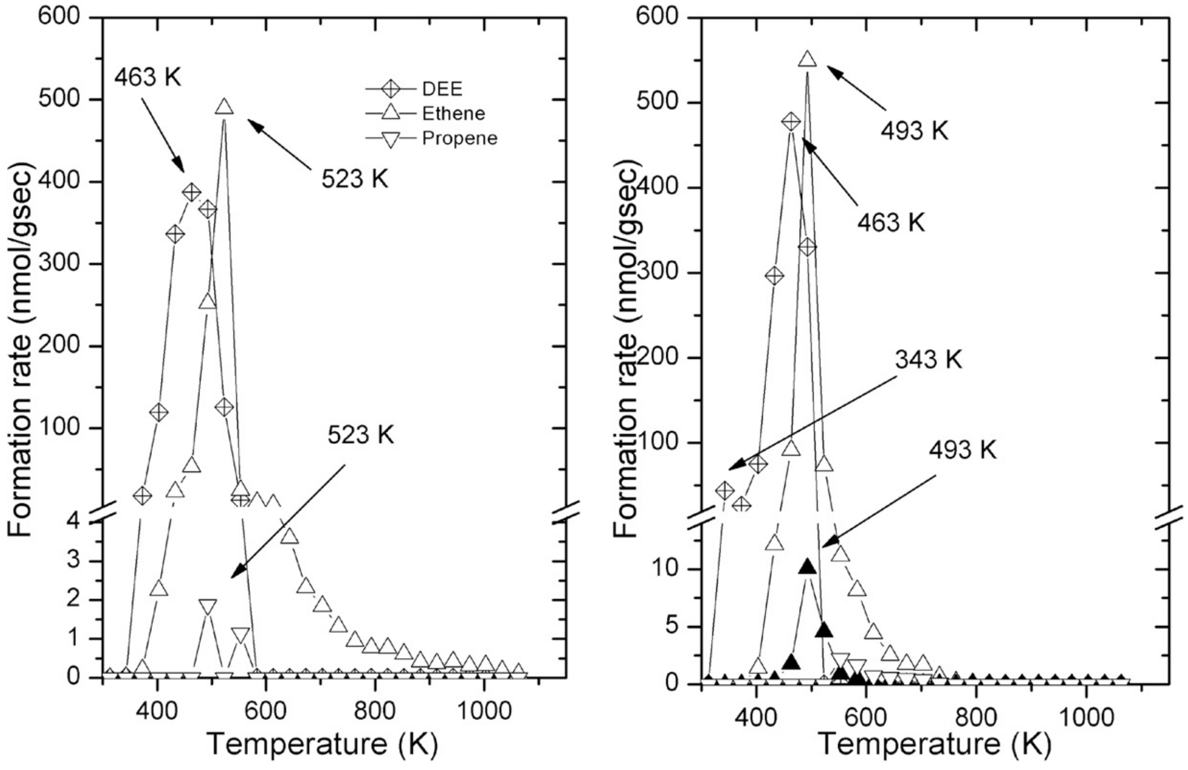
Fig. 5. FTIR spectra of ZSM-5(80) following the adsorption of diethyl ether (1.5 Torr) at 180–190 K, and after heating the samples to different temperatures during continuous degassing.

