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Reactions of Propane on Supported Mo_2C Catalysts

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The adsorption and reactions of propane over Mo_2C deposited on ZSM-5 and SiO_2 have been investigated. Propane adsorbed weakly and nondissociatively on Mo_2C catalyst at 150–273 K. At higher temperatures, the characteristic vibrations of π-bonded and di-σ-bonded propylene and propylidyne were identified by Fourier transform infrared spectroscopy. The dominant reaction of propane over Mo_2C/SiO_2 at 773–873 K is its dehydrogenation into propylene. At 873 K the selectivity of propylene formation attained a value of 35–50% at a conversion of 35–25%. The reaction pathway of propane was completely different on Mo_2C/ZSM-5: in this case the aromatization of propane was the main process. It was shown that Mo_2C improved the effect of pure ZSM-5 in this reaction. The positive influence of Mo_2C is explained by its high activity toward the dehydrogenation of propane. The effect of Mo_2C was also examined on the aromatization of propylene occurring on the acidic sites of ZSM-5, and no inhibition was observed. © 2000 Academic Press

Key Words: **supported Mo_2C catalysts; adsorption of propane; benzene from propane; dehydrogenation into propylene; FTIR spectroscopy; ZSM-5 support.**

1. INTRODUCTION

Recently it was found that Mo_2C deposited on ZSM-5 is an effective catalyst in the high-temperature conversion of methane into benzene (1–10). In order to establish the possible routes of the aromatization of methane, the reactions of ethane (11, 12) and ethylene (13) were also investigated on this catalyst. In addition, the chemistry of the possible reaction intermediates, CH_2, CH_3, and C_2H_5, formed in the activation of the above compounds was also examined on an Mo_2C/Mo(100) surface in an UHV system by means of several electron spectroscopic methods (14, 15). As we can also count the transient formation of propane and propylene during the aromatization of methane and ethane, we undertake the study of the catalytic transformation of propane and propylene on Mo_2C deposited on ZSM-5 and SiO_2.

The reactions of propane on pure and promoted ZSM-5 were the subject of extensive research in the past decade (16–20). The most important features and results are summarized in a review paper (20). The reaction of propane over H–ZSM-5 becomes significant above 700 K. Benzene, toluene, and xylenes account for most of the aromatics produced. Addition of Zn or Ga enhanced the conversion of propane and increased the yield of aromatics (20).

The primary aim of the present work is to establish the reaction pathways of propane over Mo_2C/SiO_2 and to ascertain the influence of Mo_2C on the catalytic performance of ZSM-5 in the reactions of propane.

2. EXPERIMENTAL

2.1. Materials

The gases used were of commercial purity (Linde). Ar (99.996) and H_2 (99.999) were deoxygenated with an oxytrap. H–ZSM-5 was obtained by five-times-repeated ion exchange of Na–ZSM-5 (Si/Al = 55.0) with an aqueous solution of ammonium nitrate (1 N), and calcined in air at 863 K for 5 h. The surface area of the sample was 311 m^2/g. SiO_2 was Cab-O-Sil, area 200 m^2/g.

Hexagonal Mo_2C was prepared by the method of Lee *et al.* (21). Briefly, about 0.7 g of MoO_3 was heated in a 1 : 4 methane–H_2 mixture flowing at 300 ml (STP)/min in a quartz cell with two stopcocks. The preparation temperature was increased rapidly to 773 K and then at 3 K/min from 773 to 1023 K and maintained at 1023 K for 3 h. The BET surface area of this sample is 9.6 m^2/g. MoO_3-containing catalysts were prepared by impregnating SiO_2 or 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 863 K for 5 h. Supported Mo_2C catalysts were prepared by the carburation of calcined MoO_3/ZSM-5 or MoO_3/SiO_2 in the catalytic reactor, in a way similar to that described above for the preparation of bulk Mo_2C. Before catalytic measurements each Mo_2C sample was treated in an H_2 stream at 873 K for 120 min *in situ* to remove the excess carbon and then flushed with Ar for 15 min.

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2.2. Methods

The samples were characterized by XPS measurements (5). The binding energies for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) were 227.8 and 231.0 eV, and for C(1*s*) 283.8 eV. These values are close to the values attributed to Mo_2C (22, 23).

Catalytic reactions were carried out at 1 atm of pressure in a fixed-bed, continuous-flow reactor consisting of a quartz tube (14 mm i.d.) connected to a capillary tube. The flow rate was 12 ml/min. The carrier gas was Ar. The propane content was 12.5%. 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. The propane conversion was calculated on the basis of carbon number. The selectivity values of product formation represent the fraction of propane that has been converted into specific products taking into account the number of carbon atoms in the molecules:

$$\text{conversion} = \frac{\text{number of moles of propane consumed}}{\text{number of moles of propane fed}}$$

Selectivity to a given hydrocarbon = (number of moles of the hydrocarbon produced) × (number of C atoms in the molecular formula)/(number of moles of propane consumed) × 3. Yield of a given hydrocarbon = (number of moles of the hydrocarbon produced) × (number of C atoms in the molecular formula)/(number of moles of propane fed) × 3.

Infrared spectra were recorded with a Bio-Rad Fourier transform IR spectrometer (FTS 155) with a wavenumber accuracy of ± 4 cm^{-1}. Typically 136 scans were collected. For IR measurements the catalyst samples were pressed into a 10- × 30-mm self-supporting wafer, and the carburation was performed in the infrared cell. Note that in the case of ZSM-5-containing catalyst we had great difficulty in preparing a stable, self-supporting plate. The supplementary method used was temperature-programmed desorption (TPD). The heating rate was 5 K/min.

3. RESULTS

3.1. Interaction of C_3H_8 with Supported Mo_2C

The interaction of propane with Mo_2C/SiO_2 catalyst was followed by means of IR spectroscopy. In the first experiments the following approach was used: 1.0 Torr of propane was introduced into the cell at 153 K and the IR spectra were registered as a function of temperature. Bands observed are the characteristic vibration of weakly adsorbed propane. All the bands disappeared at 273 K without any sign of the appearance of new spectral features. In the subsequent experiments the Mo_2C/SiO_2 catalyst was contacted with 10 Torr of propane at and above 300 K. The dominant absorption bands at 300 K were the same as those registered at low temperatures. New bands at 2925, 1606, 1453, (1434), 1411, and 1374 cm^{-1} appeared after treatment of the sample with propane at 573 K. After evacuation at 300 K some bands were still detectable at 2925, 1453, 1411, and 1374 cm^{-1}. To increase the surface concentration of adsorbed species the catalyst was kept in a flow of propane at 373 K for 10 min. Afterwards, the cell was evacuated at 300 K, and IR spectra were measured. Weak absorption bands remained at 1407 and 1367 cm^{-1}, which were eliminated after heating of the sample to 423 K. Selected spectra are presented in Fig. 1A, and the positions of absorption bands are collected in Table 1.

