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Aromatization of Methane over Supported and Unsupported Mo-Based Catalysts

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The interaction of methane with unsupported and supported molybdenum compounds (Mo, MoO_2, MoO_3, Mo_2C, and $MoC_{(1-x)}$) has been investigated at 973 K. ZSM-5 was used as a support. Reaction products were analyzed using gas chromatography. Changes in the composition of catalyst samples were followed by X-ray photoelectron spectroscopy. Molybdenum metal and oxides interacted strongly with methane at 973 K to give H_2 (Mo) and H_2O and CO_2 (oxides), but only a trace amount of ethane. When these compounds were contacted with ZSM-5, the reaction pathway of methane initially was the same. Afterward, however, a dramatic change occurred in the product distribution: the formation of ethane, ethylene, and benzene came into prominence. This was particularly the case when these compounds were highly dispersed on ZSM-5. The selectivity to benzene was 80–85%. XPS analysis of Mo-containing catalysts demonstrated the formation of Mo carbides during the catalytic reaction. Unsupported Mo carbides behaved like metallic Mo; the dominant process was the decomposition of methane to hydrogen and carbon. The deposition of Mo_2C on ZSM-5 in a well-dispersed state, however, produced a very active and selective catalyst for the conversion of methane into benzene. The results suggest that Mo_2C is the active surface species in the Mo-containing catalysts, which converts methane into ethylene, the primary compound for the production of benzene on the zeolite surface.

1. INTRODUCTION

Recently many attempts have been made to activate methane under nonoxidative conditions and to convert it into higher hydrocarbons and aromatic compounds. In the case of supported Pt metals the dehydrogenation of methane occurs readily, yielding a small amount of ethane in addition to the main products, H_2, and surface carbon (1–8). The subsequent hydrogenation of the most reactive carbon gives several higher hydrocarbons and even benzene (1–9). The formation of the latter compounds has been enhanced by adding Cu metal to Rh/SiO_2 catalyst which was attributed to the migration of CH_x species from the Rh onto the Cu, and to the ease of the coupling of CH_x fragments on copper surface compared to Rh (9).

Similar studies on MoO_3/ZSM-5 catalysts produced more attractive results: it appeared that methane can be directly transformed into aromatic products (10–15). Wang *et al.* (10) reported 100% selectivity of benzene formation at 7.2% conversion, but details on the calculation of this value were not given. They assumed that the activation of methane proceeds via the polarization of the CH_4 molecule on the MoO_3, and the reaction of the polarized molecule, $H^{-}-CH_3^{+}$, on the Brønsted acid sites of H−ZSM-5 zeolite (10). In our study the maximum selectivity for benzene formation (taking into account only the C-containing gaseous products) was 61–75% at 973 K and at 2.0–5.7% CH_4 conversion (11). New findings, not observed in the previous study (10), were as follows: (i) the reaction is preceded by an induction period, (ii) the reduction of Mo^{6+} to a lower oxidation state occurs and carbon is deposited during the early stage of the contact of methane with the catalyst, (iii) the high catalytic activity for methane–benzene conversion is not restricted to MoO_3/ZSM-5, as MoO_3/SiO_2 and even MoO_3/Al_2O_3 exhibited reasonable activity for this reaction. Similar features have been observed by Wang *et al.* (14). For the selectivity of benzene formation they obtained values between 60 and 65%. Recently, the conversion of methane into higher hydrocarbons and benzene was observed on K_2MoO_4/ZSM-5 catalyst with somewhat lower CH_4 conversion (1.2–6.3% at 973 K), but still with high selectivity (60–67%) of benzene formation (12). In this case the use of silica as a support led to an almost inactive catalyst (CH_4 conversion is <0.4–0.1% at 973 K), which indicates the complex nature of this catalytic system. Recently, Chen *et al.* reported on a more detailed investigation (15). In this study the reduction of MoO_3 and the deposition of carbon were also observed. It was assumed that a synergistic effect between well-dispersed molybdenum oxide species and the acidic sites of HZSM-5 is required for the catalysis of dehydrooligomerization of methane.

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The above features of the reaction of methane and the initial product formation clearly indicated that methane strongly interacted with MoO_3 at the reaction temperature. It appeared likely that the active phase for the methane conversion is produced in the high temperature surface reaction. XPS analysis of the used catalyst did reveal the reduction of Mo^{6+}; the peaks for Mo^{5+}, Mo^{4+}, Mo^{2+}, and Mo^0 were identified in the XP spectra (11). Taking into account the large amount of carbon deposited on the catalyst in the course of the high temperature methane conversion, we may also reckon with the presence of Mo_2C in the catalysts. Recently, Wang *et al.* (14) identified the formation of Mo_2C from MoO_3/ZSM-5 following the methane treatment at 973 K by means of XPS, and we did the same from K_2MoO_4/ZSM-5 and from MoO_3/SiO_2 (12, 13). It appeared, however, that the commercial Mo_2C is rather inert toward the methane decomposition (13).

The present investigation was undertaken to elucidate the nature of the active surface species involved in the conversion of methane to benzene over Mo-containing catalysts. For this purpose the effects of different Mo compounds (metallic Mo, Mo oxides, and carbides) on the activation of methane and on the formation of benzene are examined.

2. EXPERIMENTAL

Catalytic reactions were carried out at 1 atm of CH_4 pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (20-mm i.d.) connected to a capillary tube (11). The flow rate was 12 ml/min. Generally 0.5 g of loosely compressed catalyst sample was used. Reaction products were analyzed gas chromatographically using a Hewlett-Packard 5890 gas chromatograph and a Porapak QS column. In some cases the initial interaction between the catalysts and the reacting gases was followed by mass spectrometry using a Balzers quadrupole mass spectrometer (type OMS 200). The methane conversion was calculated from the H_2 and H_2O balance. The selectivity values of product formation represent the fraction of methane that has been converted to specific hydrocarbon products taking into account the number of carbon atoms in the molecules.

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, 15 mA). To compensate for possible charging effects, binding energies (BE) were normalized with respect to the position of the Si(2p) peak in SiO_2 (BE = 103.4 eV) for supported samples and 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 gases used were of commercial purity (Linde). Ar (99.996%) and H_2 (99.95%) were deoxygenated with an oxytrap. The other impurities were adsorbed by a 5A molecular sieve at the temperature of liquid nitrogen. The H−ZSM-5 support was obtained by five times repeated ion exchange of Na−ZSM-5 (Si/Al = 55.0) with an aqueous solution of ammonium nitrate (1 *M*), and calcined in air at 863 K for 5 h. MoO_3/ZSM-5 catalysts were prepared by impregnating H−ZSM-5 with a basic solution of ammonium paramolybdate to yield a nominal 2 wt.% of MoO_3. The suspension was dried at 373 K and calcined at 873 K for 5 h. Before catalytic measurements, each sample was oxidized in an O_2 stream at 973 K *in situ* and then flushed with Ar for 15 min.

MoO_2 was a product of Aldrich. It was also prepared by the reduction of MoO_3 (Aldrich) at 813 K in a thermobalance until a constant weight-loss corresponding to the formation of MoO_2 (∼2 h) was reached. Supported MoO_2 was obtained from 2 wt.% MoO_3/ZSM-5 by TPR: the highest reduction temperature reached was 808 K.

While bulk MoO_3 is readily reduced to metallic Mo by hydrogen at 973 K, similar treatment of supported MoO_3 does not give reduction below Mo^{4+} (16, 17). Supported Mo in zerovalent state was prepared following the method of Burwell *et al.* (16, 17) applied for the preparation of $Mo/Al_2O_3 \cdot$ H−ZSM-5 was dehydroxylated by the gradual heating of the sample in a dry Ar flow up to about 1173 K and then $Mo(CO)_6$ was evaporated onto the sample kept at 423 K. This was followed by the decomposition of $Mo(CO)_6$ to $Mo(CO)_x$ in an argon stream at 423–573 K, and then by hydrogenation at 973 K. In order to prevent the oxidation of metallic Mo formed, the preparation was performed in the catalytic reactor.