3.2. Diethyl ether

3.2.1. FTIR and TPD measurements

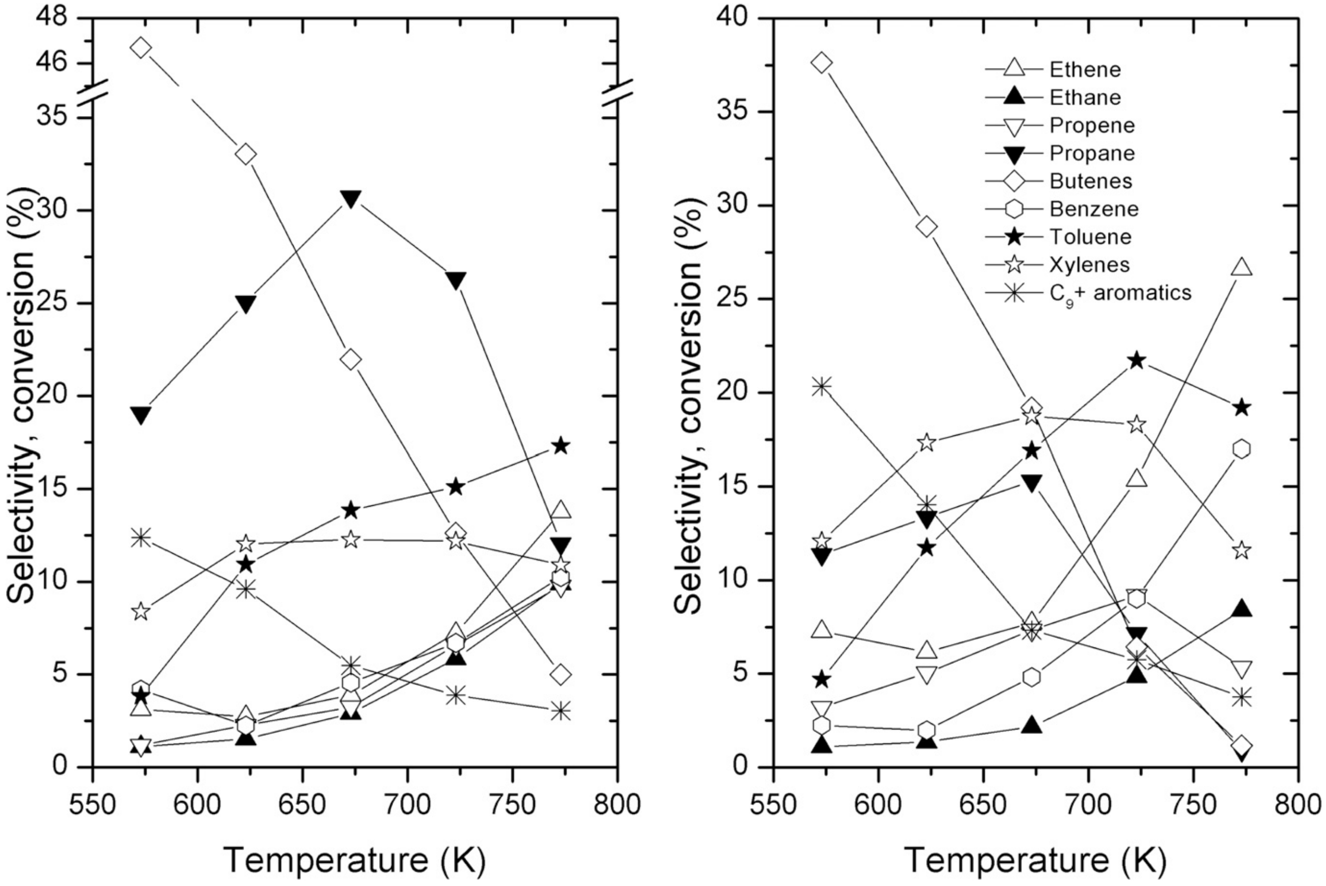
FTIR spectrum of adsorbed DEE at ∼186 K on ZSM-5(80) is presented in Fig. 5. In the C–H stretching region intense absorption bands were registered at 2981, 2934, 2908, 2870, 2806 and 2776 cm^{-1}. In the C–H deformation mode five weak peaks were detected at 1475, 1458, 1446, 1417 and 1384 cm^{-1}. The spectra remained practically unaltered up to 263 K. A dramatic change occurred when the adsorbed layer was heated to and above 300 K, when vibrational frequencies at 2930, 2870, 2806 and 2776 cm^{-1} disappeared, a shoulder developed at 2997 cm^{-1} and new weak absorption bands at 2908 and 2883 cm^{-1} appeared. These spectral features were eliminated or reduced markedly in intensities at 523 K. In the case of 5% Mo_2C/ZSM-5(80) we obtained the same absorption bands of lower intensities and at slightly different positions. In Table 3 the absorption bands of DEE and its possible primary dissociation products are shown.