In order to help in the assignment of the above absorption bands, in the subsequent measurements propylene was adsorbed on the catalyst sample. IR spectra obtained for Mo_2C/SiO_2 are displayed in Fig. 1B. We obtained relatively strong vibrations at 2956, 2924, 2894, and 2857 cm^{-1} in the high-frequency region, and somewhat weaker ones at 1637, 1613 (not shown), 1453, 1438, 1412, and 1374 cm^{-1} in the low-frequency region. On heating of the catalyst in the presence of propylene new bands, indicating the occurrence of a reaction in the adsorbed layer, developed at 1390 and 1469 cm^{-1} These features were detected first at 253–273 K. Their intensities were enhanced with further increases in the temperature. After evacuation of the cell at 300 K, spectral features were registered at 2983, 2941, 2928, 1470, 1424, 1390, and 1377 cm^{-1}. All these vibrations were eliminated by evacuation at and above 373 K. Note that in the case of pure silica no absorption band could be detected at and above 253 K, and there were no signs of the presence of the 1390 and 1469 cm^{-1} spectral features at all. Absorption bands observed and their assignments are also listed in Table 1.

The interaction of propane with the catalysts was also examined by means of TPD. The catalyst was kept in the propane gas flow for 10 min for 373 K, and then it was washed with pure argon for 30 min. Some TPD spectra are presented in Fig. 2. TPD measurements clearly showed that a small amount of propane remained adsorbed on the pure ZSM-5 and was released at 430 K. In addition, the formation of ethylene and propylene was observed with $T_p = 490$ K. A high-temperature ethylene peak was also observed at 770 K. In the case of Mo_2C/ZSM-5 somewhat larger amounts of gases desorbed and their peak temperatures shifted to higher temperatures. The release of hydrogen and methane above 900 K was also observed. Similar features were experienced for Mo_2C/SiO_2, but the amounts of gases desorbed were much lower. A possible reason is that no adsorption of propane occurs on the silica support.

3.2. Reactions of Propane on H-ZSM-5

First the catalytic behavior of the ZSM-5 support was tested. It exhibited relatively high activity (50% conversion) toward the dehydrogenation and cracking of propane

TABLE 1

Absorption Bands (in cm^{-1}) Observed Following the Adsorption of Propane and Propylene on Mo_2C/SiO_2

Assignment (24)	Propane gas (24)	Propane on Mo_2C/SiO_2 at 173 K	Assignment (25)	Propylene gas (25)	Propylene on Mo_2C/SiO_2 at 225 K	Propylene on Mo_2C/SiO_2 at 300 K	Propane on Mo_2C/SiO_2 at 573 K
$\nu_{as}(CH_3)$	2977	2963	$\nu_{as}(CH_2)$	3090	3080 (I/II)		
$\nu_{as}(CH_3)$	2973	2939	$\nu(CH)$	3010	3005 (I/II)		
$\nu_{as}(CH_2)$	2968	2904	$\nu_s(CH_2)$	2990	2975 (I/II)		
$\nu_s(CH_2)$	2887	2877				2983 (III)	
$\delta_{as}(CH_3)$	1476	1467	$\nu_{as}(CH_3)$	2960	2956 (I/II)		
$\delta(CH_2)$	1462	1450				2941 (III)	
$\delta_s(CH_3)$	1392	1388	$\nu_s(CH_3)$	2930	2924 (II/I)	2928 (II/I)	2925 (II/I)
$\delta_s(CH_3)$	1378	1371	$\nu_s(CH_3)$	2870	2894 (I/II)		
$\omega(CH_2)$	1338	1334			2857 (I/II)		
			$\nu(C{=}C)$	1650	1637 (I)		
					1613 (I)		1606 (I)
						1470 (III)	
			$\delta_{as}(CH_3)$	1470	1453 (I/II)		1453 (I/II)
			$\delta_{as}(CH_3)$	1440	1438 (I/II)	1424 (I/II)	1434 (I/II)
			$\delta(CH_2)$	1420	1412 (I/II)		1411 (I/II)
						1390 (III)	
			$\delta_s(CH_3)$	1380	1374 (I/II)	1377 (I/II)	1374 (I/II)

Note. I, π-bonded propylene. II, di-σ bonded propylene. III, propylidyne.

at 873 K. There was practically no decay in the conversion and in the rate of formation of various products. The highest selectivity, 32%, was measured for ethylene. This was followed by methane, $S = 30\%$. Propylene was produced with a selectivity of 12%, whereas that of benzene was only 10%. Other minor products were ethane, butane, and toluene. At a higher temperature, 973 K, the conversion exceeded 90%, and the selectivity of aromatics attained a value of 33–35%. On lowering the temperature the conversion of propane decreased and approached nearly zero value at around 770 K. At the same time the selectivity to ethylene increased while that for benzene drastically decreased. No change was observed in the selectivity of methane formation. The catalytic effect of silica was also tested. It exhibited very low reactivity; the conversion of propane at 873 K was around 2.5% yielding ethylene, methane, and ethane. The effects of temperature on the rate of formation and selectivity of various products are presented in Fig. 3.

