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Aromatization of n-heptane on Mo_2C-containing catalysts

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Abstract

The reaction pathways of n-heptane were studied on various Mo_2C-containing catalysts characterized by X-ray photoemission spectroscopy and surface acidity measurements. Unsupported Mo_2C catalyzed the dehydrogenation and cracking of n-heptane even at 573–623 K. Above 723 K, the dehydroaromatization of heptane became the dominant route for yielding toluene and benzene, with selectivities of 43 and 8%, respectively, at conversions of 20–23%. The catalytic performance of Mo_2C was improved when Mo_2C was deposited in a highly dispersed state on various supports, like silica, alumina, and ZSM-5. The best yield of the formation of aromatics (48.7%) was obtained for 5% Mo_2C/ZSM-5 ($SiO_2/Al_2O_3 = 80$) at 873 K. Although the deposition of coke occurred on all samples during the reaction, the latter catalyst underwent only a slight deactivation even after 20 h of reaction. The results obtained were interpreted by the monofunctional (pure Mo_2C), and bifunctional mechanism (supported Mo_2C) of the aromatization of n-heptane.

Keywords: Aromatization of n-heptane; Reaction of 1-hexene; Mo_2C; Mo_2C/ZSM-5; Mo_2C/SiO_2; Mo_2C/Al_2O_3

1. Introduction

The direct conversion of alkanes into aromatics is an important industrial process that has been the subject of extensive research. The results obtained on various catalysts and the possible mechanisms of this complex process are well documented in several excellent reviews [1–6]. Early studies focused mainly on supported Pt catalysts, which exhibited outstanding catalytic performance among the metals [7,8]. Two mechanisms were proposed: a bifunctional mechanism involving both the metal and the acid sites of the support, and a monofunctional mechanism involving only the metallic sites [5]. Coke formation in the hydrocarbon transformation reactions over Pt metals caused a serious problem, however; L-type zeolites, then later ZSM-5, loaded with Pt were found to be more active and selective for the aromatization of n-heptane [2–6,9]. The formation of coke in this case is severely restricted in the channels of ZSM-5 zeolite. But the high acidity of H-form zeolite led to increased cracking activity [5]. Therefore, it appeared necessary to balance the zeolite acidity and to compensate for its decrease with some additives, which greatly improved the catalytic performance of ZSM-5 [10].

All of these studies were exclusively restricted to the reactions of C_2–C_7 compounds, because no catalyst combination could convert methane into aromatics [1–10]. A milestone in this area occurred when a Chinese group observed that MoO_3/ZSM-5 catalyst can transform methane into benzene with 80–100% selectivity at a 10–12% conversion level [11]. Subsequent studies revealed that MoO_3 is reduced and converted into Mo_2C during the early phase of the reaction, and that Mo_2C activates methane, resulting in the formation of benzene on ZSM-5 [12–16]. Further investigations showed that Mo_2C is also an active catalyst toward the reaction of C_2–C_4 alkanes into aromatic compounds [17–24]. However, its effect was mainly exhibited when it was deposited on ZSM-5 or on silica surface containing acidic centers. Pure Mo_2C catalyzed only the decomposition and dehydrogenation of alkanes, but aromatics were produced

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only in trace amounts [11–23]. An exception was the hexane, the aromatization of which occurred on pure Mo_2C with a selectivity of ∼65% at a conversion of ∼25% [24].

Here we report on the aromatization of *n*-heptane on unsupported and supported Mo_2C catalysts. *n*-Heptane is one of the components of natural gas liquids (NGL), and its reforming to olefins and aromatics is of practical importance [25–35].

2. Experimental

2.1. Materials

Mo_2C was prepared by the carburization of MoO_3 (products of ALFA AESAR) by C_2H_6/H_2 [36]. The oxide was heated under 10% v/v C_2H_6/H_2 gas mixture from room temperature to 900 K at a heating rate of 0.8 K/min, then cooled to room temperature under argon. The carbide was passivated in flowing 1% O_2/He at 300 K. The surface area of Mo_2C is 20 m^2/g. In certain cases Mo_2C was prepared in situ in, the catalytic reactor, when the last step was missing. Supported Mo_2C catalysts have been made similarly by carburizing MoO_3-containing supports with C_2H_6/H_2 gas mixture. The MoO_3 support samples were prepared by impregnating the support with a basic solution of ammonium heptamolybdate to yield 2, 5, and 10 wt% of MoO_3. The suspension was dried and calcined at 863 K for 5 h. The following materials were used as supports: ZSM-5 with SiO_2/Al_2O_3 ratio at 80 and 280, BET area 425 and 400 m^2/g; Al_2O_3 (Degussa C, containing 0.4% Cl; 100 m^2/g); and SiO_2 (Aerosil; 200 m^2/g). To remove the excess carbon deposited on the Mo_2C during the preparation, the catalyst was reduced before the catalytic measurements in situ at 873 K in an H_2 stream for 60 min. The gases used were of commercial purity (Linde). The *n*-heptene (99% pure) was purchased from Spectrum 3D, and the 1-heptene (97% pure) was purchased from Aldrich.