TPD spectra following the adsorption of DEE on ZSM-5(80) and 5% Mo_2C/ZSM-5(80) at 300 K are shown in Figs. 6A and 6B. The weakly adsorbed DEE desorbed from undoped zeolite with $T_p = 463$ K. In addition the desorption of ethylene ($T_p = 523$ K) and a very small amount of ethane ($T_p = 463$ K) also occurred. The deposition of Mo_2C on this zeolite resulted in the release of same compounds with slightly different peak temperatures (Fig. 6B). A new feature for Mo_2C/ZSM-5 is the desorption of methane ($T_p = 493$ K).



(A) (B)

Fig. 6. TPD spectra following diethyl ether adsorption on pure ZSM-5(80) (A) and 5% Mo_2C/ZSM-5(80) (B) at 300 K.



(A) (B)

Fig. 7. Selectivities of the products formed in the reaction of diethyl ether over ZSM-5(80) (A) and 5% Mo_2C/ZSM-5(80) (B) at different temperatures.

3.3. Catalytic reaction

As in the previous case, pure Mo_2C catalyzed effectively the decomposition of DEE above 523 K to give H_2, ethane, ethylene, CO and methane as major products. Total conversion was approached at 673 K. Aromatic compounds were not identified in the temperature range of 523–773 K.

Completely different products were formed on ZSM-5(80). At 573 K, when the conversion was more than 80%, propane and butenes were the main reaction products, C_2–C_3 olefins and alkanes formed only with low selectivities. Whereas the selectivity of butenes decreased that of C_2–C_3 olefins increased with the temperature. The formation of aromatic compounds started occurred even at 573 K with 29% total selectivity. Upon increasing the reaction temperature this value slowly rises and at 773 K 41.5% was measured. Selectivity data are shown in Fig. 7A. Over 5% Mo_2C/ZSM-5(80) catalyst the conversion changed similarly as in case of non-doped catalyst. In respect of aromatic formation the positive effect of Mo_2C additive was experienced in whole temperature range. The growth of aromatic selectivity was 16–20% compared to non doped sample (Fig. 7B). Over 10% Mo_2C/ZSM-5 catalyst only a slight growth (2–5%) in the selectivity of aromatics was detected compared to 5% Mo_2C/ZSM-5. Whereas adding Mo_2C to ZSM-5 increased the total selectivity of aromatics, the distribution of aromatic compounds depended on the Mo_2C content. At 723 K the selectivity of benzene and toluene gradually increased with the loading of Mo_2C: this value for xylene and particularly for C_9 aromatics varied only little. This is well illustrated by the data plotted in Fig. 8A. The effect of Mo_2C content on the product distribution of aromatics was somewhat different at 773 K (Table 4). The ZSM-5(280) based catalysts exhibited weaker catalytic performance than ZSM-5(80) supported materials. The total aromatic selectivity varied between 31–40% at 573–773 K. Besides aromatics, C_2–C_4 olefins and C_5–C_4 hydrocarbons were the main reaction products. Adding 5% Mo_2C to ZSM-5(280) resulted in the 6–12% growth in the aromatic selectivity. Data for catalytic studies for this sample are also summarized in Table 4.

TPR measurements were also carried out for the 5% Mo_2C/ZSM-5(80) catalyst used for 5 h at 723 K. Ethylene, ethane, propane all with $T_p \approx 798$ K, and methane ($T_p \approx 973$ K) were released. Calculation based on their amounts showed that appr. 0.9% of DEE transferred decomposed completely to carbonaceous deposit.