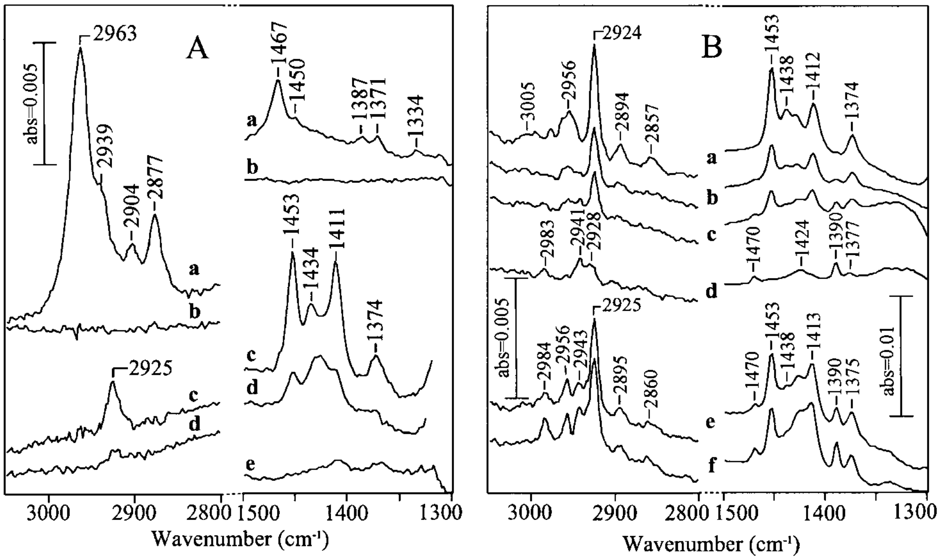

FIG. 1. Infrared spectra of Mo_2C/SiO_2 following the adsorption of propane (A) and propylene (B). For (A): 1 Torr propane at (a) 173 K and (b) 273 K; (c) 10 Torr propane at 573 K; (d) evacuation of (c) at 300 K; (e) propane flow at 373 K for 10 min and evacuation at 300 K. For (B): 1 Torr propylene at (a) 225 K, (b) 273 K, and (c) 293 (K); (d) after evacuation at 300 K; 10 Torr propylene at (e) 300 and (f) 373 K. When the spectra were taken in the presence of gases, the spectra of the gases have been subtracted.

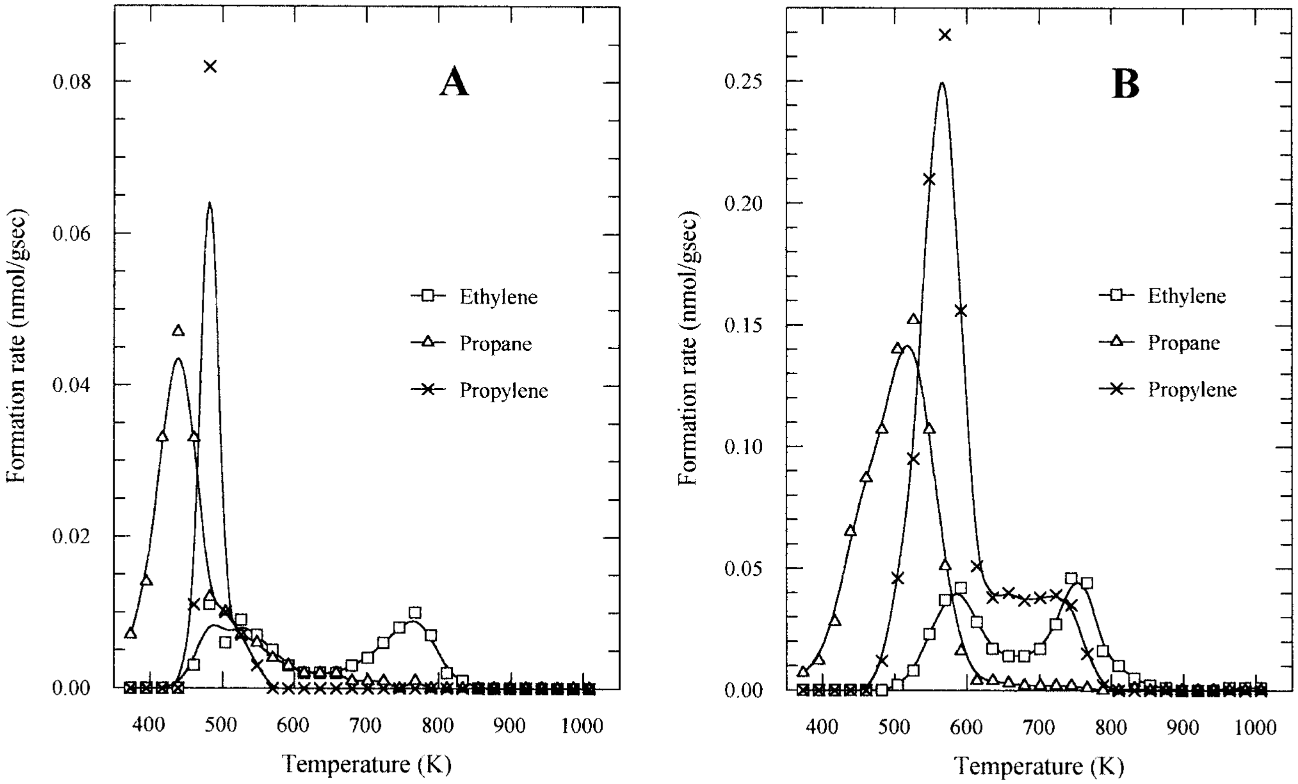

FIG. 2. TPD measurements following propane adsorption on ZSM-5 and Mo$_2$C/ZSM-5 at 373 K.