2.2. Methods

The acidic properties of catalysts were evaluated by NH_3 temperature-programmed desorption (TPD) and Fourier transform infrared (FTIR) methods using the adsorption of pyridine and CO. Infrared spectroscopic measurements were made in a vacuum infrared cell (base pressure 5×10^{-6} Torr, 1 Torr = 133 Pa) using self-supporting wafers of catalyst powders (10 mg/cm^2). The sample can be cooled by a copper block in contact with liquid nitrogen. Infrared spectra of adsorbed CO (10 Torr) were taken at 153 K. The adsorption of pyridine (0.1 Torr) was performed at 300 K for 30 min, and then the sample was evacuated at 473 K for 10 min. Spectra were registered at 300 K. A Bio-Rad (Digilab model FTS 155) FTIR spectrometer was used. Typically, 128 scans with 2 cm^{-1} spectral resolution were collected.

X-ray photoemission spectroscopy (XPS) measurements were performed in a Kratos XSAM 800 instrument at a base pressure of 10^{-8} Torr using Mg-Kα primary radiation (14 kV, 10 mA). To compensate for possible charging effects, binding energies (BEs) were normalized to the Fermi-level for the Mo_2C. TPD measurements for NH_3 were performed in the catalytic reactor. The reduced catalysts were exposed to flowing NH_3 (40 ml/min) for 30 min. After the adsorption step, the temperature was increased to 373 K in Ar stream (12 ml/min). The flushing was continued until a stable baseline on a thermal conductivity (TC) detector was achieved. The NH_3 TPD curves were detected by on-line gas chromatography (GC) with TC detection. The reactor temperature was ramped from 373 to 973 K at rate of 20 K/min. The flow rate of Ar carrier gas was 20 ml/min. The amount of coke deposited on the catalyst during the reaction was determined by temperature-programmed reaction spectroscopy (TPR). The catalyst was cooled in flowing argon, then heated in a H_2 stream at a rate of 5 K/min, and the hydrocarbons formed were measured.

Catalytic reactions were carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube connected to a capillary tube [14,22]. The flow rate was 12 ml/min. The carrier gas was Ar. The hydrocarbon content was 10%. Generally, 0.3 g of loosely compressed catalyst sample was used. Reaction products were analyzed by GC using a Hewlett–Packard 6890 gas chromatograph with a 60-m GS-GASPRO column. The conversion of *n*-heptane was calculated taking into account the amount consumed. 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 product.

3. Results

3.1. Characterization of the catalyst

All of the catalysts used in the study were characterized by XPS measurements. Similar to the catalytic studies, the Mo_2C samples were reduced in the preparation chamber attached to a UHV system in flowing H_2 at 873 K for 1 h. The BEs for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) showed some slight variation with different samples, but fell into the range 227.0–228.2 eV for Mo($3d_{5/2}$), 230.7–231.1 eV for Mo($3d_{3/2}$), and 283.8 eV for C(1s). These values are consistent with those attributed to Mo_2C [14,15,37].

In previous studies, detailed experiments were performed to detect any acidic centers on pure Mo_2C and to establish the influence of Mo_2C on the acidic properties of ZSM-5 and SiO_2 [38–44]. In the case of unsupported Mo_2C, we could not measure the adsorption of NH_3. Results of TPD measurements for pure Al_2O_3 and 2% Mo_2C/Al_2O_3 show that

Table 1
Data referring to the acidity of the catalysts

Sample	NH_3-TPD						FT-IR									
	LT-peak[a]		MT-peak[b]		HT-peak[c]		Pyridine adsorption					CO adsorption				
	mmol/g	T_{max} (K)	mmol/g	T_{max} (K)	mmol/g	T_{max} (K)	peak position (cm^{-1})					peak position (cm^{-1})				
Al_2O_3	0.04	489	0.07	542	0.07	660	1450	1494	–	1622	–	2132	2162	2187	2232	3575
2% Mo_2C/Al_2O_3	0.02	485	0.03	534	0.03	625	1452	1493	–	1623	–	2132	2162	2184	2235	3598

[a] Low-temperature peak.
[b] Medium-temperature peak.
[c] High-temperature peak.

NH_3 adsorption on alumina decreases significantly when Mo_2C is deposited on its surface. The total NH_3 adsorption capacity is 0.18 $mmol/g_{cat}$ for the pure sample, decreasing to 0.08 $mmol/g_{cat}$ for 2% Mo_2C/Al_2O_3. In the FTIR spectra of adsorbed pyridine, we obtained a strong band at 1450 cm^{-1}, indicating the presence of a Lewis acid site, but there was no spectral feature at about 1545 cm^{-1} diagnostic of pyridinium ion bonded to a Brønsted site. The integrated absorbance values and the stability to heat treatment of the band at 1450 cm^{-1} was affected only slightly by the presence of Mo_2C on Al_2O_3. After CO adsorption on Al_2O_3 and 2% Mo_2C/Al_2O_3, four bands were identified at 2234, 2198, 2162, and 2132 cm^{-1} in the CO stretching region. The two higher-frequency CO adspecies have been assigned to two families of sites involving coordinatively unsaturated tetrahedrally coordinated Al cations (Lewis acid sites). The peak at 2162 cm^{-1} has been ascribed to CO hydrogen bonded to OH groups. The weak band at 2132 cm^{-1} is assigned to physically adsorbed CO [45–47]. In harmony with the data reported in the literature, adsorption of CO yielded four negative peaks at 3794, 3770, 3735, and 3690 cm^{-1} in the OH stretching region of spectra. As an evidence of the interaction between adsorbed CO and surface OH groups on Al_2O_3, a broad positive band was also detected at about 3575 cm^{-1}. The peaks at 2162 and 3575 cm^{-1} changed coincidently during sample annealing, verifying the coherency of these peaks. The red shift value of $\Delta\upsilon_{OH} \approx 115$ cm^{-1} indicates a weak interaction between the OH groups and adsorbed CO; that is, the protons of OH groups on Al_2O_3 and 2% Mo_2C/Al_2O_3 could not be ascribed as Brønsted acidic sites. Similar to the pyridine adsorption measurements, no additional peaks and no significant integrated absorbance value changes due to Mo_2C were observed. Data characteristic of alumina-based catalysts are collected in Table 1. The acidic properties of the ZSM-5- and SiO_2-based catalysts used in our laboratory were determined previously [44].