Hexagonal Mo_2C was prepared by the method of Lee *et al.* (18). Briefly, about 0.5 g of MoO_3 was heated in 1:4 methane–H_2 mixture flowing at 300 ml (STP)/min in a quartz cell with two stopcocks. Preparation temperature was increased rapidly to 773 K and at 30 K/h between 773 and 1023 K, and maintained at 1023 K for 3 h. Following the suggestion of Lee *et al.* (18), the sample was deactivated at 300 K with air, or used *in situ* for catalytic studies. The BET surface area of this sample was 9.6 m^2/g. Cubic α-MoC_{1-x}($x = 0.45$–0.5) was made by the carburization of Mo_2N powders (19). Mo_2N was prepared by TPR between MoO_3 and ammonia (20).

Supported Mo_2C catalysts were prepared in the following ways. The first was a slurry method. ZSM-5 was suspended in triply distilled water and the fine powder of Mo_2C (prepared as above) was added slowly to a stirred slurry of ZSM-5. H_2O was evaporated while the slurry was stirred. The solid was homogenized and further dried in an oven at 403 K and ground to a powder. The powder was slightly pressed into wafers and calcined *in situ*. In another case, Mo_2C/ZSM-5 was produced by carburation of calcined MoO_3/ZSM-5 in the catalytic reactor, in a way similar to that described above for the preparation of bulk Mo_2C. Mo_2C/ZSM-5 catalysts were also prepared by the decarbonylation of the $Mo(CO)_6$/ZSM-5 sample (obtained as described above) and carburized in a CH_4/H_2 mixture (20% CH_4) at 973 K for 2 h (20). A detailed description of the properties of Mo_2C samples can be found in the reviews of Omaya and Haller (21, 22).

3. RESULTS

3.1. *Reactions of Methane on Unsupported MoO_3, MoO_2, and Mo^0 Metal*

In order to detect the primary products of the high temperature interaction of CH_4 with Mo compounds, the reaction was first followed by mass spectrometry. Results are plotted in Fig. 1A. In the case of MoO_3 (0.5 g), the product formation started after 2 min yielding H_2O (amu 18), CO_2 (amu 44), and a minor amount of C_2H_6 (amu 30). Maximum rate of their formation was reached at 20–25 min. Afterward, the amount of H_2O decreased suddenly while that of CO_2 and ethane only moderately. At the same time, the evolution of H_2 was observed.

Similar products were identified in the reaction of methane with MoO_2 (prepared by the reduction of 0.5 g MoO_3). The difference was that the evolution of H_2 was observed at the very beginning of the reaction.

Powders of Mo metal exhibited less activity toward methane: the initial products were hydrogen and a small amount of ethane. The rate of the formation of both compounds decayed by a factor of 20 and 2, respectively, after 20 min (Fig. 1B).

3.2. *Reaction of Methane on ZSM-5-Supported MoO_3, MoO_2, and Mo^0*

Mixing of fine powders of MoO_3 with ZSM-5 (weight ratio 1 : 2) caused a dramatic change in the product distribution. In the first stage of the contact of methane with the catalyst, which lasted up to 35–45 min, we observed the same features as those for unsupported MoO_3. Then the evolution of H_2 (main product) started, together with that of ethane, ethylene, benzene, and toluene. In the steady state the conversion of methane was 6.0–7.5% and the selectivity to benzene attained 83–85%. Similar catalytic performance was observed when 2 wt.% MoO_3 was dispersed on ZSM-5 by the impregnation method. The steady state conversion (6.0–7.0%) and the selectivity to benzene (83–85%) were higher on this catalyst than on the 2 wt.% MoO_3/ZSM-5 samples prepared in our laboratory in previous studies (11–13).

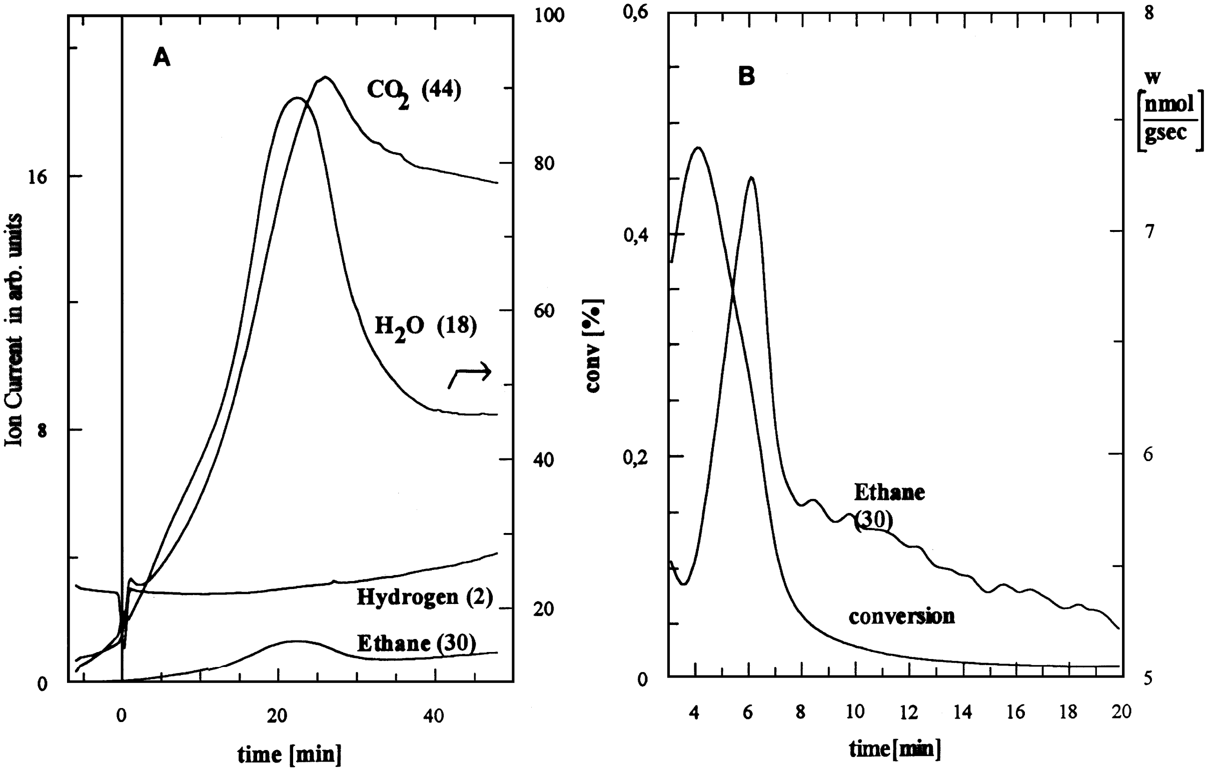

FIG. 1. Interaction of CH_4 with unsupported (A) MoO_3 (0.5 g) and (B) Mo metal (produced by the reduction of 0.5 g MoO_3) at 973 K followed by mass spectrometric analysis.