4. Discussion

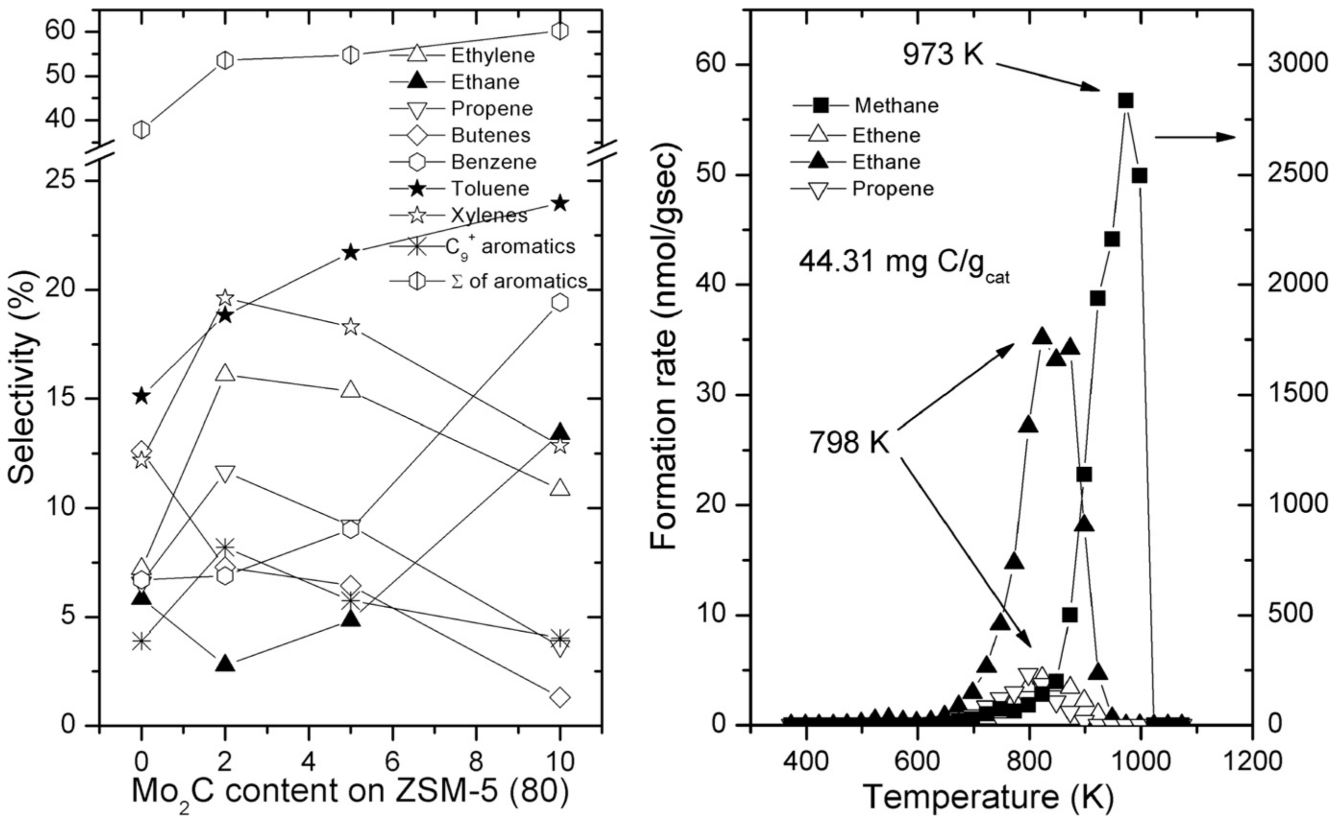
4.1. Dimethyl ether

4.1.1. Adsorption and desorption

The absorption bands 2997, 2927, 2898, 2878, 2831 and 2813 cm^{-1} determined following the adsorption of DME on pure ZSM-5(80) at ~180 K (Fig. 1) correspond very well to the vibrational motions of the molecularly adsorbed DME (Table 1). In addition, however, the appearance of spectral features at 2972, 2945 and 2840 cm^{-1} suggests the occurrence of a dissociation in the adsorbed layer even at the temperature of adsorption. This process very likely involves the scission of one of the C–O bonds of DME

$$(CH_3)_2O_{(a)} \rightarrow CH_3O_{(a)} + CH_{3(a)} \qquad (1)$$

and the formation of Al–OCH_3. The generation of Si-OCH_3 is less likely as it requires high temperature and high pressure



(A)

(B)

Fig. 8. Effects of Mo_2C content of ZSM-5(80) on the selectivities of various products formed at 723 K (A). Formation of hydrocarbons in the TPR measurements following diethyl ether reaction on 5% Mo_2C/ZSM-5(80) at 723 K for 5 h (B).