3.2. Reaction on pure Mo_2C

Mo_2C prepared by the C_2H_6/H_2 gas mixture exhibited relatively high activity. The decomposition of heptane started at 573 K, and the conversion reached an initial value of 20–23% at 823 K (Fig. 1A). To obtain more information on the initial performance of the catalysts and to avoid the effect of its deactivation, the reacting gases were replaced by argon during the product analysis in the first 30–60 min. Further increases in temperature led to a very fast deterioration of the catalyst, likely as a result of carbon deposition. At lower temperatures (573–623 K), the main process is the dehydrogenation with some cracking. Various types of heptenes were formed in this reaction. At 673–823 K, the dehydroaromatization of heptane became the dominant reaction, yielding toluene and benzene, with selectivity increasing with increasing temperature. At 823 K, these values were ∼43% for toluene and ∼8% for benzene, with heptene selectivity of ∼26–28%. Note that CO was also observed during the reaction at 823–873 K, indicating that the Mo oxide was not fully converted into Mo_2C [48]. Another possibility was that the partial oxidation of Mo_2C occurred in the passivation of freshly prepared Mo_2C. To exclude the possible role of Mo oxycarbide, the preparation was made in situ without treatment with a 1% O_2/He stream at 300 K. Although the production of a small amount of CO was seen at 823 K at the beginning of the heptane reaction, the catalytic performance of Mo_2C was practically the same as that shown in the Fig. 1A.

3.3. Reaction on supported Mo_2C

Somewhat different behavior was seen when Mo_2C was prepared on an alumina surface. Both the conversion and selectivity of toluene increased with increasing temperature. In this case, fast deactivation at 873 K was not observed; the heptane reaction was measurable for a longer period. The selectivity of toluene was 57% and that of benzene was 5–7% at 35–30% conversion on 2% Mo_2C/Al_2O_3. The selectivity of heptenes was low ($<15\%$) throughout the measurements at 723–873 K (Fig. 1B). Nearly the same values were calculated for butene and propene. 2% Mo_2C on silica exhibited similar catalytic performance. But at 873 K, the selectivity of toluene and benzene was lower, 15 and 5%, respectively, at a conversion of 34%. With a greater amount of Mo_2C (10%), toluene selectivity reached its maximum value, 55–65% at 823 K with a conversion of 10–14%. At 873 K, the initial conversion was 26.5–22.0%, but toluene selectivity decayed to 32% and then to 17–12%. On both catalysts, heptenes formed with a selectivity of 6–15%. Similar to the pure Mo_2C, the silica-based catalysts rapidly lost their catalytic efficiency at 823–873 K; some data are given in Table 2.

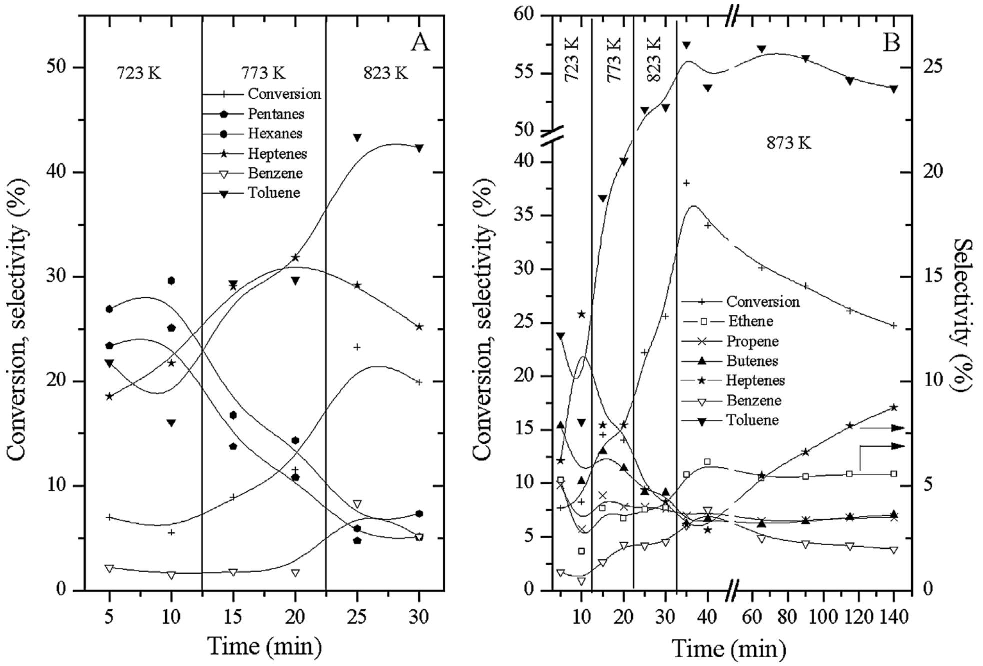

Fig. 1. Reaction of *n*-heptane over Mo_2C (A) and 2% Mo_2C/Al_2O_3 (B) catalysts at different temperatures.