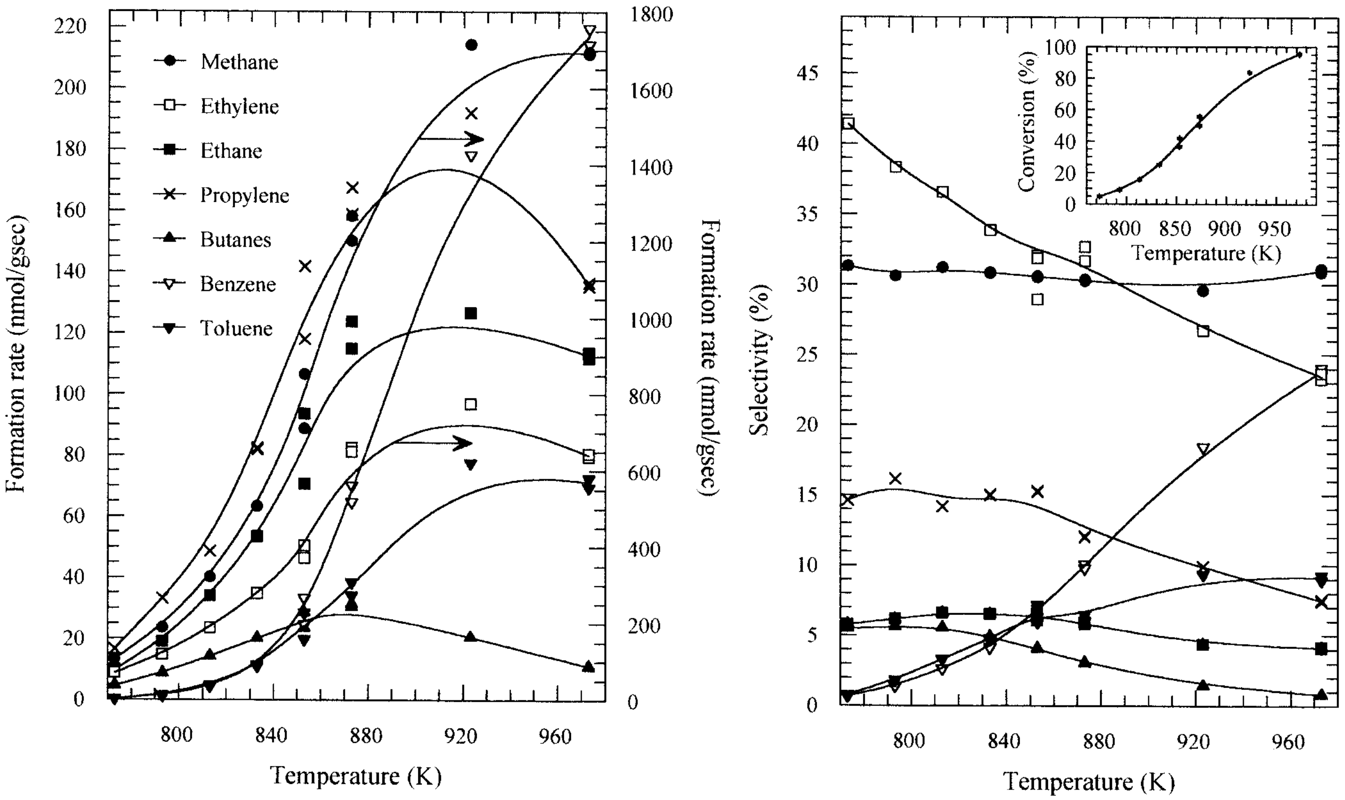

FIG. 3. Conversion of propane, rates, and selectivities of the formation of various products on ZSM-5 at different temperatures. Data were obtained after 60 min of reaction. The same sample was used at every temperature. Measurements were started at the highest temperature.

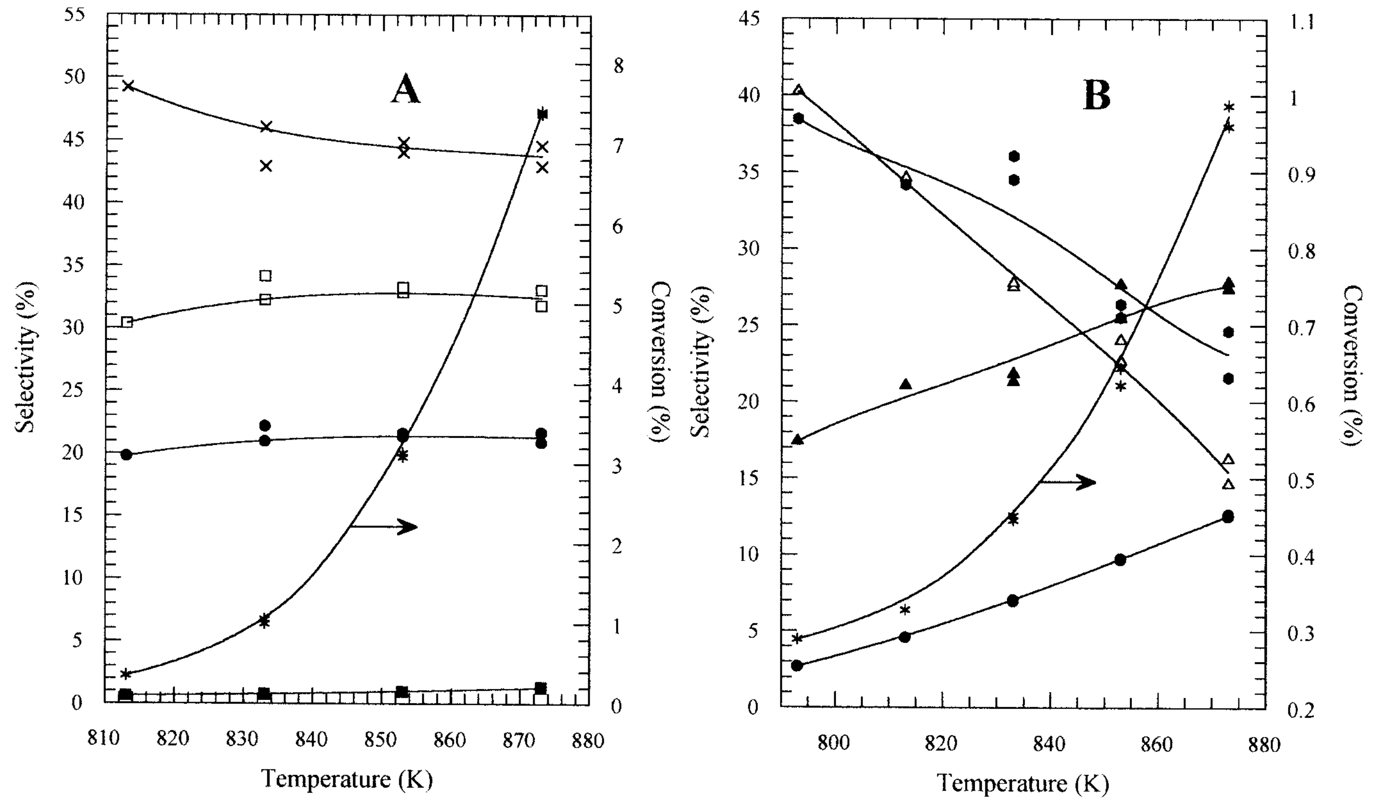

FIG. 4. Conversion of propane (A) and propylene (B), and selectivities of the formation of various products on Mo_2C at different temperatures. (×) propylene, (□) ethylene, (●) methane, (■) ethane, (△) propane, (▲) butane, and (⬢) hexanes. Data were obtained at the steady state. The same sample was used at every temperature. Measurements were started at the highest temperature.

3.3. Reactions of Propane on Mo_2C

In the next experimental series the reaction of propane was investigated on unsupported Mo_2C. The initial conversion at 873 K was 24%, which diminished to a constant value, 7.4%, in 15 min. Besides H_2, ethylene ($S = 33.0\%$), methane ($S \sim 21\%$), and propylene ($S = 44\%$) were found, but benzene was not identified. The variation of the temperature caused only slight changes in the product distribution (Fig. 4A).