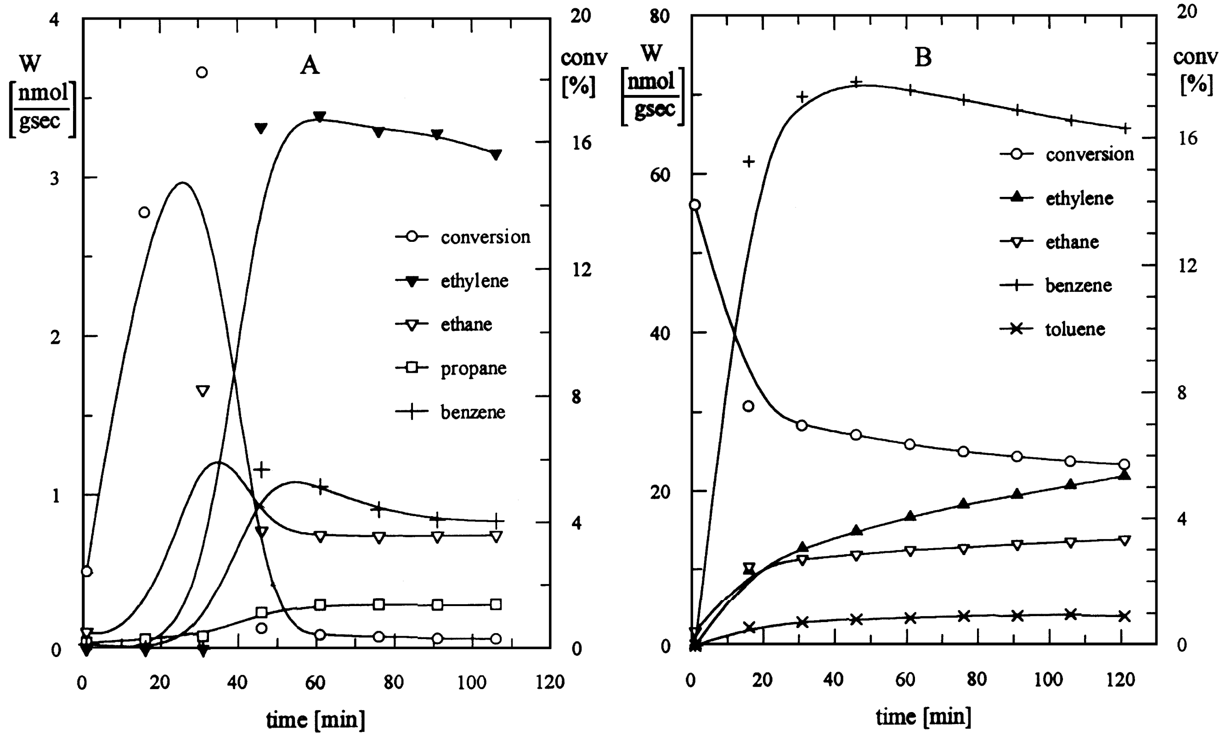

FIG. 2. Conversion of methane, rate, and selectivity of the formation of various products on (A) MoO_2/ZSM-5 by mixing MoO_2 with ZSM-5 in 1 : 2 ratio by the slurry method, and (B) MoO_2/ZSM-5 prepared by the partial reduction of 2 wt.% MoO_3/ZSM-5 *in situ*.

When MoO_2 was mixed with ZSM-5 by the slurry method (1 : 2 mol ratio), we obtained a high initial methane conversion (15–20%), which decreased to 0.5% in 40 min. During this active period only H_2O, CO_2, and CO were formed: ethylene, ethane, propane, and benzene started to evolve only after 40 min. The selectivity to benzene in this stage attains a value of 35% (Fig. 2A).

Preparation of MoO_2 *in situ* on ZSM-5 support (by the reduction of highly dispersed 2 wt.% MoO_3) resulted in a better catalyst (Fig. 2B). The decomposition of methane started with a maximum conversion (~14%), which decayed to about 7.5–6.0%. At the beginning of the reaction, the evolution of H_2O, CO_2, and CO was observed in this case as well. Afterward, the rate of hydrocarbon formation significantly increased. The main hydrocarbon product was benzene with a constant selectivity of 80–85%.

As supported metallic Mo cannot be prepared from the reduction of MoO_3 on supports (16, 17), Mo/ZSM-5 was produced from the decarbonylation of $Mo(CO)_6$. As this is a rather complicated procedure, in Fig. 3A we present the data obtained for the various steps of the preparation of this catalyst. It shows that the dehydroxylation of ZSM-5 is fast at 473–573 K, but is completed only above 873 K. The rate of decarbonylation of $Mo(CO)_6$ to $Mo(CO)_x$ exhibits a maximum at 523 K; CO evolution ceases around 573 K. In the subsequent decomposition of $Mo(CO)_x$ in hydrogen to metallic Mo, first we observed the evolution of H_2O with $T_p = 723$–753 K, then the formation of methane. The hydrogenation was continued at 973 K until methane production was detected, which took several hours. This procedure was followed by a flushing out of the hydrogen with argon for 15–30 min. The Mo/ZSM-5 catalyst so formed exhibited a high initial activity toward methane decomposition at 973 K (Fig. 3B). The conversion, determined from the amount of hydrogen produced at a reaction time of 3 min, was around 35%. Trace amounts of ethane and ethylene were also detected, but only about 0.057% of the decomposed methane was transformed into these compounds. When the next sample was taken for analysis at 24 min, the conversion of methane dropped to 0.25%. At the same time, the rate of ethane production also decreased by a factor of 5, whereas that of ethylene formation increased by a factor of 4. Afterward, both rates remained practically constant in the time of methane stream (Fig. 3B). A small amount of propane was also detected, but benzene was identified only in trace amounts.

When this sample was oxidized at 973 K after the reaction, we measured an initial methane conversion of 11.5% and a steady state conversion of 7%. The product distribution was nearly the same as observed for the 2% MoO_3/ZSM-5 catalyst; actually the selectivity to benzene was somewhat higher, 85–86%, and that to toluene was around 6%. Another feature is that the steady state values remained constant for several hours.

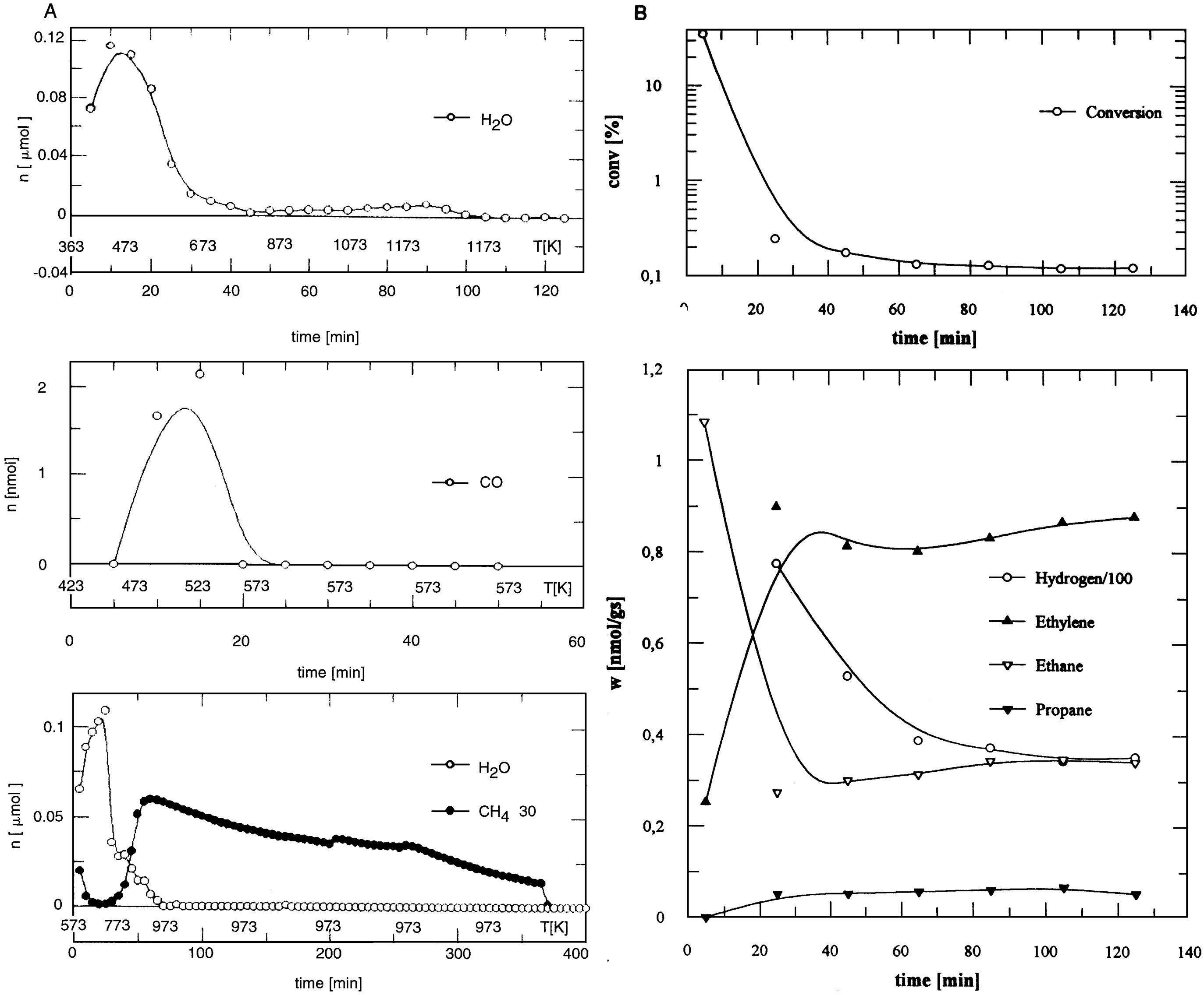

FIG. 3. (A) Dehydroxylation of ZSM-5 (a); decomposition of $Mo(CO)_6$ deposited on ZSM-5 (b) and decomposition of $Mo(CO)_x$ in H_2 stream (c). (B) Conversion of methane and rate of the formation of various products on Mo^0/ZSM-5 at 973 K.

