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Aromatization of *n*-butane and 1-butene over supported Mo_2C catalyst

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Abstract

The reaction pathways of *n*-butane were investigated on Mo_2C deposited on ZSM-5 and SiO_2. Particular attention was paid to the effects of the composition of ZSM-5, to the influence of the Mo_2C loading, and to the nature of supports. ZSM-5 itself catalyzed the reaction of *n*-butane well above 800 K. Its efficiency sensitively depended on the composition of zeolite. Whereas the conversion of butane was ∼ 90% on ZSM-5 with $SiO_2/Al_2O_3 = 30$ at 823 K, this value was only ∼ 24% on the sample with $SiO_2/Al_2O_3 = 280$. The dominant reaction was the cracking of butane yielding several C_1–C_3 compounds. Deposition of Mo_2C markedly changed the catalytic performance of ZSM-5, and the dehydrogenation and the aromatization processes came into prominence. This is particularly true in the case of less effective ZSM-5 ($SiO_2/Al_2O_3 = 280$). From the extrapolation of selectivities to zero conversion we obtained that methane, ethane, ethylene, propylene, butene, and hydrogen are the primary products on pure and Mo_2C-containing ZSM-5. Aromatics are formed in a secondary process, in the oligomerization and aromatization of butenes. The favorable effect of Mo_2C is well exhibited in the case of SiO_2, which was practically inactive. For 2% Mo_2C/SiO_2 at 823 K the selectivity of aromatics was 16–17% at a butane conversion of 26%. On this sample the main reaction was the dehydrogenation process. As the starting compound in the formation of aromatics is very likely butene, detailed measurements were performed on its reaction on the previously studied catalysts. 1-Butene exhibited a very high reactivity on pure ZSM-5 samples even at 723 K. The presence of 2% Mo_2C on the zeolites resulted only in a slight change in the conversion and product selectivities. The possible mechanism of the reactions and the role of Mo_2C are discussed, taking into account our surface science studies on the reaction of butyl species on a Mo_2C/Mo(100) surface.

Keywords: Aromatization of *n*-butane; Reaction of 1-butene; Mo_2C/ZSM-5; Mo_2C/SiO_2

1. Introduction

The upgrading of lower alkanes is an important subject of heterogeneous catalysis [1]. One of the great challenges in this area is to transform methane into higher hydrocarbons with high conversion and selectivities, which represents one route of converting the cheap raw materials into more valuable compounds. The discovery of Wang et al. [2] and Xu et al. [3] that methane can be converted into benzene on MoO_3/ZSM-5 opened a new route for the utilization of methane. It turned out, however, that Mo_2C not MoO_3 is the key component for the activation of methane, which is formed from MoO_3 during the induction period of the reaction [4–9]. In subsequent works great attention was devoted to the formation, structure, and reactivity of Mo_2C on ZSM-5 [10–15].

In our laboratory we continued our work in two directions: (i) elaborating the effect of Mo_2C on the aromatization of other hydrocarbons, ethane [16,17], ethylene [18], and propane [19], and (ii) studying the chemistry of hydrocarbon fragments, C_xH_y, the primary products of the activation of the above compounds, on Mo_2C/Mo(100) in UHV by several spectroscopic methods [20–24].

As a continuation of this research program the reaction of *n*-butane and 1-butene was investigated on the same Mo_2C/ZSM-5 catalyst used in our previous works. Attention is paid to the low-temperature interaction of butane with the catalyst, to the effects of the composition of ZSM-5 on the catalytic performance of Mo_2C, and to the influence of preparation and pretreatments of the catalysts. Detailed measurements are also performed on Mo_2C deposited on inactive oxidic supports. In order to obtain a deeper insight into the mechanism of the formation of aromatics, the reaction of

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1-butene, assumedly the starting compound in the formation of benzene, is also examined on Mo_2C-containing catalysts. In a short paper we already gave a preliminary account of the reaction of *n*-butane on Mo_2C/ZSM-5 ($SiO_2/Al_2O_3 = 80$) [25]. The interaction of *n*-butane with MoO_3 on ZSM-5 and the aromatization of *n*-butane on Mo_2C/ZSM-5 were also studied by Derouane's school [26,27]. Both laboratories showed that while *n*-butane is mainly cracked on ZSM-5, the production of aromatics is markedly promoted when Mo_2C is deposited on ZSM-5. In addition, Derouane and co-workers [26,27] also developed a method for the preparation of Mo_2C by a C_4H_{10}/H_2 mixture. The large amount of Mo_2C ($\sim 15\%$) used allowed them to perform XRD measurements and to determine the structure of Mo_2C formed under different experimental conditions. They stated that the α-Mo_2C is a better catalyst than β-Mo_2C, and the final temperature of the carburization of MoO_3/ZSM-5 effects both the conversion and the selectivity to aromatics. This observation is important in developing a more efficient Mo_2C/ZSM-5.

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 (7 mm i.d.) connected to a capillary tube [3,5,6]. The flow rate was in most cases 12 ml/min. The carrier gas was Ar. The hydrocarbon content was 12.5%. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were analyzed by gas chromatography using a Hewlett-Packard 4890 gas chromatograph with an HP-Plot Al_2O_3 and with a Poropak QS + S columns. The conversion of *n*-C_4H_{10} was calculated taking into account its amount consumed, and also on the hydrogen and carbon basis. The first two gave practically similar values. The selectivity for reaction products, S_i, was defined as

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

where x_i is the fraction of product i, and n_i is the number of carbon atoms in each molecule of gaseous products.

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 and then heated in a H_2 stream with a rate of 5 K/min and the hydrocarbons formed were measured. The acidity of ZSM-5 samples was determined by the method described before [28], which consists of the adsorption and desorption of NH_3.

The XPS measurements were performed in a Kratos XSAM 800 instrument at a base pressure of 10^{-8} Torr using Mg-K_α 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 pass energy was set at 40 eV, and an energy step width of 50 meV and dwell time of 300 ms were used. Typically 10 scans were accumulated for each spectrum. Fitting and deconvolution of the spectra were made using the VISION software (Kratos). The pretreatments of the samples were performed in the preparation chambers attached to the UHV system.

Table 1
Characteristic data for ZSM-5 samples

SiO_2/Al_2O_3 ratio	BET area (m^2/g)	Total acid sites/unit cell
30	400	9.79
50	425	6.94
80	425	3.22
250	400	1.32

2.2. Materials

The gases used were of commercial purity (Linde). Four ZSM-5 samples with different compositions were used. The starting materials were NH_4-ZSM-5 (Zeolite International), which was calcined to produce H-ZSM-5 in air at 863 K for 5 h. Silica used were the products of Aerosil and Degussa. The surface areas of the samples obtained are shown in Table 1. The acidity of the zeolites are also listed in Table 1.