Table 2
Characteristic data for the reaction of *n*-heptane on different catalysts at 873 K[a]

Catalyst	Conversion (%)	Selectivity (%)									Yield of aromatics
		Methane	Ethene	Propene	Propane	Butenes	Heptenes	Benzene	Toluene	Xylenes	
Mo_2C	18.8	2.6	4.1	5.0	0.4	2.8	23.9	3.0	19.7	0.1	3.9
Mo_2C[b]	21.5	1.0	0.5	1.9	0.2	4.0	31.4	6.0	43.0	0.0	8.6
2% Mo_2C/Al_2O_3	34.1	3.3	6.1	7.4	1.7	6.7	2.9	7.5	53.8	0.3	21.0
2% Mo_2C/SiO_2	34.4	3.4	10.2	25.5	0.8	27.4	5.5	5.4	15.4	0.8	7.4
10% Mo_2C/SiO_2	22.5	6.9	1.7	3.2	0.3	7.2	15.3	6.2	18.7	0.5	5.8
10% Mo_2C/SiO_2[b]	12.5	1.0	0.5	1.0	0.1	1.6	20.0	4.0	60.0	0.9	7.9
H-ZSM-5(80)	96.7	5.8	24.0	20.0	9.8	5.9	–	8.4	9.3	2.9	20.2
2% Mo_2C/ZSM-5(80)	99.6	11.0	14.2	7.3	8.9	1.7	–	22.7	20.2	5.7	48.7
5% Mo_2C/ZSM-5(80)	99.9	14.1	11.4	4.9	5.4	0.6	–	27.4	23.3	6.0	57.2
10% Mo_2C/ZSM-5(80)	80.6	5.7	15.5	31.3	5.9	14.6	0.2	8.5	8.8	0.4	14.3
ZSM-5(280)	91.5	3.3	19.9	28.4	11.2	11.3	–	2.6	3.4	1.8	7.2
2% Mo_2C/ZSM-5(280)	82.6	2.5	14.6	27.6	10.0	13.3	0.1	4.5	8.8	1.6	12.4

[a] Data were taken at 10 min of time on stream.
[b] At 823 K.

More attractive results were obtained when Mo_2C was combined with zeolites. We choose two ZSM-5 samples with SiO_2/Al_2O_3 ratios of 80 and 280, respectively. In harmony with previous studies [28,31,34], even in a pure state the ZSM-5(80) is active toward the conversion of heptane into other compounds. The reaction on ZSM-5(80) was observed at very low temperature (∼523 K), but the formation of aromatics, xylene, and benzene occurred to a measurable extent only above 573 K. At 773 K, the main products were propane, propene, ethene, butanes, and butenes. The conversion reached ∼92% at 823 K and ∼96% at 873 K. At the latter temperature, propene ($S = 20\%$), ethylene ($S = 24\%$) formed with the highest selectivity; this value was ∼9% for both the xylene and benzene. ZSM-5(280) was less active and its aromatizing property was also lower. The total selectivity of aromatics was <4–5% even at 873 K. Heptenes were not identified on these zeolites at 450–873 K.

Deposition of 2% Mo_2C on the ZSM-5(80) samples enhanced the rate of heptane decomposition measured on pure ZSM-5(80). The formation of cracking products, hexane, pentane, propane, propene, butane, and butenes was observed even at 473–523 K. With increasing temperature, their evolution increased up to 673 K, then decreased. Hexane was an exception, because its production above 673 K decreased. At the same time, dehydrogenation set in at 573 K, as indicated by the formation of H_2 and heptenes with