3.3. *Reactions of Methane on Unsupported Mo_2C Samples*

As reported earlier, Mo_2C (Aldrich) exhibited very little activity toward the decomposition of methane even at 973 K (12). The initial conversion was very low (0.1–0.2%) and decreased further with time.

A higher initial activity was measured for the Mo_2C prepared by the method of Lee *et al.* (18). The reaction started with a maximum rate (3–4% conversion at 973 K) which gradually decayed to a very low value, 0.1–0.3%. The only gaseous product was H_2. Ethane, the other product observed in the decomposition of CH_4 on supported Pt metals (1–8), was not formed in detectable amounts. No change in the product formation occurred after several hours of reaction. It was observed before that during the preparation of Mo_2C a significant amount of excess carbon is deposited on Mo_2C (18), which may influence its catalytic performance. This excess carbon can be removed by hydrogenation at 873 K. This treatment led to an appreciable increase in the catalytic activity of Mo_2C (the initial conversion of methane attains 6–8%), but it also decreased with time. A small amount of ethane was also detected: interestingly, its formation rate exhibited a maximum with time on methane stream. Variation of the temperature gave the same picture. The C_2H_6/H_2 ratio at the maximum of ethane production was about 2.0×10^{-3} at 943 K, and increased with the reaction temperature to the value of 6.0×10^{-3} at 973 K. Figure 4 shows the formation of H_2 and C_2H_6 in the decomposition of methane at different temperatures. A new sample was used for each temperature.

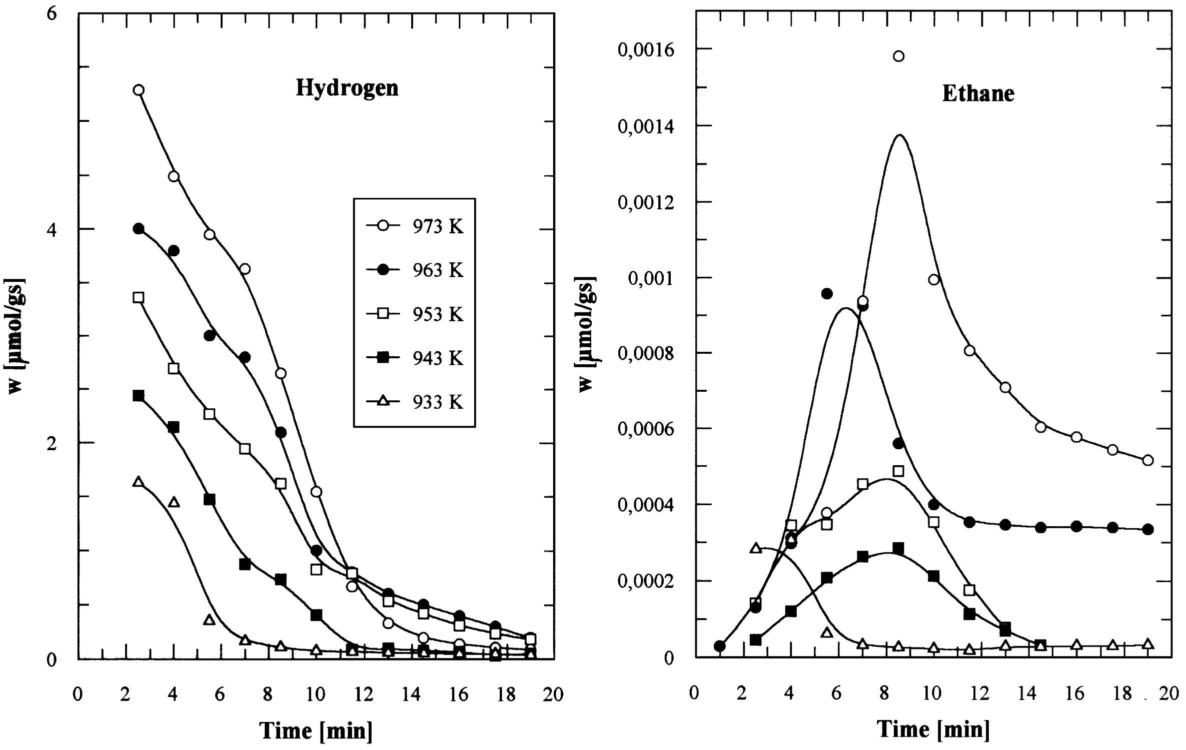

FIG. 4. Decomposition of CH_4 on Mo_2C at different temperatures. 0.5 g Mo_2C was used.

The decomposition of methane on Mo_2C at 973 K produced additional surface carbon, which reacted with hydrogen to give methane above 800 K. No other products of the hydrogenation of this carbon were identified.

Some experiments have been performed with the cubic MoC_{1-x} sample. We obtained a very high initial conversion, ~28–30%, which subsequently decreased to about 2.0–2.5%. The main product was hydrogen. CO was also produced initially: its formation practically ceased after 20 min. Small amounts of ethane and ethylene were also produced (Fig. 5). The C_2H_x/H_2 ratio varied between 2.8×10^{-4} and 6.5×10^{-4}.

3.4. *Reactions of Methane on Supported Mo_2C*

First the catalytic behavior of 2 wt.% Mo_2C/ZSM-5 prepared by the slurry method was tested. The conversion of CH_4 at the first point of the product analysis (~2 min) was around 1.0%. In this case only a small amount of ethane was detected. Afterward, the conversion decreased to about 0.6% (60 min) and, besides hydrogen, the formation of all the hydrocarbons identified on the most active MoO_3/ZSM-5 catalysts occurred (Fig. 6A). The selectivity to benzene was around 53–55%. When this sample was treated with hydrogen at 873 K before the catalytic test, to remove the excess carbon, the conversion of methane determined after 2 min contact time was about 5%, and ethane, ethylene, and benzene were also formed at the very begin-

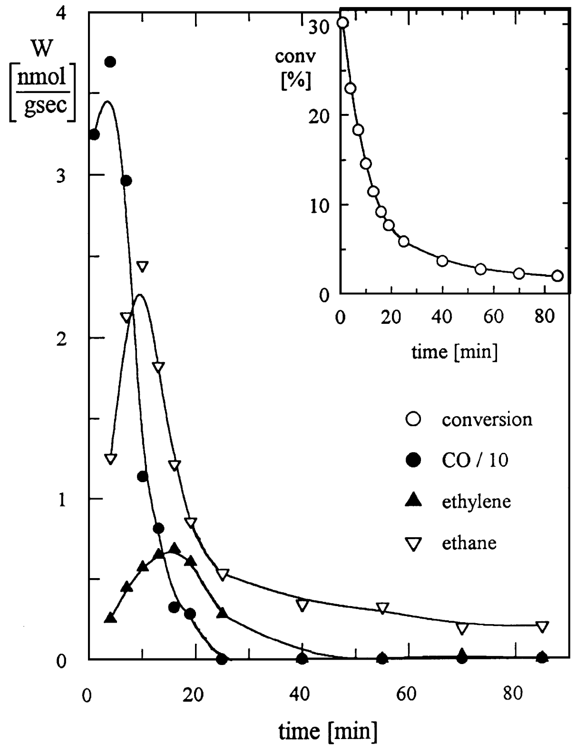

FIG. 5. Conversion of methane, rate, and selectivity of the formation of various products on α-MoC_{1-x} at 973 K.