Table 4
Main results obtained in the reaction of diethyl ether on ZSM-5-based catalysts

Catalyst	Temp. (K)	Selectivity (%)									
		Methane	Ethylene	Ethane	Propylene	C_4 aliph.	Benzene	Toluene	Xylenes	C_{9+} arom.	∑aroma
ZSM-5(80)	673	1.1	3.9	2.9	3.3	22.0	4.6	13.9	12.3	5.5	36.1
	773	7.7	13.8	9.9	9.8	5.0	10.3	17.3	10.9	3.1	41.5
2% Mo_2C/ZSM-5(80)	673	0.4	6.2	1.2	6.9	15.8	4.0	15.5	24.5	13.4	57.2
	773	2.4	29.5	4.7	10.9	2.8	13.2	20.0	10.9	2.6	46.7
5% Mo_2C/ZSM-5(80)	673	0.5	7.7	2.2	7.3	19.2	4.8	16.9	18.7	7.3	47.8
	773	3.5	26.6	8.4	5.3	1.1	17.0	19.2	11.6	3.8	51.6
10% Mo_2C/ZSM-5(80)	673	1.3	4.5	4.3	3.5	10.7	9.6	22.1	17.1	4.9	53.8
	773	4.5	16.1	15.0	3.3	0.6	24.5	19.4	7.6	2.6	54.2
ZSM-5(280)	673	0.4	12.2	1.5	11.9	26.4	2.9	9.1	13.6	9.9	35.6
	773	4.2	29.7	4.1	19.2	7.7	6.0	12.4	9.0	2.8	30.1
5% Mo_2C/ZSM-5(280)	673	0.4	13.0	1.9	10.7	21.2	2.6	12.1	17.4	9.1	41.2
	773	2.7	33.9	6.5	7.6	2.2	13.0	17.4	10.1	3.1	43.6

[52]. The spectral features detected at 300 K can readily be assigned to the normal modes of the surface methoxy species (Table 1). As we found no vibrational modes for adsorbed CH_3 we assume that it also interacted with the surface oxygen of the zeolite yielding CH_3O species. Similar spectral features were measured for DME adsorbed on the Mo_2C-promoted ZSM-5(80). This is not surprised if we take into account the large surface area of the zeolite. The fact that the intensities of vibrational modes were lower than in the previous case indicates that Mo_2C occupies some of the adsorption sites on the ZSM-5, which also leads to the decrease of the number of Brönstead sites [49].

4.1.2. *Catalytic reactions*

ZSM-5 zeolites effectively catalyzed the reaction of DME. As shown in Fig. 3, whereas at lower temperatures C_4 olefins are the main products, at higher temperature the formation of C_2H_4 and C_3H_6 became the dominant compounds. Aromatics, benzene, toluene, xylene and C_9 are also produced: their total selectivity is decreased with the temperature (Fig. 3A, Table 2). The conversion of DME to olefins (DTO process) is closely related to methanol to olefins (MTO) process, which is well studied due to its great technological importance. The most effective catalysts for the MTO process are the zeolites, which due to their acidic sites can promote the formation of C–C bond, which is the vital step in the