MoO_3-containing catalysts were prepared by impregnating H-ZSM-5 or SiO_2 with a basic solution of ammonium heptamolybdate to yield different wt% of MoO_3. The suspension was dried at 373 K and calcined at 863 K for 5 h. Supported Mo_2C catalysts were prepared by the carburization of calcined MoO_3/ZSM-5 or MoO_3/SiO_2 by ethane following the description of Green and co-workers [29]: the MoO_3-containing sample was heated under 10% v/v C_2H_6/H_2, from room temperature to 900 K at a heating rate of 0.8 K min^{-1}. After preparation the catalysts were cooled down to room temperature under argon. The carbides were passivated in flowing 1% O_2/Ar at 300 K. The same catalysts were made by carburization of supported MoO_3 by a CH_4/H_2 mixture [30]. Before most of the catalytic experiments, the samples were treated with H_2 at 873 K for 60 min to remove the excess carbon. Unsupported Mo_2C was also prepared by carburization of MoO_3 with ethane.

Some characteristic XPS spectra for supported Mo_2C are presented in Fig. 1. The binding energies for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) were 227.8–228.2 and 230.7–231.1 eV, and for C(1s) 283.8 eV. These values are consistent with those attributed to Mo_2C [6,9,31].

3. Results

3.1. Interaction of n-butane with supported Mo_2C

Butane adsorbed weakly and nondissociatively on Mo_2C/ZSM-5 at 140–250 K. By means of FTIR spectroscopy we detected the characteristic absorption bands of *n*-butane. Above 300 K new bands appeared at 2960, 2873, 1381, and 1330 cm^{-1}, which remained on the spectra even

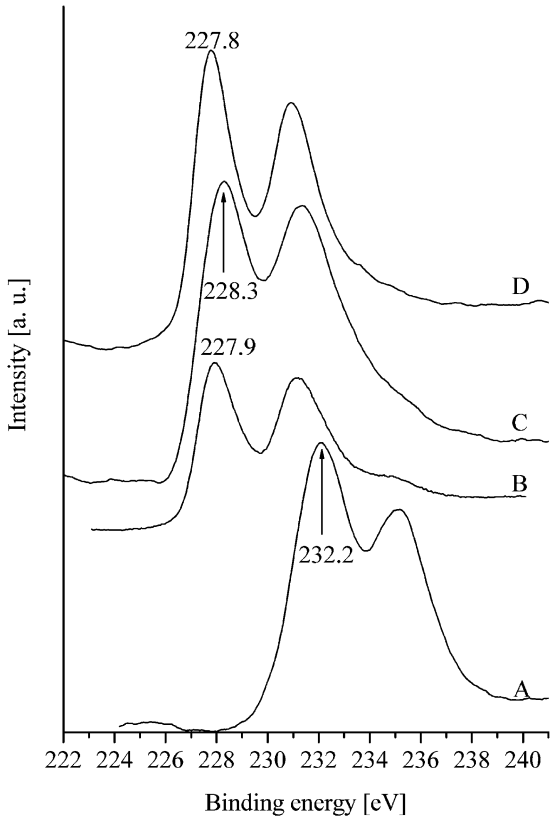

Fig. 1. XPS spectra of Mo_2C/ZSM-5 and Mo_2C/SiO_2 catalysts: (A) MoO_3/ZSM-5; (B) Mo_2C (Aldrich); (C) Mo_2C/SiO_2; (D) Mo_2C/ZSM-5.

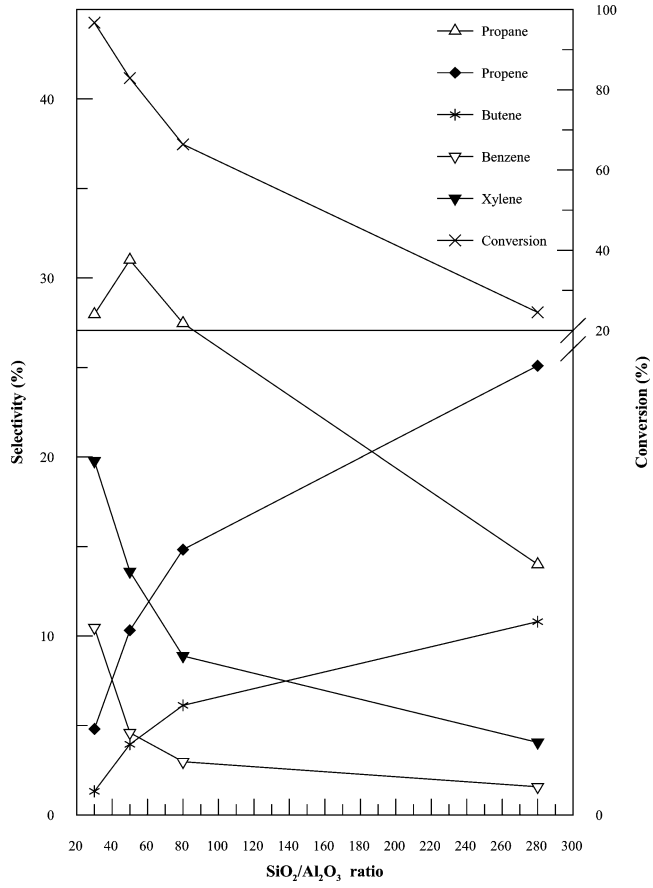

Fig. 2. Effects of SiO_2/Al_2O_3 ratio on the reaction of *n*-butane at 823 K. Data were taken at 40 min on stream.

after degassing the sample at 300–400 K. These bands can be attributed to the vibrations of butylidyne formed in the strong interaction of *n*-butane with Mo_2C [32]. No such spectral features were observed on pure ZSM-5 under similar conditions.

3.2. Reaction of *n*-butane

3.2.1. Effects of the composition of ZSM-5

First we examined the catalytic behavior of four ZSM-5 samples with different compositions. Characteristic data for the effect of the composition of ZSM-5 are plotted in Fig. 2. As regards the conversion of *n*-butane, the ZSM-5 with $SiO_2/Al_2O_3 = 30$ (further $Si/Al = 30$) was found to be the most active catalyst. At 823 K the conversion was above 90%. Another feature is the high stability of the catalyst, which is characteristic for all ZSM-5 samples used. The highest selectivity was measured for propane (26–28%), xylene (18–20%), ethane (14.6%), methane (14.0%), benzene (11–12%), ethylene (6.7%), and propene (4.9%). It is interesting that butenes were formed with low selectivity, $\sim 1.0\%$.

The efficiency of the ZSM-5 gradually decreased with the increase of the SiO_2/Al_2O_3 ratio, and at the value of 280, the conversion of butane was only 23–24%. At the same time the selectivity of benzene and xylene diminished, whereas that of the olefins increased. This is particularly true for the formation of butenes, the selectivity of which was more than an order of magnitude higher on ZSM-5 ($Si/Al = 280$) compared to the value measured for zeolite ($Si/Al = 30$). We note here that toluene was formed on all zeolites, but its selectivity remained at a low level (0.12–0.47%).