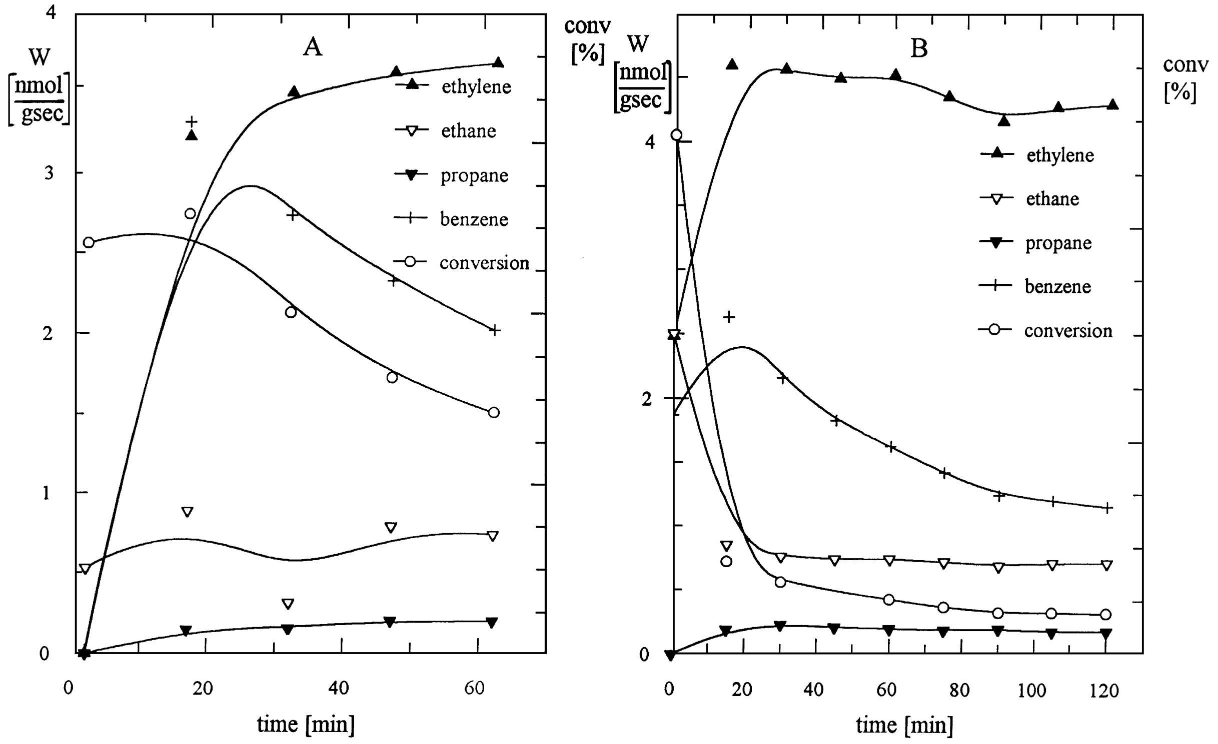

FIG. 6. Conversion of methane, rate, and selectivity of the formation of various products on Mo_2C/ZSM-5 at 973 K. The catalyst was prepared by mixing Mo_2C with ZSM-5 by the slurry method. The Mo_2C content was 1.5 wt.%. (A) No H_2 treatment, (B) H_2 treatment before the catalytic test at 873 K for 2 h.

ning of the reaction (Fig. 6B). The conversion of methane, however, suddenly decreased below 1% at the next analysis (17 min). At the same time, the rate of ethylene formation increased and that of ethane production decreased. The rate of benzene production slowly decreased after a transitory maximum. The selectivity to benzene diminished from 47 to 40% in 120 min.

When the amount of Mo_2C was significantly increased (the Mo_2C/ZSM-5 weight ratio was 1 : 2), we observed similar picture. The initial conversion of methane on the prereduced catalyst attained 18%, but it decayed soon to 1%. The product distribution and selectivities were practically the same as before.

A completely different picture was obtained when Mo_2C was prepared from 2 wt.% MoO_3 deposited on ZSM-5 by the impregnation of molybdenum compound. The induction period observed for supported MoO_3 was missing: the reaction started with the highest rate. The initial conversion of methane was about 10% which diminished slowly to 5–6%. At the very beginning of the reaction CO was also produced but its amount soon decreased to a low level. The other products of the reaction of methane were H_2, C_2H_6, C_2H_4, and C_6H_6. The rates of their formation increased with time on stream. The selectivity to benzene became practically constant after 15 min and reached a value of 85%. The selectivity to ethane was 17–20% and that to ethylene was below 2%. In Fig. 7 we show the rates and slectivities of the formation of various products on this catalyst.

When Mo_2C was prepared by decarbonylation and carburization of $Mo(CO)_6$ deposited on ZSM-5 we also obtained an active and selective catalyst. The initial conversion of methane was 7.5%, which decayed to 2% in 120 min (Fig. 8). In addition to hydrogen, the hydrocarbons ethane, ethylene, propane, benzene, and toluene were produced. H_2O, CO, and CO_2 were not detected even in the initial phase of the reaction. (Note that we found these compounds when the catalyst sample was prepared not *in situ* and was exposed to air.) The selectivity to benzene was high, >85%, and constant during the experiment. The reoxidized catalyst exhibited the same behavior as MoO_3/ZSM-5 prepared by impregnation. After an induction period, the conversion of methane attained a value of 10–12%.

Similarly as in the previous papers (10–15), in the calculation of the selectivities to various products only the C-containing gaseous compounds were taken into account. During the CH_4 conversion, however, a significant fraction of CH_4 decomposed to carbon. In order to be clear as regards the reaction pathways of CH_4, we evaluated quantitatively the amount of CH_4 transformed into carbon deposit and also into hydrocarbons and aromatic compounds. Data are given in Table 1. It appears that the complete

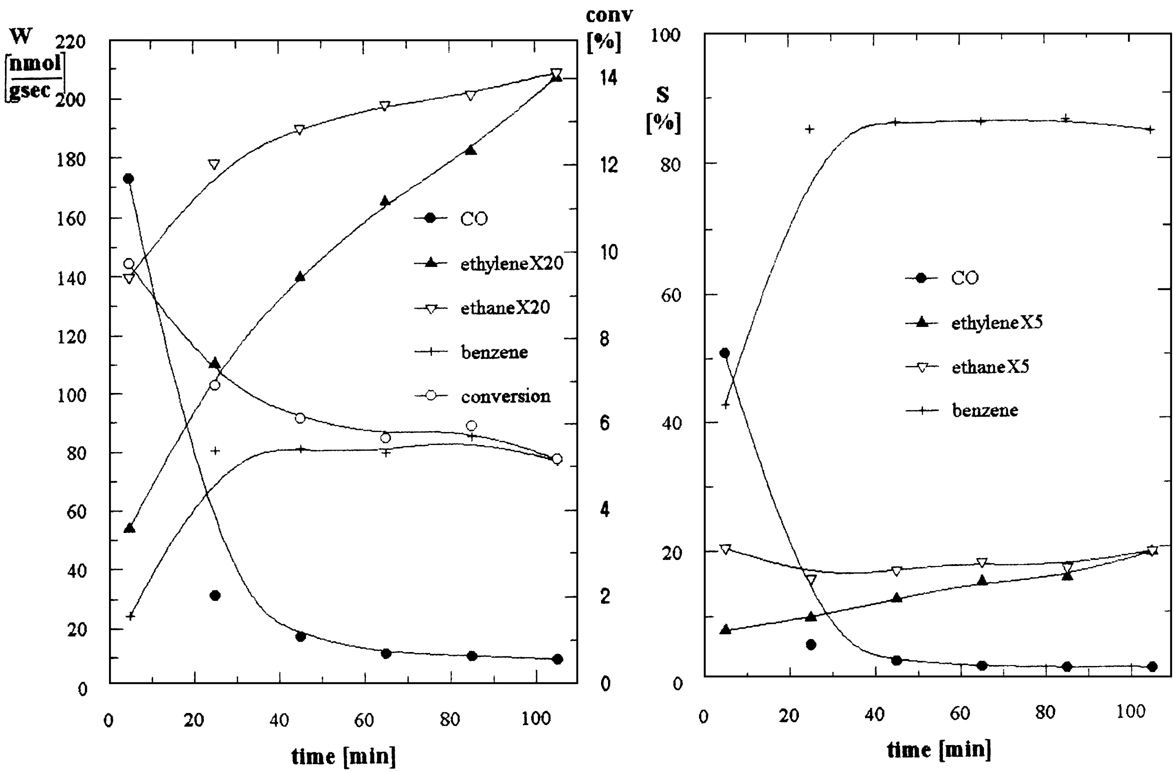

FIG. 7. Conversion of methane, rate, and selectivity of the formation of various products on Mo_2C/ZSM-5 at 973 K. Mo_2C was prepared by the carburization of 2 wt.% MoO_3 on ZSM-5.