Some measurements were also performed with propylene. The initial conversion was 3.8% at 873 K, which decayed to a constant value (~1.0%) in 15 min. The main products are butane, hexane, propane, ethylene, and methane in commensurate amounts. Benzene and toluene were produced in trace amounts ($S \sim 1$–2%). Lowering the temperature resulted in a decrease in the selectivity of butane, methane, and ethylene, and an increase in that of propane and hexane (Fig. 4B).

3.4. Reactions of Propane on Supported Mo_2C

A completely different picture was obtained for Mo_2C/ZSM-5. Results are presented in Fig. 5. The reaction of propane was observed at 773 K. The initial conversion at 773 K was about 2.0%, which increased to 45.0% at 873 K. Whereas there was only a slight decay in the activity of the catalyst at 773 K, at higher temperatures the attainment of a steady state required 50–60 min. During the conditioning period a slight enhancement occurred in the rate of formation of propylene and benzene. The products were practically the same as those measured for Mo_2C-free ZSM-5, but the product distribution was drastically different. The main compound formed was benzene followed by methane and ethylene. Other products were toluene, propylene, and butane. An increase in the temperature was favorable for the formation of benzene and toluene, and was disadvantageous for that of ethylene and propylene. At 873 K, the selectivity to benzene reached a value of 34%.

The effect of contact time on the reaction of propane was determined by varying the flow rate of the reacting gas mixture. Results for Mo_2C/ZSM-5 are plotted in Fig. 6A. We determined that with the increase of the flow rate the conversion and the selectivity to aromatics decreased while the selectivity to ethylene and propylene increased. No change occurred in the selectivity to methane.

Similar measurements have been performed on Mo_2C/SiO_2 catalyst. The product distribution basically differed from that observed for Mo_2C/ZSM-5. The initial main products were methane and ethane. These were followed by propylene, ethylene, benzene, toluene, and butane. A

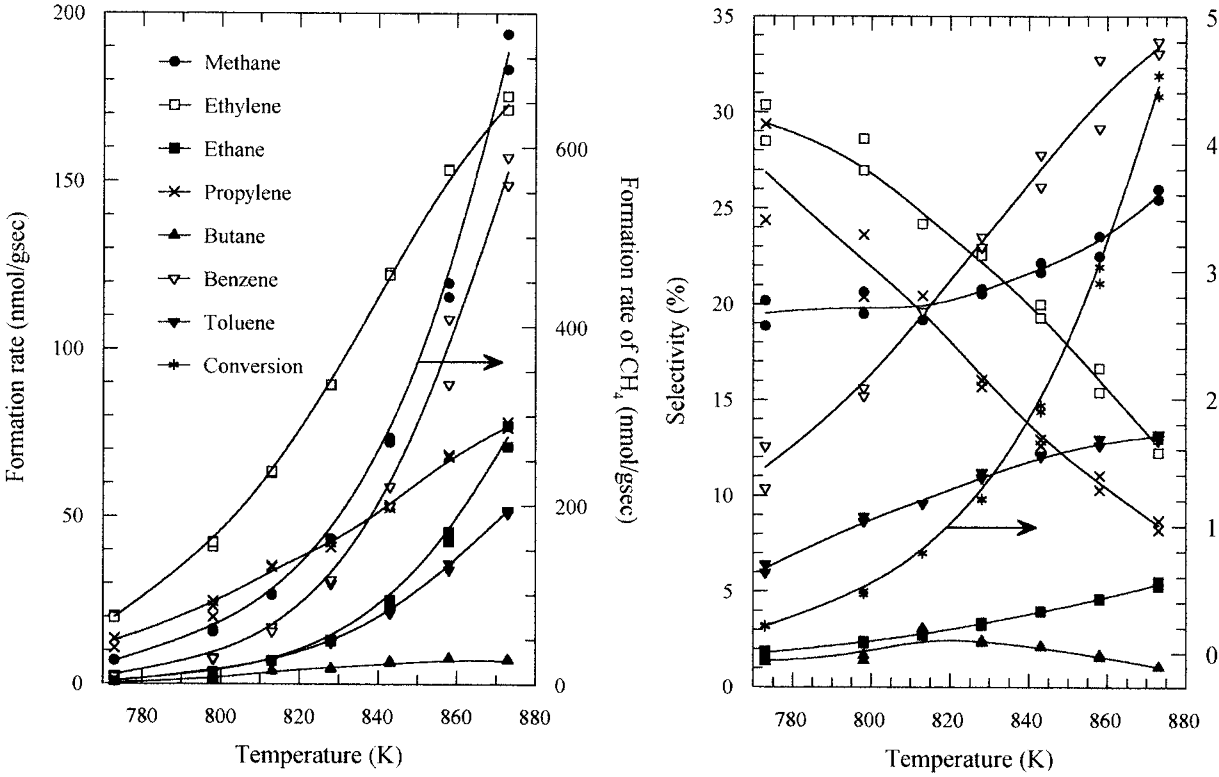

FIG. 5. Conversion of propane, rates, and selectivities of the formation of various products on Mo_2C/ZSM-5 at different temperatures. Data were obtained after 60 min of reaction. The same sample was used at every temperature. Measurements were started at the highest temperature.