Table 2
Distribution of butenes formed in the reaction of *n*-butane on different catalysts at 823 K

Catalyst	Si/Al ratio	Selectivity (%)			
		trans-2-Butene	1-Butene	Isobutene	*cis*-2-Butene
H/ZSM-5	(30)	0.36	0.18	0.51	0.25
2% Mo_2C/ZSM-5	(30)	0.85	0.74	1.34	0.66
H/ZSM-5	(50)	0.94	0.74	1.59	0.72
2% Mo_2C/ZSM-5	(50)	1.26	1.03	2.09	0.97
H/ZSM-5	(80)	1.52	1.18	2.55	1.16
2% Mo_2C/ZSM-5	(80)	2.38	1.95	3.79	1.83
H/ZSM-5	(280)	3.59	2.54	5.75	2.67
2% Mo_2C/ZSM-5	(280)	8.93	7.40	14.42	6.92

Data were taken at 75 min of time on stream.

Detailed analysis of butenes showed that it consists of 1-butene, *trans*-2-butene, isobutene and *cis*-2-butene. Their distribution is shown in Table 2. It appears that isobutene is produced with higher selectivities on all ZSM-5 samples.

3.2.2. Effects of Mo_2C

From the study of the effect of the preparation of Mo_2C we observed that the preparation of Mo_2C by carburization of unsupported or ZSM-5-supported MoO_3 by ethane always produced a better catalyst compared to that made by methane. This feature appeared in both the conversion and the selectivity to formation of aromatics. The possible reason is the higher surface area or dispersion of Mo_2C. Therefore in the subsequent measurements the Mo_2C samples were made using ethane. As regards the catalytic performance of unsupported Mo_2C (0.5 g) we found a well measurable reaction of *n*-butane at 823 K. The initial conversion was 10–15%, which decayed to a constant value, 4–5% after 20–30 min of reaction. The main process was the dehydrogenation yielding various butenes and hydrogen. The selectivity to butenes was 75–80%, but the products of cracking reactions were also observed. Benzene and xylene were also formed, but their total selectivity was below 0.5%.

Next, the effects of different amounts of Mo_2C were examined on all ZSM-5 samples. As ZSM-5 (Si/Al = 30) itself exhibited high activity (see results in Fig. 2), a great improvement of its catalytic performance with Mo_2C addition was not expected. The deposition of 2% Mo_2C onto this ZSM-5 led to a decay in the conversion of butane of a few percent, and somewhat improved the aromatization capability of ZSM-5, as indicated by the higher selectivity of aromatics. As shown in Fig. 3, the selectivities of various products changed very little with time on stream. A further increase in the amount of Mo_2C produced a less effective catalyst, and was also unfavorable for the formation of aromatics. A dramatic enhancement in the selectivity of the formation of butenes occurred and, at the same time, a significant reduction in the selectivity of propane.

We experienced similar phenomena in the case of less effective ZSM-5 samples. The addition of 2% Mo_2C to ZSM-5 (Si/Al = 80) increased the selectivity to aromatics from 12 to 27% and markedly diminished that to propane. On increasing the amount of Mo_2C we observed a decrease in the conversion and in the selectivities of aromatics, methane, ethane, and propane, and a marked increase in that of butenes (Fig. 4A). The results obtained for ZSM-5 (Si/Al = 280) are plotted in Fig. 4B. While this zeolite exhibited a very little aromatizing tendency, the presence of Mo_2C promoted the formation of both benzene and xylene and slightly increased the conversion too. The selectivity of aromatics rose from 6 to 13–15%. A significant enhancement was observed in the selectivity of butenes, whereas the formation of lower hydrocarbons, particularly that of propane, has been reduced. Mo_2C exerted only a slight influence on the formation of toluene measured on the ZSM-5 samples.

When the temperature was raised to 873 K, the selectivities of all aromatic compounds, benzene, xylene, and toluene were considerably increased, mainly at the expense of the formation of propane, and resulted in higher yields of aromatics. This is well illustrated in the Table 3, where the yields of various products are collected.

As regards the distribution of butenes on Mo_2C/ZSM-5 samples we found the same features as for pure ZSM-5. Isobutene formed with higher selectivities on all Mo_2C-containing catalyst (Table 2).

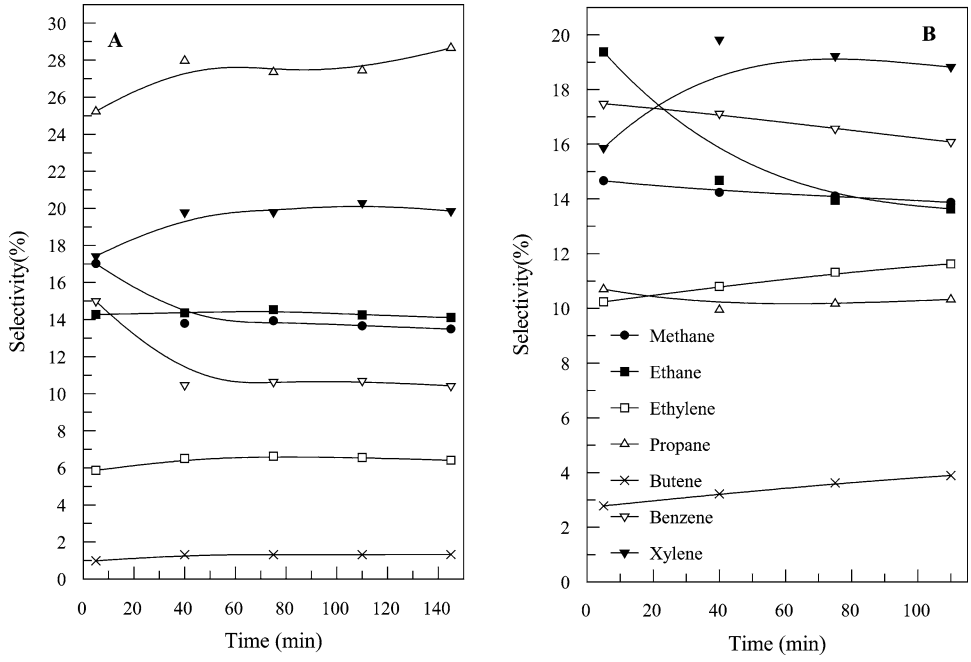

Fig. 3. Selectivities for various products formed in the reaction of *n*-butane on ZSM-5 (Si/Al = 30) (A) and 2% Mo_2C/ZSM-5 (Si/Al = 30) (B) at 823 K in time on stream.