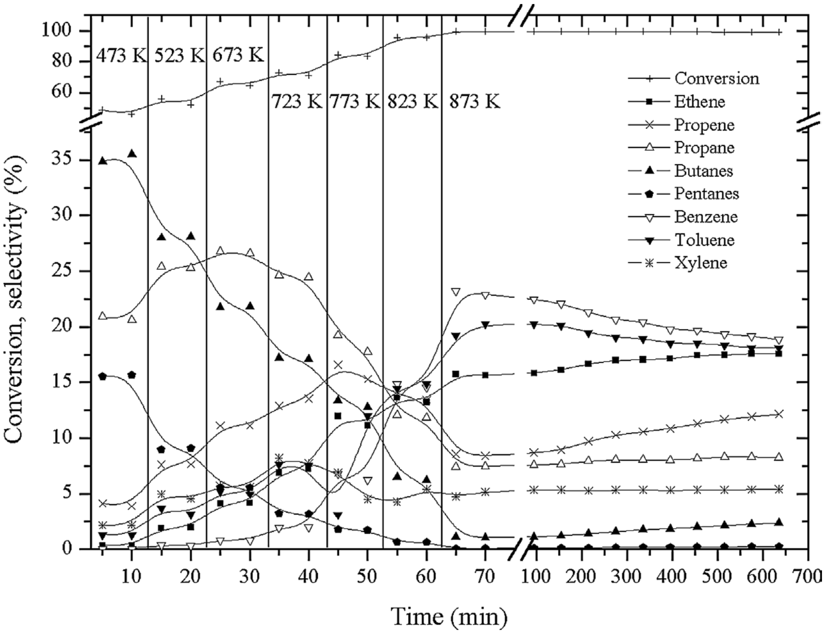

Fig. 2. Reaction of *n*-heptane over 2% Mo_2C/ZSM-5(80) at different temperatures.

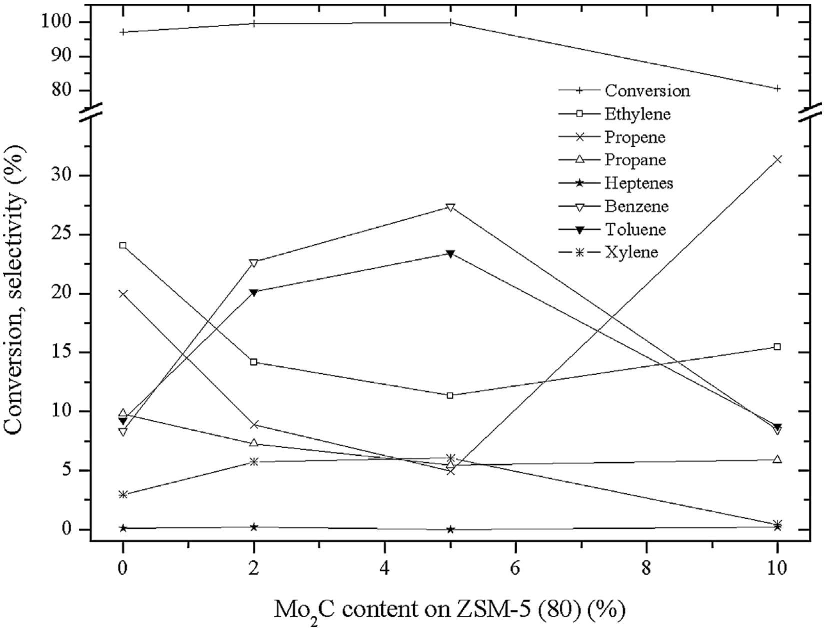

Fig. 3. Effects of Mo_2C content of ZSM-5(80) on the conversion of *n*-heptane and selectivities of various products formed at 823 K.

a very low selectivity of 2%. Heptenes disappeared from the products at 623–673 K, when the formation of toluene, benzene, and xylene became prominent. In contrast to the previously studied catalysts, in which toluene was the main aromatic compound on 2% Mo_2C/ZSM-5, the selectivity of benzene approached that of toluene at 823 K and became even higher at 873 K. At 873 K, the total selectivity of aromatics reached a value of ~49%. This catalyst exhibited a very stable activity, with conversion decaying by only a few percentage points even after 10 h and the aromatizing capability remaining high. These findings are illustrated in Fig. 2.

Higher loading of Mo_2C (5%) further increased the selectivity of aromatics to ~57%, while decreasing the selectivity of ethylene, propene, butene, and butane. Heptenes were practically absent. Less activity was exhibited by 10% Mo_2C/ZSM-5. The effects of loading of Mo_2C are displayed in Fig. 3. The promoting effect of Mo_2C was experienced in the case of less-active ZSM-5(280), when it enhanced both the conversion and selectivity of aromatics (Table 2). We performed some kinetic measurements on Mo_2C/ZSM-5(80) and found that the concentration of *n*-heptane varied between 1.3 and 8.0% and the decomposition rate of heptane