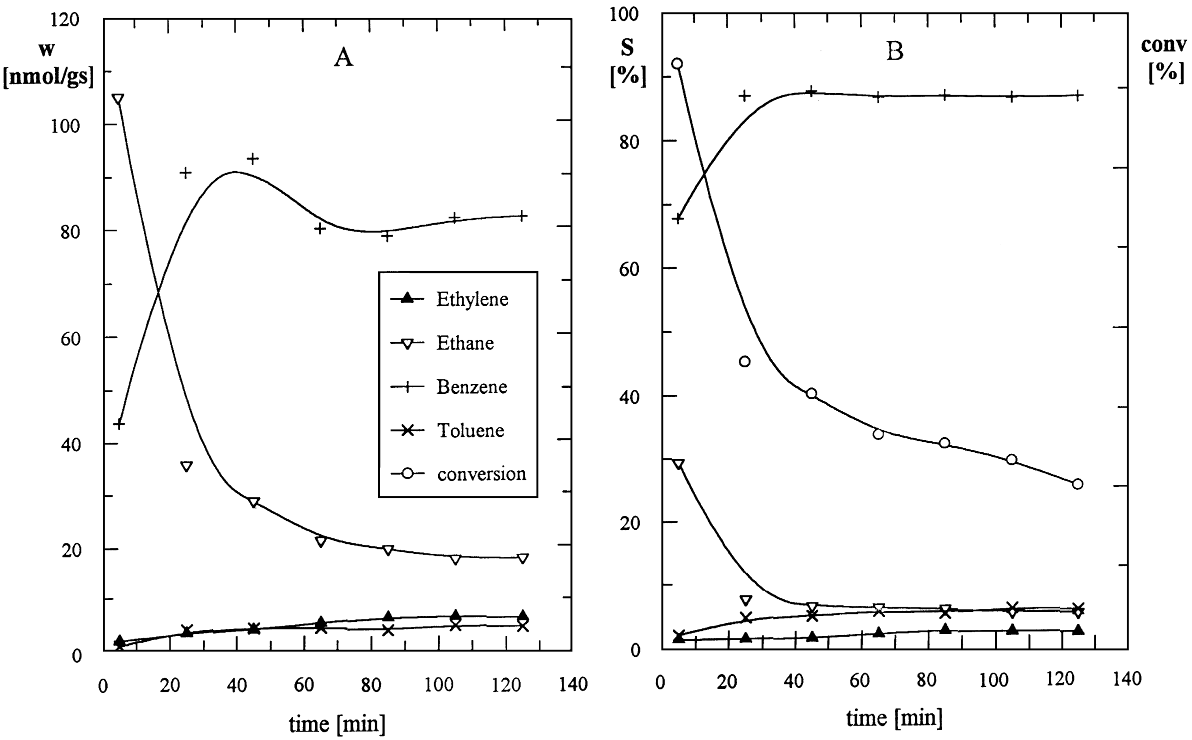

FIG. 8. Conversion of methane, rate, and selectivity of the formation of various products on Mo_2C/ZSM-5 at 973 K. Mo_2C was prepared by decarbonylation and carburization of $Mo(CO)_6$ deposited on ZSM-5.

TABLE 1

Characteristic Data for the Conversion of CH_4 into Various Products on Different Mo-Based Catalysts at 973 K

			Amount of CH_4 transformed [%]									
	Conversion [%]		Ethylene		Ethane		Benzene		Toluene		Coke	
Catalysts	2 min	60 min	2 min	60 min	2 min	60 min	2 min	60 min	2 min	60 min	2 min	60 min
MoO_3/ZSM-5	1.6	4.15	0	5.52	0.59	2.92	0	36.8	0	2.76	0	50.5
MoO_2/ZSM-5	14.0	6.42	0	3.49	0.15	2.29	0	39.5	0	2.23	39.5	52.4
Mo/ZSM-5	35.5	0.12	0.01	7.83	0.05	3.07	0	0	0	0	99.9	89.2
Mo_2C/ZSM-5 from MoO_3/ZSM-5	9.72	5.71	0.37	1.74	0.97	2.09	10.1	50.0	0.2	3.15	88.39	42.86
Mo_2C/ZSM-5 from $Mo(CO)_6$	7.23	2.62	0.19	1.26	10.15	5.06	12.69	57.32	0.33	3.18	76.9	40.8

decomposition of CH_4 is significant even for the Mo_2C deposited on ZSM-5.

3.5. *Characterization of Mo Catalysts*

The surface area of the Mo_2C sample prepared by us is about 4.5–5.0 times larger than that of the commercial Mo_2C.

All the catalysts used in this study have been characterized by XPS measurements before and after the reaction. Some spectra are presented in Fig. 9. For oxidized, unsupported MoO_3 we found the doublet for Mo(3d) at 236.2 and 233.0 eV. The BE for 0(1s) was located at 530.8 eV. When the MoO_3 was deposited on ZSM-5 and calcined in air at 873 K, we observed a slight shift of these binding energies (BE) to 235.7 and 232.7 eV. On treatment of this sample with CH_4 at 973 K for 2 h, the BE values for Mo(3d) were registered at 231.2 and 227.9 eV. A strong C(1s) peak appeared at 283.8 eV. Note that the carbon contamination of MoO_3 and MoO_3/ZSM-5 gave a peak at higher energies, 285.1–284.9 eV. The BE values for Mo(3d) in MoO_2 were found at 232.9 and 229.8 eV, and that for 0(1s) at 529.8 eV, corresponding well to literature data for MoO_2 (23, 24). When MoO_2/ZSM-5 was applied as a catalyst after 1 h of reaction with methane, we obtained practically the same BE