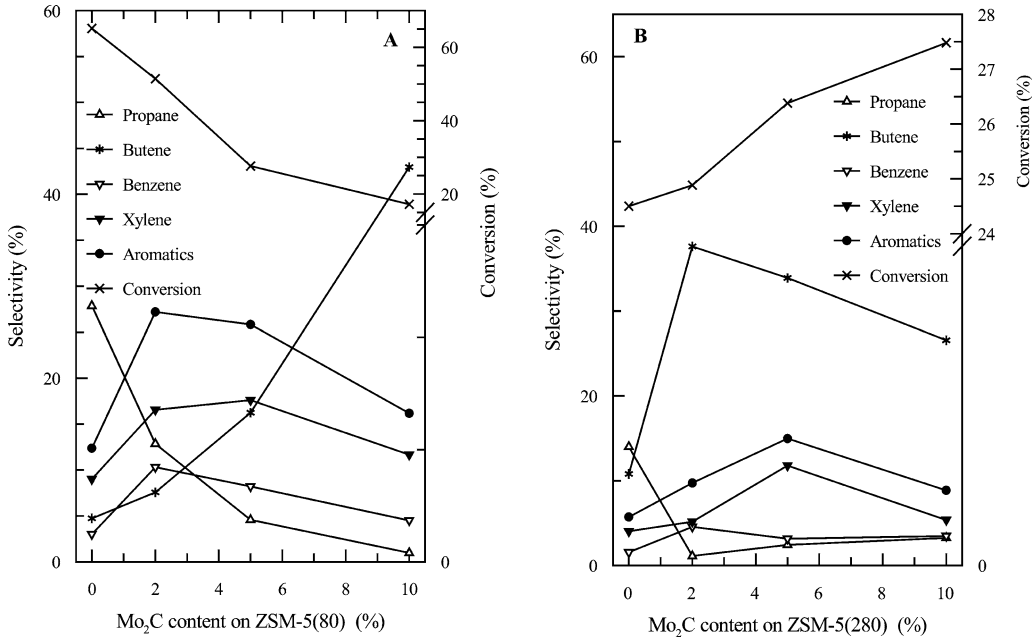

Fig. 4. Effects of Mo_2C content of ZSM-5 on the reaction of *n*-butane at 823 K: (A) Si/Al = 80; (B) Si/Al = 280. Data were taken at 40 min on stream.

Table 3
Some characteristic data for reaction of *n*-butane on various ZSM-5 and Mo_2C/ZSM-5 catalysts at 823 and 873 K

Catalyst	Si/Al	Conversion	Yields				
	ratio	(%)	Propane	Butene	Benzene	Xylene	Aromatics
ZSM-5	(30)	96.74	27.05	1.27	10.12	19.13	29.71
2% Mo_2C/ZSM-5	(30)	86.40	8.59	2.78	14.79	17.13	32.30
2% Mo_2C/ZSM-5[a]	(30)	99.18	2.08	0.50	28.00	21.14	49.14
ZSM-5	(50)	82.91	25.70	3.27	3.81	11.28	15.41
2% Mo_2C/ZSM-5	(50)	85.18	9.41	2.37	12.09	16.81	28.90
2% Mo_2C/ZSM-5[a]	(50)	96.79	4.51	1.29	23.53	18.34	41.86
ZSM-5	(80)	66.39	18.23	4.06	1.97	5.90	8.09
2% Mo_2C/ZSM-5	(80)	52.03	6.71	4.91	5.38	8.62	14.17
2% Mo_2C/ZSM-5[a]	(80)	65.43	3.85	4.26	8.34	9.86	18.20
2% Mo_2C/ZSM-5[b]	(80)	70.49	7.43	3.17	8.07	12.2	30.27
ZSM-5	(280)	24.54	3.44	2.65	0.38	0.99	1.41
2% Mo_2C/ZSM-5	(280)	24.89	0.28	9.36	1.14	1.29	2.43
2% Mo_2C/ZSM-5[a]	(280)	30.96	1.02	5.03	1.88	2.22	4.11
2% Mo_2C/SiO_2	(Aerosil)	14.69	0.05	7.90	0.97	0.79	1.47
2% Mo_2C/SiO_2[b]	(Aerosil)	36.95	0.25	15.74	4.07	3.00	7.07
2% Mo_2C/SiO_2[a]	(Aerosil)	32.80	0.17	11.40	4.20	3.21	7.42
10% Mo_2C/SiO_2	(Aerosil)	35.15	0.18	19.46	2.54	2.58	5.12
10% Mo_2C/SiO_2	(Cabosil)	33.24	0.09	20.34	2.14	2.04	4.18

[a] Data were taken at 873 K.
[b] Data were taken at a flow rate of 7.5 ml/min.

3.2.3. TPR measurement for used catalysts

In order to establish the amount and the reactivity of carbonaceous species formed on the catalyst surface during the reaction, TPR measurements were performed with hydrogen. When the excess carbon formed on Mo_2C during carburization was removed with H_2 treatment at 873 K, the subsequent TPR measurements gave only few carbon-containing compounds. As the data presented in Fig. 5 show a small amount of carbon (1.76 mg/g catalyst) was deposited on 2% Mo_2C/ZSM-5 (Si/Al = 80) during the reaction of *n*-butane, which reacted with hydrogen above 500 K yielding methane (T_p = 853 K), ethane (T_p = 773 K), ethylene (T_p = 753 K), and propane (T_p = 713 K). In the absence of Mo_2C, the T_p values appeared at somewhat higher temperatures, but the amount of carbon calculated from the hydrocarbons formed was more than an order of magnitude lower (0.105 mg/g).

3.2.4. Effects of space velocity

Results showing the influence of space velocity on the conversion and selectivities for various products are presented in Fig. 6. As expected the conversion is decreased