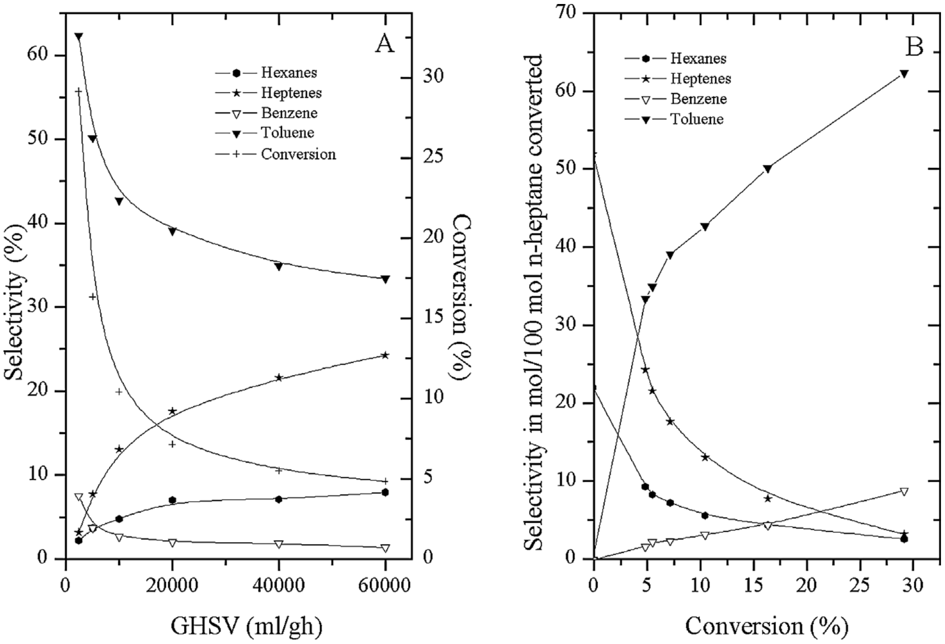

Fig. 4. Effects of space velocity on the reaction of *n*-heptane (A) and product selectivity as a function of *n*-heptane conversion (B) over 2% Mo_2C/Al_2O_3 at 873 K.

followed first-order kinetics. The same results were found for the formation of benzene and toluene, which assumedly did not undergo secondary reactions. We obtained an activation energy of 83 kJ/mol for the heptane decomposition.

The results showing the effect of space velocity on the conversion and selectivity of the important compounds for 2% Mo_2C/Al_2O_3 are displayed in Fig. 4A. As shown, the conversion and selectivity of aromatics decreased, whereas the selectivity of heptenes and hexanes increased with increasing space velocity.

3.4. *TPR measurements for used catalyst*

The amount and the reactivity of coke deposited on the catalysts during the reaction were determined by TPR with hydrogen. The samples were treated with the reacting gas mixture for 2 h at 823 K, then cooled to around room temperature in argon flow. In the case of pure fresh, unreduced, and unused Mo_2C, the evolution of methane started above 600 K and reached a peak at 798 K. Repeating the experiment with the same sample, we still found a very small amount of methane ($T_p = 848$ K) corresponding to 0.003 mg_C/g_{cat} (Fig. 5A). Similar experiments with Mo_2C demonstrated that the hydrogenation of the carbon started at ~800 K and peaked at 948 K (Fig. 5B) with 5.53 mg/g catalyst. In addition to methane, traces of ethane and propylene were also identified in the temperature range 700–900 K. A smaller amount of coke (2.69 mg/g_{cat}) was found under the same experimental conditions over 2% Mo_2C/ZSM-5(80) with $T_p = 898$ K (Fig. 5C). We measured a smaller amount of carbon-containing deposit (1.83 mg/g_{cat}) in the case of 2% Mo_2C/Al_2O_3, which exhibited the lowest reactivity ($T_p =$ 1048 K).

3.5. *Reaction of 1-heptene*

To gain better insight into the reaction mechanism of *n*-heptane aromatization, we also examined the reaction of 1-heptene over some catalysts. Heptene reacted at a higher rate than heptane on all samples. On pure Mo_2C, the conversion was ~34% at 773 K and increased to ~70% at 873 K. Qualitatively, the same cracking products in both hexane and hexane reactions. For the aromatic compounds, the selectivity of toluene was the highest (~34%) at 723–773 K and decreased with increasing temperature.

High conversion values (55–95%) were measured for alumina- and silica-supported Mo_2C samples at 773–873 K. Butenes, ethene, ethane, and propene were the main products. On 2% Mo_2C/Al_2O_3 at 873 K, toluene selectivity was 27% and benzene selectivity was 6%; xylene formation was also observed. On Mo_2C/SiO_2, aromatics were produced with lower selectivity. The maximum value 11% was attained at 873 K. The catalytic behavior of pure ZSM-5(80) and 5% Mo_2C/ZSM-5(80) was also tested. The conversion of heptene was near 100% on both solids at 723–873 K; the aromatic selectivity values were similar. The positive influence of Mo_2C was exhibited at lower temperatures (723–773 K), where it increased the selectivity and yield of aromatics (Table 3).

4. Discussion

4.1. *Main characteristics of the catalysts*

XPS measurements showed that the binding energies obtained for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) and C(1s) correspond