MTO reaction and also in the subsequent reactions [25–28]. Despite the intensive research, however, many details of this very complex transformation has been the subject of a great debate. As regards the C–C formation more than 20 different proposals may be discerned. The formation of free carbene radicals [26], formation of trimethyloxonium and ylide intermediates [57], carbocations [27], and mechanisms involving ketene intermediate and CO as the active catalyst [58] have been proposed. Intermediate surface methoxy species formation has also been suggested [59]. The hydrocarbon-pool mechanism has also gained increasing acceptance [60]. It proceeds via repeated methylations and dealkylations of organic reaction centers trapped inside the zeolite voids. Methyl benzenes, and the higher homologues have been identified as key intermediates [60]. According to Oláh and Molnár [57] it is now generally accepted that methanol undergoes preliminary Brönsted acid catalyzed dehydration step, and DME, or equilibrium mixture of DME and methanol, acts as the precursor to hydrocarbon formation. An important contribution to this subject was provided by the use of density functional theory (DFT). Blaszkowszki and van Santen [61] analyzed several reaction paths for C–C formation bond with this method. They confirmed the experimental results of Manson et al. [62], namely that ethanol and ethyl methyl ether are formed from surface methoxy groups, methanol, and/or dimethyl ether. Formation of trimethyl oxonium, proposed to be an intermediate in initial C–C bond formation, was also considered as a possible intermediate.

Depending on the nature of the catalysts the light olefins formed can be also activated on the Brönsted sites of ZSM-5 to give higher olefins, aromatics, alkanes and naphthalenes. As regards the production of aromatics the extent of the activation, however, is limited, as a result the yield of aromatics from methanol was only 25.1% on pure ZSM-5(80) and 7.0% on ZSM-5(280) [24]. Similar processes will occur on zeolites when the starting compound is DME. The Brönsted sites of ZSM-5 obviously play a decisive role both in the activation of DME and also in the further reaction of light olefins into aromatics via hydrogen transfer, alkylation and polycondensation. The yields of aromatics was, however, somewhat less compared to those measured in the reaction of methanol (Table 2). When Mo_2C was added to ZSM-5 the product distribution changed, and the formation of aromatics was clearly enhanced. At 723 K the total selectivity of aromatics increased with the rise of the amount of Mo_2C on ZSM-5(80) (Fig. 4A). This result is mainly due to the higher formation of xylenes and C_9 aromatics. Similar feature was experienced in the case of ZSM-5(280). In this case the optimum amount of Mo_2C is 5%, as at higher loading the formation of aromatics falls down (Table 2).

The question to be answered is the way of the effect of Mo_2C. Previous studies on Mo_2C/Mo(100) surface showed that the Mo_2C, or more precisely the metal-terminated carbide is a reactive surface [63]. It can activate the C–O bond in the adsorbed CO and CO_2 [64] and even the C–I bond in various alkyl iodides by forming a strong bond with the oxygen and iodine [65]. The release of iodine from Mo_2C proceeds above 900 K with $T_p \sim 950$ K [65]. Mo_2C/Mo(100) model catalyst also exhibited a high reactivity towards DME under UHV conditions [50]. 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 long pair of DME to the carbide surface [50]. 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. Both intermediates, however, are unstable on Mo_2C and decompose to hydrogen, CO, CH_4 and surface carbon. The formation of C_2 compounds was not detected.

In harmony with this behavior unsupported polycrystalline Mo_2C catalyzed the decomposition of DME above 523 K yielding the same products with a small amounts of C_2 compounds. There was, however, no sign of the formation of aromatics. We cannot rule out the decomposition of DME proceeds in this way on Mo_2C when it supported by ZSM-5. As Mo_2C reduces the number of Brönsted sites of ZSM-5 [49], we have to assume that it opens a new route for the activation of DME and/or for the further reaction. As was mentioned above pure Mo_2C catalyzes the decomposition of DME by facilitating its dissociation to the reactive CH_3 and CH_3O species (Eq. (1)). Another role of the Mo_2C very likely 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 different C_xH_y products, which are converted into aromatics on the acidic sites of the zeolite [4,13,23].