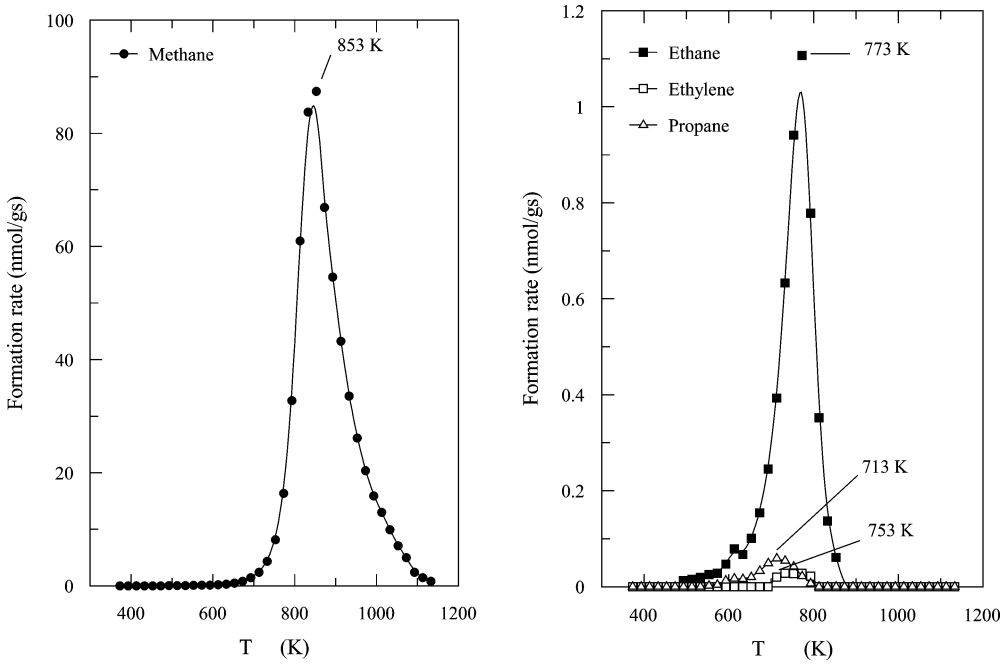

Fig. 5. TPR spectra of 2% Mo_2C/ZSM-5 (Si/Al = 80) after reaction of *n*-butane at 823 K for 120 min.

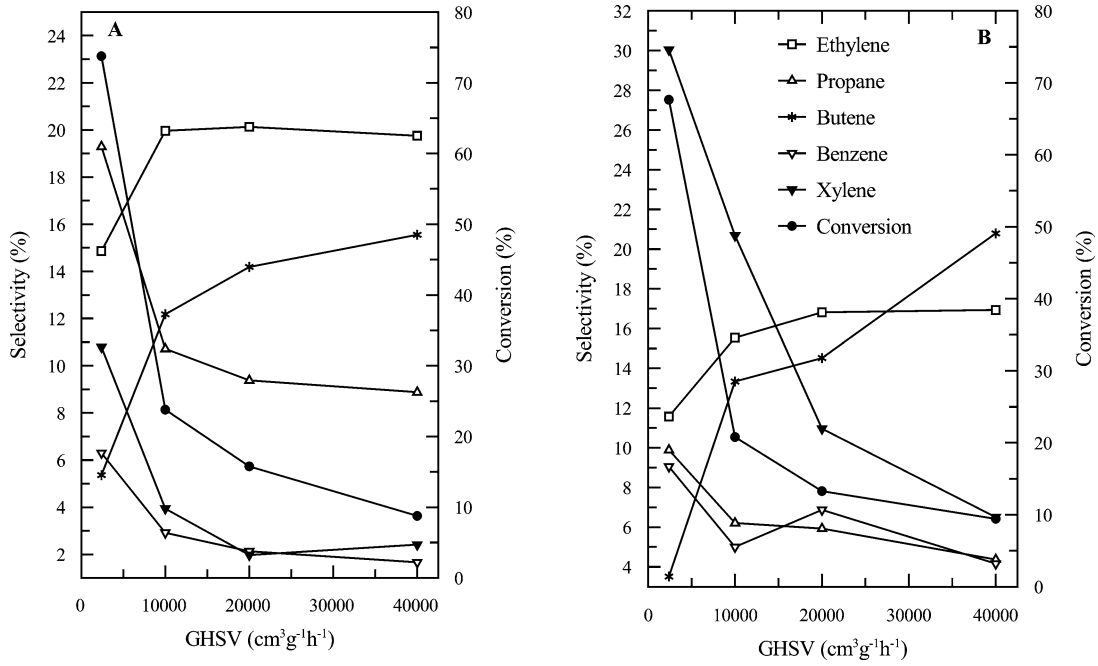

Fig. 6. Effects of space velocity on the reaction of *n*-butane on ZSM-5 (Si/Al = 80) (A) and on 2% Mo_2C/ZSM-5 (Si/Al = 80) (B) at 823 K.

with the rise of the space velocity. The selectivities of aromatics also decreased, whereas an increase was observed in these values of all unsaturated compounds, like ethene, propene, and butene.

3.2.5. *Effects of supports*

Mo_2C deposited on other oxidic supports (alumina, titania, magnesia, and silica) was found to be an active catalyst for the dehydrogenation and decomposition of *n*-butane. At 823 K we measured 8–12% of conversion. As regards the formation of aromatics Mo_2C/SiO_2 exhibited the higher activity; therefore, more detailed measurements were carried out only with this catalyst.

The pure silica showed very little activity toward the reaction of *n*-butane. Even at 873 K, the conversion was below 2%. It was interesting to see first how the start-

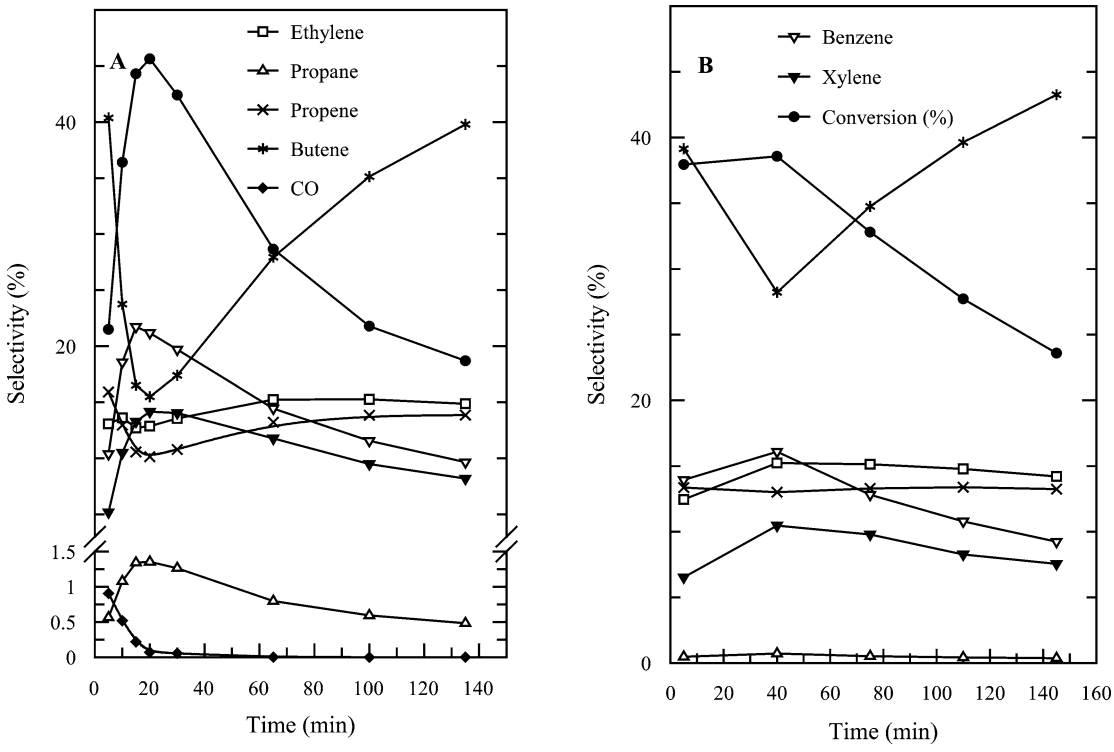

Fig. 7. Reaction of *n*-butane on 2% MoO_3/SiO_2 (A) and on 2% Mo_2C/SiO_2 (B) at 873 K in time on stream.