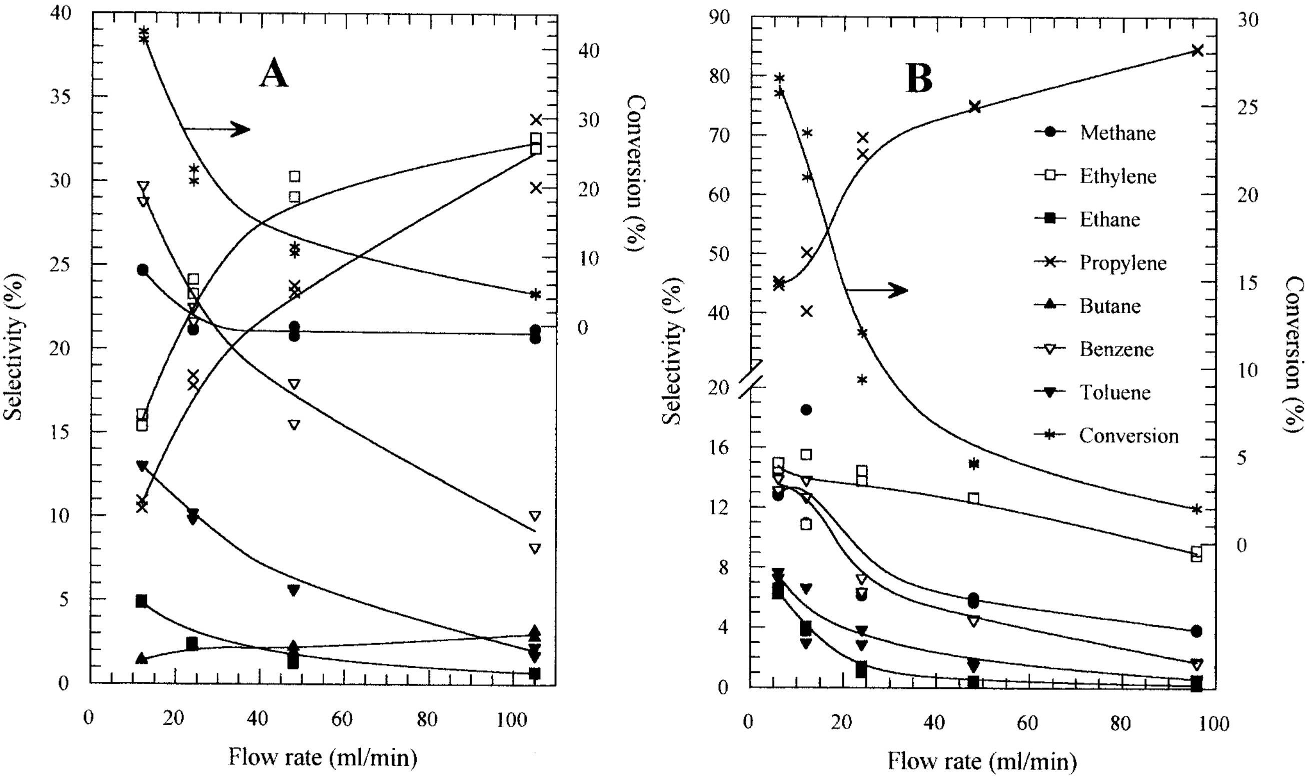

FIG. 6. Effects of the flow rate on the conversion of propane and on the selectivities of the formation of various products on (A) Mo_2C/ZSM-5 and (B) Mo_2C/SiO_2 at 873 K.

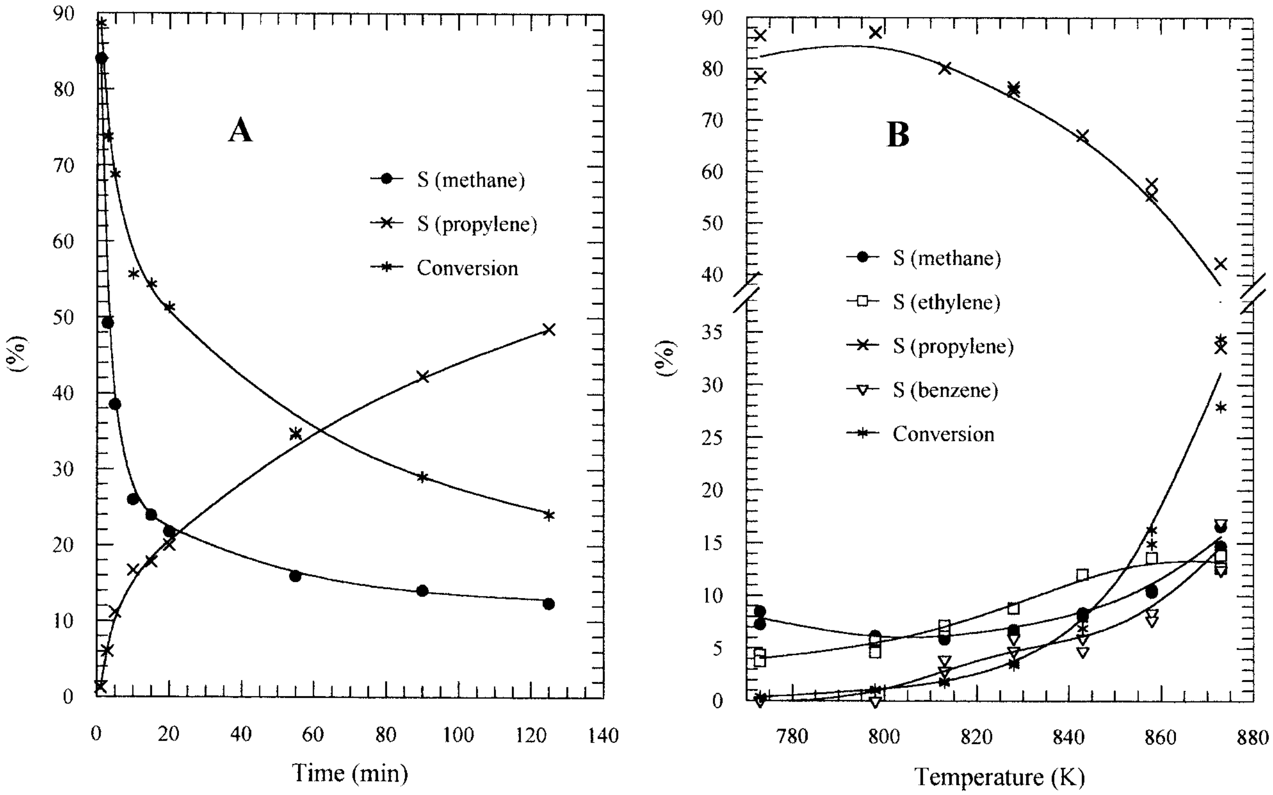

FIG. 7. (A) Conversion of propane, rates, and selectivities of the formation of various products on Mo_2C/SiO_2 at 873 K; (B) effects of reaction temperatures.

gradual decay in the conversion and in the rate of all product formation occurred. An exception was propylene; its formation increased with time on stream. After the initial stage, ~20 min, it became the dominant product, and its selectivity reached values of 35–50% at 873 K (Fig. 7A). The selectivities of all other products were below 15%. Interestingly, the initial high selectivity to benzene, 23%, gradually diminished to 13% after 120 min. When the temperature was lowered after 2 h of reaction at 873 K, we obtained a significant enhancement in the selectivity to propene (Fig. 7B). The same features were observed when the measurements were started at lower temperatures. The effect of contact time was examined at 873 K. We determined that the conversion drastically decreased at high flow rate, and at the same time the selectivity to propylene increased (Fig. 6B). For instance, at a flow rate of 50 ml/min, the selectivity to propylene attained a value of 75% at a propane conversion of ~5%.

Some important data for the transformation of propane on different catalysts are collected in Table 2.