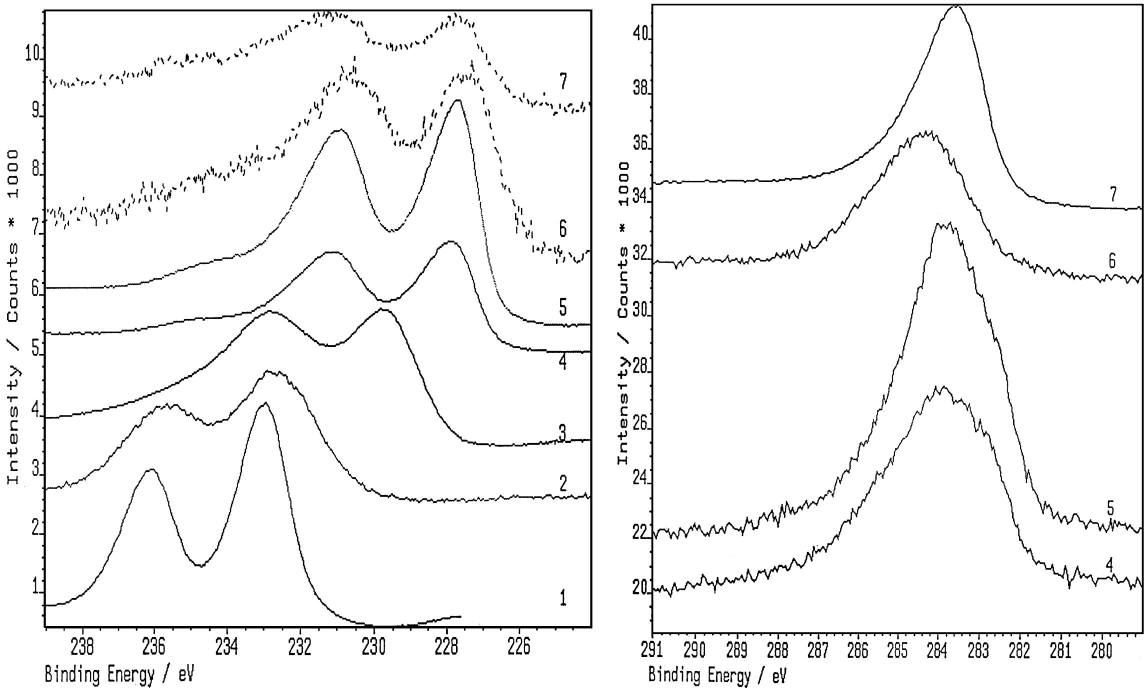

FIG. 9. XPS spectra of Mo-containing catalysts. (1) MoO_3 (oxidized at 973 K for 1 h); (2) 2 wt.% MoO_3/ZSM-5 (oxidized at 973 K for 1 h); (3) MoO_2 (Aldrich, bombarded with argon ions for 15 min); (4) Mo_2C (Aldrich); (5) Mo_2C (prepared by the method of Lee *et al.* (18)); (6) Mo_2C/ZSM-5 (Mo_2C was prepared from $Mo(CO)_6$); (7) 2 wt.% MoO_3/ZSM-5 treated with CH_4 at 973 K for 2 h. Samples (4–7) have been treated with H_2 at 873 K for 2 h to remove the excess carbon.

TABLE 2

XPS Data for Mo Catalysts

Sample	Binding energy (eV)		
	$Mo(3d_{5/2})$	$Mo(3d_{3/2})$	C(1s)
MoO_3	233.0	236.2	
MoO_3/ZSM-5	232.7	235.7	
MoO_2	229.8	232.9	
Mo_2C (Aldrich)	228.0	231.1	283.85
Mo_2C^a	227.8	231.0	283.85
Mo_2C/ZSM-5^b	227.6	230.7	284.5
MoO_3/ZSM-5^c	227.9	231.2	283.8

[a] From MoO_3 [18].
[b] From $Mo(CO)_6$ [19].
[c] Treated with CH_4 at 973 K for 2 h.

as for MoO_3/ZSM-5 treated in the same way. The situation was similar when the Mo^0/ZSM-5 catalyst was examined after its use as a catalyst.

In Fig. 9 we also show the XPS spectra for Mo_2C samples received from Aldrich and prepared by us. The binding energies of $Mo(3d_{5/2})$ were 228.0 eV (Aldrich) and 227.8–227.6 eV, respectively. A value of 227.9 eV was measured for the MoO_3/ZSM-5 catalyst used for CH_4 conversion. Note that these values are slightly lower than obtained previously for Mo_2C prepared by other methods (229.0 eV (24) and 228.1–228.3 (25)), but agree well with the value (227.8 eV) reported by Wang *et al.* (14) for Mo_2C produced from MoO_3/ZSM-5 during the CH_4 conversion into benzene. The C(1s) peaks were relatively broad indicating the coexistence of several forms of C with different binding energies. Following the XPS work of Bonzel and Krebs (26) three C species can be distinguished (24, 25): carbidic carbon (283.3 eV), polymeric carbon (284.5 eV) and amorphous or graphitic carbon (285.0 eV). For our Mo_2C samples we obtained a value of 283.8 eV, which is close to the value attributed to Mo_2C (14, 24, 25). XPS data for Mo-containing catalysts used in this study are collected in Table 2.

4. DISCUSSION

The primary aim of this work was to elaborate the nature of the active surface site involved in the conversion of methane to benzene over MoO_3/ZSM-5 catalysts. The basic requirements for that center are to activate the methane molecule to produce CH_3 and CH_2 fragments, to exhibit less activity toward the subsequent decomposition of these CH_x species to carbon, and to promote their couplings to ethane and particularly to ethylene. Taking into account the high efficiency of the acidic sites of H−ZSM-5 in the oligomerization and cyclization reactions (27, 28), it was envisaged that the transformation of ethylene into benzene is accomplished on the ZSM-5 surface (12–15). Before making a final conclusion as regards the active sites and the possible pathways of the transformation of methane into ethylene, let us summarize the main findings of previous and present studies.

4.1. Characteristic Features of the Reaction of Methane on Mo Oxides and Mo Metal

The results of the present study clearly show that methane reacts readily with unsupported MoO_3 and MoO_2 at high temperature to give H_2O and CO_2. The product formation in the initial stage of the surface reaction can be described by the overall equation

$$CH_4 + 4O_s = CO_2 + 2H_2O. \qquad [1]$$

The obvious first step in the activation of CH_4 is an oxidative dehydrogenation process

$$CH_4 + O(s) = CH_3 + OH \qquad [2]$$

followed by the recombination of OH groups

$$2OH = H_2O + O(s) \qquad [3]$$

and by the oxidation of CH_3 species

$$CH_3 + O_s = CH + H_2O \qquad [4]$$

$$CH + 2O_s = CO_2 + \tfrac{1}{2}H_2 \qquad [5]$$

by surface oxygen. Competing processes are the dehydrogenation of CH_3 species

$$CH_3 = CH_2 + H \qquad [6]$$

$$CH_2 = CH + H \qquad [7]$$

$$CH = C + H \qquad [8]$$

$$2H = H_2 \qquad [9]$$

as indicated by the evolution of H_2.

The respective couplings of CH_3 and CH_2 species

$$2CH_3 = C_2H_6 \qquad [10]$$

$$2CH_2 = C_2H_4 \qquad [11]$$

on molybdenum oxides are negligible as compared to the oxidation and decomposition steps of CH_x fragments, but become detectable on partially reduced surfaces. In the case of the Mo metal, the dominant process is the decomposition of methane to carbon and hydrogen, similarly as on supported Pt metals (1–9); only about 7–8% of decomposed methane is transfomed into ethane and ethylene.

In all three cases a significant decay in the rate of CH_4 reaction and changes in the product distribution were experienced after the initial interaction of methane with the catalysts at high temperature. As a result, the formation of C_2H_6 and C_2H_4 in very small amounts was observed.

The above results showed that although Mo oxides and metallic Mo can activate the CH_4 molecule and catalyze its decomposition, neither of these catalysts alone is selective enough to produce C_2H_6 and/or C_2H_4, the assumed starting componds of benzene and aromatics, in larger quantity ($>1\%$ of decomposing methane).

When Mo oxides were mixed with ZSM-5, or particularly when they were dispersed on the ZSM-5 support, at the very beginning of the contact of methane with the catalyst we observed similar features. In the latter stages, however, the production of hydrocarbons, particularly benzene, with a selectivity of 60–80%, came into prominence. This dramatic change in the catalytic behavior can be attributed to the formation of a new compound from the catalyst during the high temperature reaction. The situation was different for Mo^0/ZSM-5. In this case the initial interaction of Mo^0 with methane at 973 K was followed by a drastic deactivation as indicated by the decrease of CH_4 conversion from 35 to 0.25% in 24 min. It appears that the deposition of coke and/or polymeric carbon (18) in a large quantity poisoned the active sites of the catalyst.

4.2. *Catalytic Behavior of Mo_2C and Mo_2C/ZSM-5*

XPS examination of MoO_x-containing catalysts supported by ZSM-5 clearly showed that the oxides are not only reduced by methane at 973 K, but at least the surface layers of oxides have been transformed into some kind of Mo carbide. The same holds when the starting catalyst was Mo^0/ZSM-5. The binding energies of Mo(3d) and C(1s) agree with those obtained for commercial Mo_2C and for Mo_2C samples prepared by us. This is not surprising as the conditions used for the preparation of Mo_2C are nearly the same as applied for the catalytic conversion of methane. Accordingly, we may assume that the dramatic change in the product distribution following the strong interaction of methane with supported Mo oxides is due to the formation of Mo_2C.