ing material, 2% MoO_3/SiO_2 used for the preparation of Mo_2C/SiO_2, behaves toward the reaction of *n*-butane. At the beginning of the reaction, up to about 30 min, the formation of CO and H_2O was observed, very likely as a result of the reduction of MoO_3. Other compounds were methane, propane, and propene. Benzene and xylene were detected even at 5 min of reaction, but only in minor amounts. With the progress of the reduction of MoO_3, and possibly with the formation of carbide layer, the conversion and the selectivities to aromatics significantly increased attaining maximum values at 20 min, when the production of CO and H_2O ceased. At the same time the selectivities to propene and butene decreased. After 20–25 min opposite changes were experienced. Similar features were registered at 823 K, where the maximum occurred at 30 min. Data are shown in Fig. 7A.

When Mo_2C was prepared on SiO_2, the formation of CO and H_2O was not observed and only slight changes were experienced in the selectivities of products with time on stream (Fig. 7B). The catalytic behavior of Mo_2C/SiO_2 was sensitive to the preparation of the sample, to the origin of the silica, and particularly to the amount of excess carbon formed during the preparation of Mo_2C. The 2% Mo_2C/SiO_2 (Aerosil) exhibited a somewhat better catalytic performance compared to Mo_2C on Cabosil SiO_2. In this case the conversion of *n*-butane at 873 K approached 40%, which gradually decreased with the time. Similarly as in the case of Mo_2C/ZSM-5, removing the excess carbon with H_2 enhanced the activity of the catalyst; the extent of the enhancement depended on the amount of coke deposited on the catalyst during the carburization process. At 2% Mo_2C content, the major products were various butenes, their total selectivity attained a value of 40–45%. Interestingly, benzene, xylene, and toluene also formed with a total selectivity of 20–25%. Other products were in decreasing selectivities: methane, propene, ethylene, propane, ethane, and isobutane. Higher Mo_2C loading resulted in the enhanced selectivity of butenes and in the slight diminution of that for the formation of benzene. Some characteristic data obtained for various samples are also listed in Table 3.

3.3. Reaction of 1-butene on supported Mo_2C

As the products of the dehydrogenation of *n*-butane are butenes, it was important to examine the reaction of 1-butene on the previously studied catalysts. The reactivity of 1-butene on ZSM-based catalysts is very high: the conversion of 1-butene on pure ZSM-5 samples (Si/Al = 30 and 80) was more than 90% even at 723 K. In the calculation of the conversion, the isomerization of 1-butene, which occurred to a great extent, was not taken into account. The main products were propane followed by xylene, isobutane, and benzene. The selectivities of aromatics were lower on ZSM-5 (Si/Al = 80) compared to ZSM-5 (Si/Al = 30) and their values slightly increased on the effect of 2% Mo_2C. The selectivities of the main products formed on pure and Mo_2C-containing ZSM-5 (Si/Al = 80) at 723 K are plotted with time on stream in Fig. 8. At a lower temperature, 623 K, the selectivities of all the three aromatic compounds

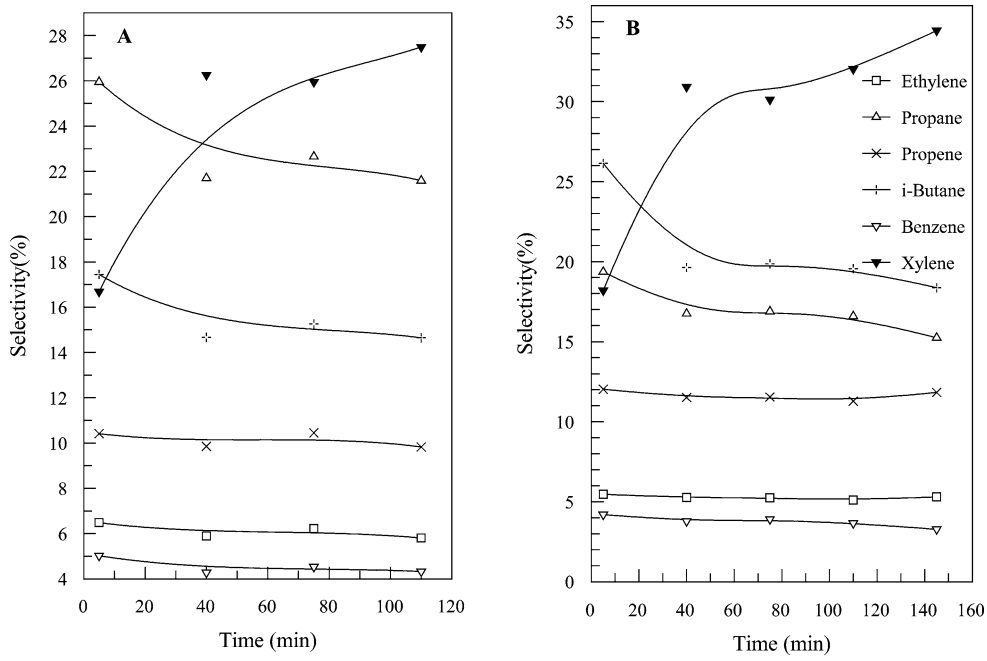

Fig. 8. Selectivities for various products in the reaction of 1-butene on ZSM-5 (Si/Al = 80) (A) and on 2% Mo_2C/ZSM-5 (Si/Al = 80) (B) at 773 K in time on stream.

Table 4
Characteristic data for the reaction of 1-butene on ZSM-5 and 2% Mo_2C/ZSM-5 samples at 723 K

Catalyst	Si/Al ratio	Conversion (%)	Selectivity(%)								Yield of aromatics
			Methane	Ethane	Ethylene	Propane	Propene	Isobutane	Benzene	Xylene	
H/ZSM-5	(30)	98.5	1.42	2.33	2.57	35.37	3.63	9.82	8.83	27.74	36.38
2% Mo_2C/ZSM-5	(30)	98.0	1.32	2.33	2.70	30.94	3.30	9.63	10.94	30.12	40.60
H/ZSM-5	(80)	95.1	0.62	1.25	5.80	21.59	9.82	15.31	5.16	26.65	30.26
2% Mo_2C/ZSM-5	(80)	88.5	0.25	0.60	5.10	16.58	11.28	19.28	3.65	32.02	31.63
H/ZSM-5	(280)	84.5	0.21	0.39	8.39	8.76	23.55	12.82	1.71	18.93	18.08
2% Mo_2C/ZSM-5	(280)	83.84	0.114	0.57	6.87	6.28	26.2	9.95	1.69	20.53	19.28

Data were taken at 40 min of time on stream.

were reduced, whereas the formation of isobutane, *n*-butane, and pentane greatly increased.