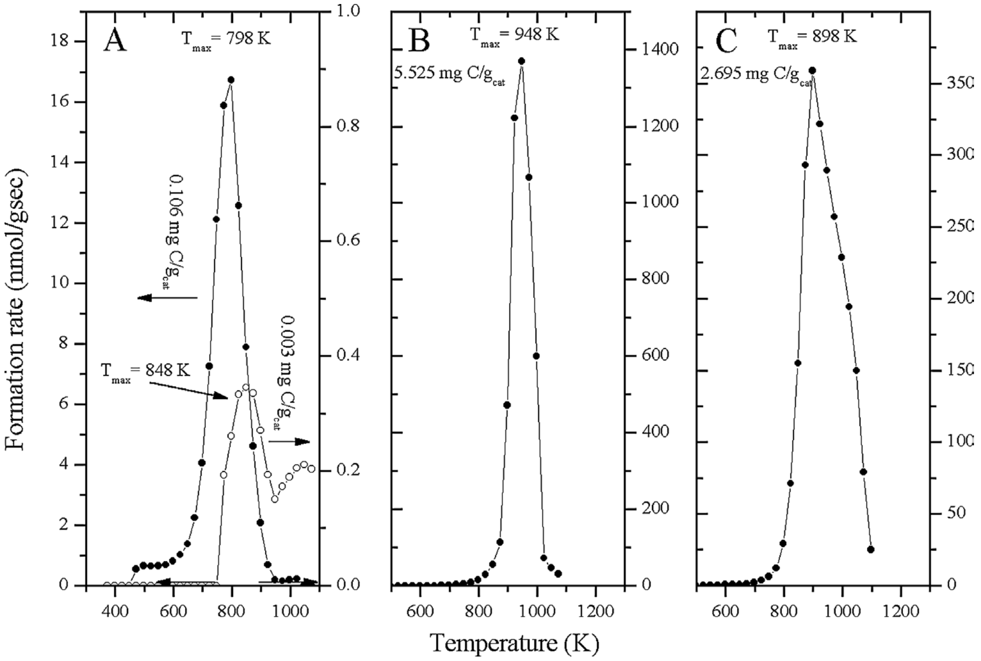

Fig. 5. Formation of methane in the TPR measurements for unused and unreduced Mo_2C (●) and after repeating the measurement with the same sample (○) (A), and following *n*-heptane reaction at 823 K for 120 min on Mo_2C (B) and 2% Mo_2C/ZSM-5(80) (C).

Table 3
Characteristic data for the reaction of 1-heptene on different catalysts[a]

Catalyst	Temperature (K)	Conversion (%)	Selectivity (%)									Yield of aromatics
			Methane	Ethene	Ethane	Propene	Propane	Butenes	Benzene	Toluene	Xylenes	
Mo_2C	773	34.3	0.8	2.8	1.5	10.3	1.0	17.4	2.0	33.8	0.1	12.3
	873	70.4	7.0	4.3	7.8	8.4	2.7	20.2	4.9	15.8	0.1	14.6
2% Mo_2C/Al_2O_3	773	54.1	0.8	2.6	0.6	10.2	0.5	22.4	1.0	27.7	0.4	17.4
	873	94.6	5.7	10.4	5.1	11.6	2.1	18.5	5.8	27.3	0.2	33.0
2% Mo_2C/SiO_2	773	72.5	0.1	0.6	0.1	38.4	0.1	55.6	0.5	0.8	0.3	1.1
	873	73.7	4.5	5.8	6.1	18.5	1.3	30.2	2.6	7.3	0.9	8.4
H-ZSM-5(80)	723	99.5	0.5	8.5	1.1	13.8	20.2	8.9	3.8	8.4	0.1	12.3
	773	99.7	1.3	14.9	2.0	19.1	18.1	9.5	4.5	12.7	0.1	17.2
	873	99.9	5.3	26.5	4.7	18.3	5.9	5.0	9.4	16.3	6.0	32.0
5% Mo_2C/ZSM-5(80)	723	99.2	0.3	9.6	0.7	18.3	9.8	12.8	3.4	13.3	3.4	20.3
	773	99.6	0.5	15.7	0.7	23.6	9.2	12.6	4.2	13.2	4.2	21.8
	873	99.9	2.1	21.7	1.7	29.5	3.7	10.7	10.2	15.8	1.4	27.4

[a] Average data determined during gradual heating from 723 K.

well to those ascribed to Mo_2C [14,15,37]. Our previous study concerning the acidity of Mo_2C/ZSM demonstrated that the deposition of Mo caused the consumption of Brønsted acidic OH groups of HZSM-5, as indicated by the changes in the ν(OH) region of the spectra and also by pyridine and low-temperature CO adsorption measurements [44]. Carburization of the sample did not result in the restoration of acidic OH groups of the zeolite. Mo reacted with OH groups during its deposition on SiO_2. The results of both pyridine and CO adsorption measurements did not indicate the generation of Brønsted acidic sites on MoO_3/SiO_2 and carburized MoO_3/SiO_2; however, Lewis acidic sites were formed on the deposition of Mo, and carburization of MoO_3 led to stronger Lewis centers [44]. We obtained similar results for the samples used in the present study.

This type of study has now been extended to alumina-based catalysts. NH_3 TPD measurements indicate that number of acid sites of alumina decreased markedly as a result of Mo_2C deposition. Analysis of the FTIR spectra of adsorbed pyridine reveals no acid sites on the Al_2O_3 and 2% Mo_2C/Al_2O_3 strong enough to protonate the pyridine characteristic of Brønsted sites. The findings of spectroscopic experiments suggest that only Lewis acidic centers are present on the surface of Al_2O_3, and that Mo_2C does not induce new acid centers (Table 1).

4.2. *Reaction of n-heptane on pure Mo_2C*

The reaction of heptane on different catalysts has been the subject of extensive research [5,25–35]. Supported Pt was found to be an active catalyst for the dehydrocyclization process. Significant progress was made in this area when zeolite was used as a catalyst and/or as a support. A bifunctional mechanism involving both the metal and the acid sites of the support and a monofunctional mechanism involving only the metallic sites were assumed [5,49,50].