4.2. Diethyl ether

4.2.1. Adsorption and desorption

Taking into account the similarity of IR spectra of DEE and its possible dissociation products (Table 3), it is not easy to distinguish between these compounds. The intense absorption bands at 2981, 2930 and 2870 cm^{-1} observed on the IR spectra of adsorbed DEE on ZSM-5(80) at 180–200 K correspond very likely to the vibration of the molecularly adsorbed DEE. The presence of weak spectral features at 2939 and 2908 cm^{-1} suggests that dissociation of DEE

$$(C_2H_5)_2O_{(a)} = C_2H_5O_{(a)} + C_2H_{5(a)} \tag{3}$$

already occurred at 180–200 K, and they reflect the formation of Al–OC_2H_5 surface species. The vibration of C_2H_5 formed may also contribute to these spectral features (Table 3). Upon heating the adsorbed layer the vibrational modes of DEE gradually attenuated, while those belonging to ethoxy species, 2984, 2939–2943, 2908 and 2883 cm^{-1}, remained almost unaltered up to 423 K.

4.2.2. Catalytic reaction

The reaction of DEE on ZSM-5 catalyst produced mainly C_2–C_4 olefins and various aromatics at 523–773 K. For the description of the formation of these compounds it should be pointed out an important difference between DME and DEE. In the latter case the C–C bond already exists in the molecule, consequently there is no need to consider and assume the complex reaction sequence described for the activation and reaction of DME. This is probably the reason that the formation of aromatics from DEE proceeds more easily compared to the case of DME. Apart from this the acidic sites of pure ZSM-5 still play an important role in the activation of the molecule, and in the production of aromatics (Fig. 7).

In addition to the rupture of C–O bond (Eq. (4)) we may count with the dehydration of DEE

$$(C_2H_5)_2O_{(a)} = 2C_2H_{4(g)} + H_2O_{(g)} \tag{4}$$

or

$$(C_2H_5)_2O_{(a)} = C_4H_{8(a)} + H_2O_{(a)}. \tag{5}$$

This process occurs readily in the case of ethanol over zeolites of high Brönsted acidity [22,23]. The fact that at low temperature, 523–573 K, butanes are the main products suggests that the coupling of C_2H_5 groups in the adsorbed DEE on ZSM-5(80) (Eq. (5)) is more favorable than the simple dehydrogenation step (Eq. (4)).

As in the previous case Mo_2C exerted a considerable influence on the product distribution and enhanced the formation of aromatics. In the study of the interaction of DEE with Mo_2C/Mo(100) surface it was found that the adsorption of DEE also causes a marked decrease (maximum 2.8 eV) in the work function of Mo_2C/Mo(100) at 100 K [50], which was again attributed to the electron donation from oxygen lone pair of DEE to the carbide. This electronic interaction may lead to an increased activation of C–O bond in the adsorbed DEE on Mo_2C. Analysis of the HREEL spectra of adsorbed and annealed layer led to the assumption of the occurrence of primary process (Eq. (3)) followed by the decomposition of adsorbed reaction intermediates mainly to CO, H_2, methane and ethylene [50]. Similar features and products were found in the present case on polycrystalline Mo_2C without any traces of aromatics. However, the situation is different, when Mo_2C is deposited on ZSM-5 containing Brönsted sites. The carbide changed the product distribution and promoted the aromatization of DEE. Following the previous discussion (Section 4.1), the effect of Mo_2C can be again attributed to the dehydrogenation property of Mo_2C, which is the first step in the oligomerization, cyclization, and hydrogen transfer of olefins [66,67]. As was reported before Mo_2C markedly facilitates the aromatization of butanes and butenes on ZSM-5 zeolites [68].

5. Conclusions

(i) FTIR spectroscopic measurements showed that both the DME and DEE undergo partial dissociation on pure and Mo_2C-containing ZSM-5(80) at 180–200 to yield methoxy from DME and ethoxy from DEE.
(ii) TPD measurements following the adsorption of ethers showed the formation of methane, ethene and propene from DME and ethene, ethane and propene from DEE.
(iii) ZSM-5 zeolite is an active catalyst for the decomposition of DME and DEE. Depending on its composition, it also catalyzes the formation of aromatics at high temperatures.
(iv) The deposition of Mo_2C on ZSM-5, however, markedly enhances the formation of aromatics (benzene, toluene, xylene, and C_{9+}), very likely by activation of ethylene and other olefins formed.

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