It was interesting to examine the reaction of 1-butene on ZSM-5 (Si/Al = 280), too, which exhibited very little aromatizing behavior of *n*-butane. On pure ZSM-5 the conversion of 1-butene was 84.5% at 723 K: the major process was the cracking of butene yielding propene isobutane, propane, ethylene, methane, and ethane in decreasing selectivities. In addition, xylene ($S = 18.7\%$), benzene ($S = 1.7\%$), toluene ($S = 1.0\%$), and several C_5 compounds were also formed. On 2% Mo_2C/ZSM-5 neither the conversion of 1-butene nor the product distribution were altered to an appreciable extent. Most important data are collected in Table 4. Since the reaction pathways of hydrocarbons, particularly the aromatization of alkanes and alkenes, are strongly influenced by the temperature, an attempt was made to measure the reaction at 823 K, where the conversion of *n*-butane was studied. The cracking processes of butene were very fast at this temperature resulting in a larger deposition of coke, too. This caused a more significant deactivation. Nevertheless, selectivities for aromatics determined on both pure and Mo_2C containing ZSM-5 (Si/Al = 280) were only with a few percent higher.

Mo_2C/SiO_2 was a much less active catalyst for the 1-butene. The conversion was only 13% at 723 K, and selectivities to aromatics were 3–5%. At 823 K the conversion approached 20%, and the total selectivity of aromatics attained a value of 7–8%.

4. Discussion

4.1. Reaction of n-butane

4.1.1. Pure ZSM-5 samples

It has been disclosed before that ZSM-5 is an efficient catalyst for the reaction of *n*-butane [1]. The predominant product on ZSM-5 (Si/Al = 56) at high conversion and at 773 K was propane. The yield of aromatics was found to be very small. Several attempts have been made to enhance the catalytic activity of zeolites and to alter the product distribution

by adding different metals and oxides to ZSM-5 [33–41]. As regards the aromatization of *n*-butane, Zn and Ga proved to be the most active promoters [41–46].

By extrapolating the selectivities to zero percent conversion, on pure ZSM-5 (Si/Al = 56) the following compounds were found: methane, ethane, propene, ethylene, butenes, and hydrogen, which were considered as the primary reaction products [44]. This product distribution was described by the following reactions,

$$\nearrow CH_4 + C_3H_7^+ \quad (1)$$

$$n\text{-}C_4H_{10} + H^+ \rightarrow C_2H_6 + C_2H_5^+ \quad (2)$$

$$\searrow H_2 + C_4H_9^+, \quad (3)$$

assuming the transient formation of pentacoordinated carbonium ions. The carbenium ions may release protons to give lower alkenes. As the selectivities for the above compounds decreased in the later stage of the process, the formation of propane came into the fore, another mode of activation of *n*-butane, namely the hydride transfer reaction was assumed [44].

Our systematic study showed that the conversion of *n*-butane on ZSM-5 samples sensitively depends on the composition of zeolites, although there is no significant difference in their surface area. The composition also exerted a drastic influence on the reaction pathway of *n*-butane; at a low Si/Al ratio the aromatics are formed with higher selectivities and relatively higher yields, whereas at a high Si/Al ratio (280) aromatic compounds were produced with low (2–3%) selectivities (Fig. 2). This change in the selectivities can be attributed to the variation of acidic sites, which decrease with the increase of Si/Al ratio (Table 1).

From the extrapolation of selectivities determined for ZSM-5 (Si/Al = 80) to zero percent conversion (Fig. 8), we obtained the same primary products as above for zeolite (Si/Al = 56) [44]. The values of the three reactions are in the ratio 38:29:15 (Table 5). This suggests that the rupture of the C–C bond on this ZSM-5 is more dominant than that of the C–H bond. A change occurred in this ratio for ZSM-5 (280) (Table 5), indicating that on zeolites with decreased acidity the cleavage of the C–H bond became more dominant.

As the total conversion increases, benzene and xylene appear in the products. This suggests that the primary products, very likely the butenes, undergo secondary reactions involving oligomerization, cyclization, and hydrogen transfer before they leave the pore system of ZSM-5.

4.1.2. Effects of Mo_2C

The addition of Mo_2C to ZSM-5 markedly influenced the catalytic performance of all ZSM-5 samples, and this feature was well exhibited on the less effective ZSM-5 samples. The main effects of Mo_2C are as follows:

(i) With the exception of ZSM-5 (Si/Al = 280), the total conversion of *n*-butane is slightly decreased,
(ii) The selectivities and yields for aromatics are enhanced at the expense of the cracking reactions. Higher Mo_2C loading leads to a less active and selective catalysts.
(iii) The production of hydrogen and butenes is markedly increased.

The latter feature indicates that Mo_2C promotes the dehydrogenation of *n*-butane by providing new dehydrogenation centers. As a consequence the production of aromatics is considerably increased very likely through dimerization and oligomerization of butenes on the Brönsted sites of ZSM-5. When the selectivities of various products are extrapolated to zero conversion for 2% Mo_2C-containing ZSM-5 (Si/Al = 80), we obtained the data listed in Table 5. This shows that although the product ratios are different for Mo_2C/ZSM-5 samples, the primary products are the same as on the pure ZSM-5. The dehydrogenation of *n*-butane is more favored on Mo_2C/ZSM-5. Another important result is that aromatics are not primary products, as they are missing at zero conversion even on Mo_2C-containing ZSM-5, too. This implies again that both benzene and xylene are produced in the secondary processes.

In previous studies it was established that zeolite acidity is an important parameter not only for the oligomerization of alkenes but also for the production of alkenes from alkanes [1]. The number of acid sites and acid strength are, however, considerably reduced by loading Mo_2C onto ZSM-5 [47], so we have to assume that this drawback is overcompensated by the enhanced production of butenes in the dehydrogenation process.

The significant effect of Mo_2C on the activation of *n*-butane and on the subsequent reactions is well exhibited by the results obtained on Mo_2C/SiO_2. In this case the situation is simpler as silica is practically inactive for the reaction of *n*-butane. Loading the silica with Mo_2C produced a relatively active catalyst (Table 3). The main process is the dehydrogenation of *n*-butane, which occurs with a selectivity of 50–70%. Cracking reactions may also proceed as indi-

Table 5
Selectivities in *n*-butane conversion at zero conversion (extrapolated) at 823 K

Catalyst	Si/Al ratio	Selectivity (in moles produced per 100 mol butane converted)							
		Methane	Propene	Ethane	Ethylene	Hydrogen	Butene	Isobutane	Aromatics
H-ZSM-5	(80)	38	36	29	40	15	16	4	0
2% Mo_2C/ZSM-5	(80)	40	35	14	34	20	20	7	0
H-ZSM-5	(280)	39	35	33	35.5	22	22	7	0
2% Mo_2C/SiO_2	(Aerosil 380)	1	2	1	3	120	80	29	0

Data were taken from the measurements of the effect of space velocity.