3.5. *Examination of Used Catalyst*

In the infrared spectra of the Mo_2C/ZSM-5 at 873 K for 120 min we detected several absorption bands, which indicated the presence of strongly adsorbed C_xH_y species. Treating this catalyst with hydrogen at 873 K, we observed the formation of methane with small amounts of ethane and ethylene at the beginning of the hydrogenation. The production of methane decayed to a very low level only after 100–120 min, but did not cease completely. This treatment only slightly improved the catalytic performance. When hydrogenation of the catalyst was performed at 973 K, the initial high activity was somewhat restored but a subsequent deactivation occurred again. The amount of carbonaceous species measured at 873 K was 4.4 mmol/g catalyst. This value was 6.8 mmol/g at 973 K.

TABLE 2

Characteristic Data for the Reactions of Propane at 873 K for Steady State

	Mo_2C/SiO_2	ZSM-5	Mo_2C/ZSM-5
Conversion of propane	24%	53%	46%
Selectivity for			
propylene	48%	12%	8%
ethylene	14%	32%	13%
methane	13%	30%	26%
ethane	5%	6%	5%
benzene	12%	10%	33%
toluene	5%	6%	13%

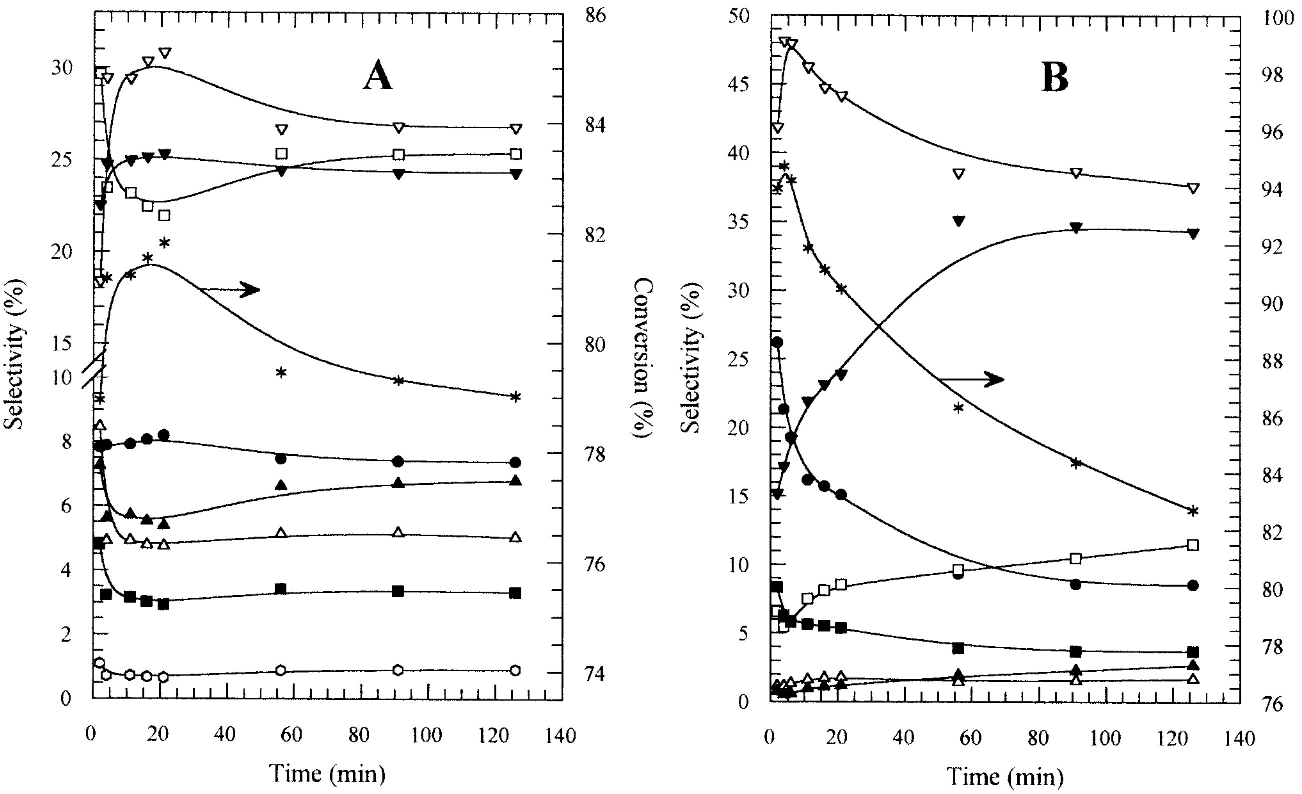

FIG. 8. Conversion of propylene and selectivities of the formation of various products on (A) ZSM-5 and (B) Mo_2C/ZSM-5 at 873 K. (×) propylene, (□) ethylene, (●) methane, (■) ethane, (△) propane, (▲) butane, (⬢) hexanes, (▽) benzene, (▼) toluene, and (○) pentanes.

3.6. *Reactions of Propylene on ZSM-5 and Mo_2C/ZSM-5*

As in the aromatization of lower alkanes the oligomerization of alkenes on the acidic sites of ZSM-5 plays an important role, it seemed necessary to examine the influence of Mo_2C on the reaction of propylene on ZSM-5. Under the reaction conditions used 80% of propylene reacted on pure ZSM-5 at 873 K, producing all the products measured in the reaction of propane. The selectivity to benzene and toluene was 27 and 24%, respectively. The other main product was ethylene with 25% selectivity (Fig. 8A). The main effect of Mo_2C over ZSM-5 is that the formation of ethylene was reduced, and at the same time the selectivity to benzene and toluene was somewhat increased (Fig. 8B). The conversion of propylene remained at a high level, above 80%. Note that on unsupported Mo_2C the cracking of propylene was the main reaction route, and aromatics were only very minor products (Fig. 4B).

4. DISCUSSION

4.1. *Interaction and Reactions of Hydrocarbons with Supported Mo_2C*

There are very few studies dealing with the interaction of alkanes with Mo_2C catalyst. Methane adsorbs weakly and nondissociatively on supported and unsupported Mo_2C samples (4, 5). The decomposition of methane was observed only above 900 K producing several hydrocarbon species, ethane, ethylene, propane, and the deposition of carbonaceous species (5). Above 873 K, the aromatization of methane proceeded on both silica- and ZSM-5-supported Mo_2C catalysts (3–10). The highest selectivity, 80–85%, was measured for Mo_2C/ZSM-5 (5, 6). Ethane was more reactive than methane. By means of FTIR spectroscopy, spectroscopic evidence was obtained for the formation of adsorbed ethylene at 270–300 K, which transformed into ethylidyne at higher temperature (26). The aromatization of ethane occurred on Mo_2C/ZSM-5 above 773 K (11). A deeper insight into the role of Mo_2C in the conversion of the above hydrocarbons was provided by the surface science studies of the reactions of different hydrocarbon species, CH_2, CH_3, and C_2H_5, on Mo_2C produced on an Mo(111) single crystal surface (14, 15). We found no report in the literature concerning the interaction and reaction of propane on unsupported and supported Mo_2C.