The results obtained in the present study show that pure Mo_2C can catalyze the aromatization of heptane with a maximum selectivity of ~51% at 823 K. This suggests the action of the monofunctional mechanism. Accordingly, Mo_2C can activate the heptane molecule, catalyze its dehydrogenation, and affect subsequent processes leading to the production of aromatics. The catalytic performance of Mo_2C remained the same when the presence of Mo–O was completely eliminated, suggesting that Mo oxycarbide is not required for the activation of heptane and the subsequent processes. We delineate the following main steps:

With cracking and dehydrogenation,

$$C_7H_{16} \rightarrow C_3H_6 + C_4H_{10}, \tag{1}$$

$$C_7H_{16} \rightarrow C_7H_{14} + H_2, \tag{2}$$

with cracking and dehydrocyclization of heptene,

$$C_7H_{14} \rightarrow 2C_2H_4 + C_3H_6, \tag{3}$$

$$C_7H_{14} \rightarrow C_6H_5\text{–}CH_3 + 3H_2. \tag{4}$$

Studying the reaction of 1-heptene shows that Mo_2C can convert this compound into aromatics, mainly to toluene. Nevertheless, a significant fraction of heptene formed in the reaction of *n*-heptane remained unreacted (Table 2), likely because pure Mo_2C contains no acidic sites advantageous for these processes.

At higher temperature (873 K), the unsupported Mo_2C lost its catalytic activity very rapidly, likely due to the deposition of coke. TPR measurements revealed that its reactivity toward hydrogen is relatively low, with a peak temperature, $T_p = 948$ K, higher than that measured for the hydrogenation of excess carbon produced during the preparation of Mo_2C (Fig. 5A).

4.3. *Effects of supported Mo_2C*

The conversion of heptane was markedly increased when Mo_2C was deposited on alumina and silica of high surface area (Table 2). The formation of toluene and benzene occurred with enhanced selectivity, particularly on 2% Mo_2C/Al_2O_3 (Fig. 1B). In these cases we may assume the operation of a bifunctional mechanism. Mo_2C is mainly responsible for the dehydrogenation reaction, whereas the Lewis acidic sites of the supports facilitate the dehydrocyclization of heptene into toluene (Eq. (4)). In accordance with this picture, heptene was formed with much lower selectivity (6–20%) on supported Mo_2C than on pure Mo_2C (Table 2). Separate studies on the reaction of 1-heptene confirmed that the Mo_2C-containing catalysts were effective in converting hexene into aromatics (Table 3). From the extrapolation of the selectivities to zero percent conversion, we determined the primary products of the reaction on 2% Mo_2C/Al_2O_3 to be hydrogen, heptene, and hexane (Fig. 4B). This finding suggests that dehydrogenation is the primary process on Mo_2C/Al_2O_3 and that all of the other reactions, including aromatization, occur subsequently.

The role of acidic sites is clearly exhibited by the results obtained using ZSM-5, which contained even Brønsted sites in high concentration. Depending on the number of this site, ZSM-5 alone catalyzed the aromatization of heptane [5]. In this case, the first step is the formation of carbonium ions,

$$C_7H_{16(a)} + H_{(a)}^+ \rightarrow C_7H_{17(a)}^+, \tag{5}$$

which undergo dehydrogenation and cracking, followed by the dehydrocyclization of olefins into different aromatics. Deposition of Mo_2C on ZSM-5, particularly on ZSM-5(80), markedly increased the selectivity and yield of aromatics at the expense of the formation of alkene. In this sample, heptene was completely absent from the reaction products at temperatures >673–723 K, indicating that it reacted rapidly after its formation. The better aromatization property of Mo_2C/ZSM-5(80) compared with pure ZSM-5 suggests that a fraction of the intermediate formed at the Mo_2C/ZSM-5 interface, or, more precisely, on the highly dispersed Mo_2C interacting with the acid sites of ZSM-5, was effectively converted into aromatics before being transformed into other molecules. This intermediate is very likely a hexyl species formed in the activation of *n*-hexane on Mo_2C,

$$C_7H_{16(a)} \rightarrow C_7H_{15(a)} + H_{(a)}. \tag{6}$$

We mention that an alternative route for the formation of aromatics was also considered on supported Pt [5]. Accordingly, the first main step in the aromatization of heptane is its dehydrocylization into C_7 cycloalkane,

$$C_7H_{16} \rightarrow C_6H_{11}\text{–}CH_3 + H_2, \tag{7}$$

followed by dehydrogenation of the cycloalkane into aromatics,

$$C_6H_{11}\text{–}CH_3 \rightarrow C_6H_5\text{–}CH_3 + 3H_2. \tag{8}$$

However, C_7 cycloalkane has not been identified in the products using Mo_2C-containing catalysts.

5. Conclusions

1. Deposition of MoO_3 and its carburization on various supports (alumina, silica, and ZSM-5) decreased the number of different acidic sites, but did not eliminate these sites.

2. Unsupported Mo_2C was a relatively effective catalyst for the aromatization of n-heptane at 723–873 K. The main aromatic product was toluene. The greatest selectivity of aromatics (toluene, benzene, and xylene) measured was 51% at a conversion of 20–23%.
3. The catalytic performance of Mo_2C was considerably enhanced on SiO_2, Al_2O_3, and particularly ZSM-5, where the yield of aromatics attained a value of 48%.
4. All of these catalysts effectively promoted the cyclization-aromatization of 1-heptene assumed to be the main product of the primary reaction of n-heptane.

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