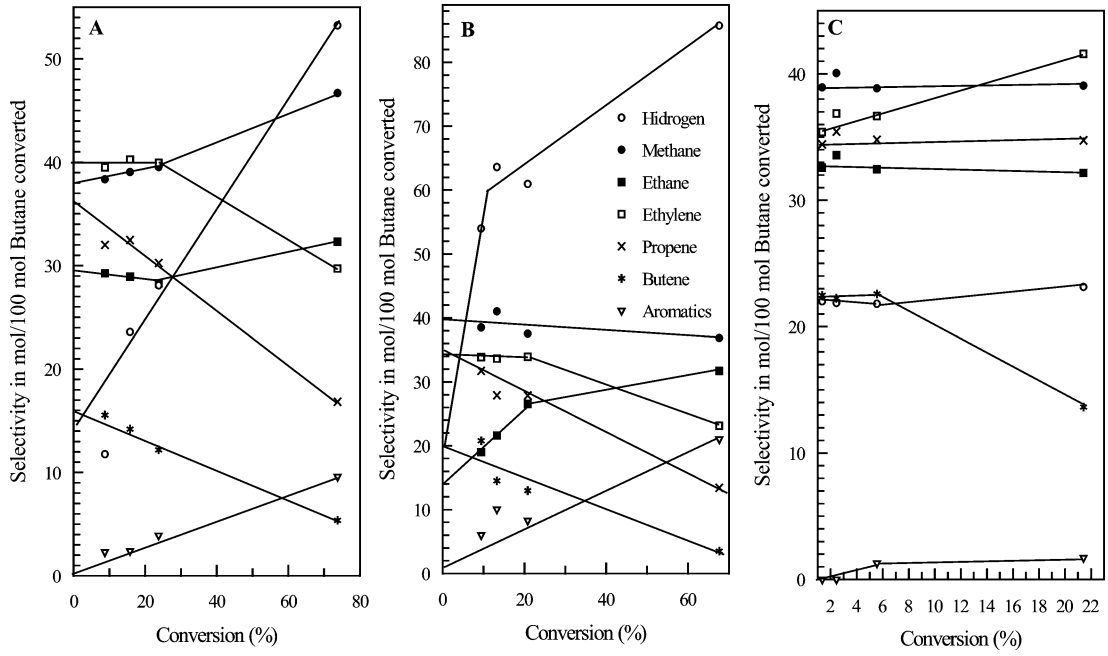

Fig. 9. Product selectivity as a function of *n*-butane conversion over ZSM-5 (Si/Al = 80) (A), ZSM-5 (Si/Al = 280) (B), and 2% Mo_2C/ZSM-5 (Si/Al = 80) (C).

cated by the formation of various lower hydrocarbons. An interesting feature of this catalytic system is the formation of aromatics, benzene and xylene.

From the extrapolation of the selectivities to zero percent conversion we determined the primary products of the reaction on this sample, too (Fig. 9). These are basically different compared to ZSM-5-based catalysts. The predominant products were hydrogen and butenes, and methane, ethane, propane, and ethylene appeared only in traces (Table 5). This suggests that the dehydrogenation is the primary process on Mo_2C/SiO_2, and all the other reactions, including cracking and aromatization, occur subsequently. The formation of aromatics over this catalyst strongly supports the idea that the role of Mo_2C is not only the activation of *n*-butane and the production of butenes, but somehow Mo_2C also participates in the steps leading to aromatics. As silica contains no Brönsted sites we may speculate that during the carburization of MoO_3 or the deposition of Mo_2C itself creates Brönsted sites on silica. Detailed infrared spectroscopic measurements, however, did not prove this assumption [47]. Nevertheless, it was demonstrated that the Mo deposited on SiO_2 reacted with OH groups of the support and induced Lewis acidity. Carburization resulted in further OH consumption and the appearance of stronger Lewis acid sites. Accordingly, we may assume that the oligomerization and aromatization processes of butenes may proceed on Lewis acidic sites of the Mo_2C/SiO_2 catalyst.

The study of the reaction of 1-butene on the previously applied catalysts shed more light on this complex system. We obtained that Mo_2C exerted only slight promotion on the aromatization of 1-butene on ZSM-5 samples. In harmony with this, the formation of aromatic compounds from 1-butene was very limited on Mo_2C/SiO_2. This feature suggests that the direct transformation of the primary product of *n*-butane activation on Mo_2C plays a crucial role in the process leading to the formation of aromatics. In other words, a fraction of the intermediate formed at the Mo_2C/ZSM-5 or Mo_2C/SiO_2 interface, or more precisely on the highly dispersed Mo_2C interacting with the acid sites of these support, is effectively converted into aromatics before they can be transformed into other molecules. This intermediate is very likely butyl species,

$$C_4H_{10(a)} \rightarrow C_4H_{9(a)}$$

which is formed in the activation of *n*-butane on Mo_2C. This idea seems to be supported by the results obtained in the study of the reactions of butyl species on Mo_2C/Mo(100) in UHV system [48]. A C_4H_9 fragment was prepared by the thermal and/or photo dissociation of C_4H_9I. TPD measurements revealed that beside the dehydrogenation and hydrogenation processes the coupling of C_4H_9 species also occurred to a very limited extent.

5. Conclusion

(i) The conversion and reaction pathways of *n*-butane on ZSM-5 sensitively depend on the composition of zeolite. The main reaction is the cracking, and the aromatization proceeds mainly on the sample with a low Si/Al ratio.

(ii) Deposition of Mo_2C changed the catalytic performance of the ZSM-5 and promoted the dehydrogenation and aromatization processes.

(iii) Reaction products determined at zero conversion on Mo_2C/ZSM-5 samples suggested that aromatics are formed in the secondary processes very likely in the reactions of butenes on the acidic sites of ZSM-5.

(iv) Mo_2C catalyzed the dehydrogenation and aromatization of *n*-butane even when it was deposited on an inactive silica support, which suggested that the oligomerization and aromatization processes of butenes might proceed on the Lewis sites of the Mo_2C/SiO_2.

(v) As Mo_2C exerted much less influence on the reaction of 1-butene occurring on ZSM-5 and only slightly enhanced the formation of aromatics, it was inferred that the butyl species, the primary product of the activation of butane on Mo_2C, is effectively converted to a compound leading to aromatics.

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