4.2. *Interaction of Propane with Supported Mo_2C*

As shown in Table 1 the absorption bands observed following the adsorption of propane on Mo_2C/SiO_2 at 150–250 K correspond very well with the different vibrations of adsorbed propane. At higher temperatures, however, new spectral features appeared at 2925, 1453, 1429, 1411, and 1374 cm^{-1}, which suggests that a fraction of propane interacted strongly with Mo_2C. As the possible process was the dehydrogenation of propane, the interaction of propylene with supported Mo_2C was also investigated. The characteristic absorption bands of π-bonded and di-σ-bonded propylene can be clearly established in the IR spectra (Fig. 1B). In addition, the appearance of bands at 2983, 2941, 1470, and 1390 cm^{-1} suggests that adsorbed propylene is converted into propylidyne at 273 K. Taking into account the spectral features of adsorbed propylene and propylidyne on Mo_2C/SiO_2, the absorption bands at 2925, 1453, 1411, 1374 cm^{-1} found following the adsorption of propane at 573 K can be attributed to adsorbed propylene. We cannot exclude that the vibration of propylidyne also contributes to these absorption bands. We assume that the two weak features remaining on spectrum (e) in Fig. 1A are definitely due to the strongly adsorbed propylidyne. The characteristic absorption bands of propylidyne are as follows: 2960, 2920, 2870, 1450, 1410, and 1365 cm^{-1} (27–31). These spectral features were also established following the adsorption of propane on Pt/SiO_2 by Sheppard *et al.* (27–31). Accordingly, the reactivity of highly dispersed Mo_2C toward propane and propylene is not much less than that of supported Pt catalyst.

The failure to prepare a stable, self-supporting disc from ZSM-5-containing catalyst prevented us from performing similar IR spectroscopic measurements. We could only establish that the adsorption of propane at 173–273 K resulted in the same absorption bands on both ZSM-5 and Mo_2C/ZSM-5 as on Mo_2C/SiO_2, and the propane bonded more strongly compared to that on Mo_2C/SiO_2.

The presence of strongly adsorbed species remaining on supported Mo_2C after contact with propane is also suggested by TPD measurements. This species is converted into propylene and ethylene at higher temperatures (Fig. 2).

4.3. *Reactions of Propane on Mo_2C and Mo_2C/SiO_2*

The dominant reaction on unsupported Mo_2C at 873 K is the dehydrogenation process to give propylene with ∼44% selectivity. The cracking of propylene also occurred, and the main products were ethylene and methane. As the surface area of Mo_2C is low (∼8–10 m^2/g), the conversion of propane was only 7.4%.

Deposition of Mo_2C on silica in a highly dispersed state produced a much more effective catalyst. The initial products determined at 873 K suggest that the main reaction in the first stage is the decomposition of propane into methane and ethylene,

$$C_3H_8 \rightarrow CH_4 + C_2H_4, \qquad [1]$$

followed by the dehydrogenation of propane into propylene,

$$C_3H_8 \rightarrow C_3H_6 + H_2. \qquad [2]$$

A fraction of C_2H_4 is hydrogenated into ethane. After the initial stage the dehydrogenation of propane became the dominant reaction pathway; propylene was produced with a maximum 50% selectivity at 873 K (Fig. 7A). At lower temperatures much higher selectivities, 85–75%, were reached. The change in the selectivities of product formation with time on stream suggests that the deactivation of the catalyst, very likely due to the deposition of carbon, is disadvantageous for the cracking of propane.

4.4. *Reactions of Propane on ZSM-5 and on Mo_2C/ZSM-5*

A completely different picture was obtained on Mo_2C/ZSM-5 catalysts. The formation of aromatics came into prominence, which was negligible on silica-supported Mo_2C. The aromatization of propane proceeds readily on undoped ZSM-5 alone at and above 823 K; the preparation, the composition of the ZSM-5, and the experimental conditions all influence the conversion and product distribution (16–20). On our ZSM-5 sample, the reaction of propane was measurable at 773 K (Fig. 3). The main products were ethylene, methane, and propylene, suggesting the occurrence of the reactions observed for Mo_2C/SiO_2. The selectivity of the aromatics (benzene and toluene) at 873 K was around 16–18%, which increased to ∼34% at 973 K. When Mo_2C was deposited over ZSM-5, the catalytic performance of ZSM-5 markedly changed. The conversion of propane slightly decayed, but the selectivity to benzene and toluene significantly increased (Table 2).

In the description of the aromatization of propane on ZSM-5 it is assumed that propane is activated through the abstraction of hydride ions by carbonium ion (20). The dimethyl carbonium ions formed may give propylene or react with alkenes. Parallel with this reaction route the cracking of alkenes (ethylene and propylene) also proceeds to yield lower alkanes. The oligomerization of propylene on the acidic sites in the zeolite cavities leads to the formation of aromatics (20).

The favorable effect of Mo_2C can be explained by its high activity toward the dehydrogenation of propane. The results obtained for Mo_2C/SiO_2 clearly showed that Mo_2C is an effective catalyst to produce propylene from propane. It remained, however, an open question as to how the highly dispersed Mo_2C affects the oligomerizing property of ZSM-5. In the case of ethylene we found that Mo_2C only slightly influenced the conversion of ethylene, but lowered by about 10–15% the selectivity to aromatics. In the present case, no unfavorable effect of Mo_2C on the aromatization capability of ZSM-5 was experienced; moreover, a slight increase in the selectivities of the formation of both benzene and toluene occurred (Fig. 8).

CONCLUSIONS

(i) Propane adsorbed weakly and reversibly on supported Mo_2C below 273 K. A stronger interaction occurred above 300 K, when vibrations of adsorbed propylene and propylidyne were observed. (ii) Mo_2C dispersed on silica is an effective dehydrogenating catalyst for propane: the highest selectivity to propylene is 50% at a conversion of 25% at 873 K. (iii) The reaction pathway of propane is completely different over Mo_2C/ZSM-5. In this case the dominant reaction is the aromatization of propane. The change in the reaction route is attributed to the capability of ZSM-5 to aromatize propylene produced over Mo_2C.

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