In a preliminary study, however, Mo_2C exhibited very little activity toward methane decomposition, and mixing it with ZSM-5 brought no positive result (13). This Mo_2C, however, was a commercial product of very low surface area ($\sim$1.1 m^2/g). The use of a more advanced method in the preparation of Mo_2C resulted in a more active catalyst toward CH_4 reactions. However, the dominant process was still the complete decomposition of methane to give H_2, C, and a small amount of ethane (C_2H_6/H_2 ratio was between 2.0×10^{-4} and 6.0×10^{-4}). The initial catalytic activity of Mo_2C was greatly enhanced when the excess carbon deposited during the preparation was removed by H_2 treatment at 873 K (Fig. 4). In this case, however, we cannot exclude the possibility that the high temperature treatment with H_2 removes not only the excess carbon, but also a fraction of surface carbon of Mo_2C, creating very active centers for the subsequent decomposition of CH_4. This latter reaction restores the surface stoichiometry of Mo_2C leading to a much less active catalyst. The fact that MoC_{1-x} was found to be considerably more active in the decomposition of CH_4 (Fig. 5) than the Mo_2C may support this speculation. The catalytic activity of this sample, however, also soon diminished. Coupling reactions of CH_x species were very limited on this sample, too.

The situation was completely different when Mo_2C was added to ZSM-5 or deposited on its surface. In these cases, in addition to H_2, we detected all the hydrocarbons (ethylene, ethane, benzene, and small amounts of propane and toluene), the formation of which was observed on the highly active 2 wt.% MoO_3/ZSM-5 catalyst. As in these cases the Mo_2C samples were prepared by the carburization of supported or unsupported MoO_3, one can assume that the high catalytic performance of Mo_2C/ZSM-5 samples is due to the presence of unreacted MoO_3 and/or Mo_2C/MoO_x contact. This idea was apparently supported by the observation that a partial oxidation of a less active Mo_2C mixed with ZSM-5 improved the yield of hydrocarbons and benzene produced (13). However, in the present case, we could not identify the formation of H_2O and CO_2 even at the beginning of the reaction. Therefore, we can exclude the dominant role of MoO_3 in the catalytic performance of Mo_2C/ZSM-5.

This conclusion may be supported by the results obtained for Mo_2C/ZSM-5 prepared *in situ* by decarbonylation and carburization of $Mo(CO)_6$ (Fig. 8). This sample also proved to be an active and selective catalyst in the conversion of methane into benzene. In this case we cannot count on the presence of Mo oxides, although if the reactive OH groups of the support are not removed completely, $2\sigma-O^{-}-Mo^{2+}$ species can be transitorily formed during the preparation in the reaction

$$2\sigma\text{–OH} + \text{Mo(CO)}_3 \rightarrow 2\sigma\text{–O}^{-}\text{–Mo}^{2+} + 3\text{CO} + \text{H}_2, \quad (12)$$

as it was postulated for alumina (17). However, we did not find H_2O, CO, and CO_2 in the reaction products which suggests that the Mo–O species was not present.

Accordingly, we may conclude that Mo_2C on the ZSM-5, produced by the transformation of highly dispersed MoO_3, is the active site for the cleavage of the C–H bond in the methane molecule, but it is far less active for the further decomposition of CH_3 and CH_2 species produced. As a result, these radicals have a certain lifetime to recombine into C_2H_6 and C_2H_4 either on the catalyst surface or in the gas phase. Further reactions, the oligomerization and aromatization of ethylene, occur on the ZSM-5 support (12–15, 27, 28).

5. CONCLUSIONS

1. MoO_3 and MoO_2 interact strongly with methane at 973 K to give H_2O and CO_2 with trace amounts of ethylene and ethane. The reaction of methane on metallic Mo produces H_2 with a very small amount of ethane. The catalyst is soon poisoned due to carbon deposition.

2. Mixing of these compounds with ZSM-5 changes the product distribution, and the formation of ethylene, ethane, and benzene comes into prominence. High selectivity to benzene was attained when these Mo compounds were dispersed on ZSM-5.

3. XPS results suggest that the major part of molybdenum metal and oxides is transformed into Mo carbides during the high temperature reaction with methane.

4. Unsupported Mo_2C and $MoC_{(1-x)}$ catalyzed the decomposition of methane to hydrogen, carbon, and to a minor amount of ethane.

5. Preparation of Mo_2C on ZSM-5 in high dispersion produced catalyst which is active and selective in the aromatization of methane (selectivity to benzene is 80–85% at a conversion of 6.0–7.0%). It appears that Mo_2C is responsible for the production of ethylene from methane which is converted to benzene on the acidic sites of the ZSM-5 support.

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REFERENCES

1. van Santen, R. A., de Koster, A., and Koerts, T., *Catal. Lett.* **7**, 1 (1990); Koerts, T., and van Santen, R. A., “Proc. 10th Int. Congr. on Catalysis (Budapest 1992)” (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 1065, (Akadémiai Kiadó, Budapest, 1993).
2. Koerts, T., Deelen, M. J. A. G., and van Santen, R. A., *J. Catal.* **138**, 101 (1992).
3. Belgued, M., Pareja, P., Amariglio, A., and Amariglio, H., *Nature* **352**, 789 (1991).
4. Solymosi, F., Kutsán, Gy., and Erdöhelyi, A., *Catal. Lett.* **11**, 149 (1991).
5. Solymosi, F., Erdöhelyi, A., and Cserényi, J., *Catal. Lett.* **16**, 399 (1992).
6. Erdöhelyi, A., Cserényi, J., and Solymosi, F., *J. Catal.* **141**, 287 (1993).
7. Solymosi, F., Erdöhelyi, A., Cserényi, J., and Felvégi, A., *J. Catal.* **147**, 272 (1994).
8. Solymosi, F., and Cserényi, J., *Catal. Today* **21**, 561 (1994).
9. Solymosi, F., and Cserényi, J., *Catal. Lett.* **34**, 343 (1995).
10. Wang, L., Tao, L., Xie, M., Xu, G., Huang, J., and Xu, Y., *Catal. Lett.* **21**, 35 (1993); Xu, Y., Liu, S., Wang, L., Xie, M., and Guo, X., *Catal. Lett.* **30**, 135 (1995).
11. Solymosi, F., Erdöhelyi, A., and Szöke, A., *Catal. Lett.* **32**, 43 (1995).
12. Solymosi, F., and Szöke, A., **39**, 157 (1996).
13. Solymosi, F., Szöke, A., and Cserényi, J., *Appl. Catal. A* **142**, 361 (1996).
14. Wang, D., Lunsford, J. H., and Rosynek, M., paper presented at the 14th Meeting of the North American Catalysis Society, Snowbird, 1995; Lunsford, J. H., Rosynek, M. P., and Dingjun, W., paper presented at the 4th Intern. Natural Gas Conversion, Kruger National Park, South Africa, 1995.
15. Chen, L., Lin, L., Xu, Z., Li, X., and Zhang, T., *J. Catal.* **157**, 190 (1995).
16. Burwell, R. L., and Brenner, A., *J. Mol. Catal.* **1**, 77 (1975/76).
17. Bowman, R. G., and Burwell, R. L., *J. Catal.* **63**, 463 (1980).
18. Lee, J. S., Oyama, S. T., and Boudart, M., *J. Catal.* **106**, 125 (1987).
19. Lee, J. S., Locatelli, S., Oyama, S. T., and Boudart, M., *J. Catal.* **125**, 157 (1990).
20. Volpe, L., and Boudart, M., *J. Solid State Chem.* **59**, 348 (1985).
21. Oyama, S. T., and Haller, G. L., *in* “Catalysis, Specialist Periodical Reports” (G. C. Bond and G. Webb, Eds.), Vol. 5, p. 333. The Chemical Society, London, 1981.
22. Oyama, S. T., *Catal. Today* **15**, 179 (1992).
23. Spevack, P. A., and McIntyre, N. S., *J. Phys. Chem.* **97**, 11020 (1993).
24. Leclercq, L., Provost, M., Pastor, H., Grimblot, J., Hardy, A. M., Gengembre, L., and Leclercq, G., *J. Catal.* **117**, 371 (1989).
25. Ledoux, M. J., Huu, C. P., Guille, J., and Dunlop, H., *J. Catal.* **134**, 383 (1992).
26. Bonzel H. P., and Krebs, H. J., *Surf. Sci.* **91**, 499 (1980).
27. Anderson, J. R., Foger, K., Mole, T., Rajadhyaksha, R. A., and Sanders, J. V., *J. Catal.* **58**, 14 (1979).
28. Chu, P., U.S. Pat. 4120910 (1978); Chester, A. W., and Chu, Y. F., U.S. Pat. 4350835 (1982).