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Aromatization of *n*-hexane on Mo_2C catalysts

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The reaction of *n*-hexane and 1-hexene has been investigated on unsupported and supported Mo_2C catalysts. Pure Mo_2C catalyses the dehydrogenation and aromatization of *n*-hexane at and above 723 K. Benzene was formed with the highest selectivity, ~65%, at 773–823 K at a conversion of ~25%. Mo_2C also exhibited high activity towards the reaction of *n*-hexane when it was deposited in a small amount (2–10%) on SiO_2. It is assumed that the production of benzene occurs through the formation and subsequent dehydrogenation–cyclization of hexene. Catalysts prepared *in situ* revealed that the activation and aromatization of hexane and hexene do not require the presence of Mo–O species in the Mo_2C.

KEY WORDS: Mo_2C; dehydrogenation; aromatization; *n*-hexane; 1-hexene.

1. Introduction

In searching new catalyst materials Mo_2C is one of the candidates, which exhibits excellent catalytic behavior in several reaction [1–5]. Recently, it was found that its combination with ZSM-5 zeolite effectively catalyses the aromatization of methane with 80% selectivity at about 10–12% conversion [6–11]. As the aromatization of methane was not observed either on pure Mo_2C [6,7] or ZSM-5 alone, it was assumed that the role of Mo_2C is to activate the methane molecule yielding CH_3 and for CH_2 radicals, which – in contrast to the Pt metals – have a certain lifetime to couple into C_2H_4 [6,7]. Ethylene formed can be readily oligomerized and aromatized on the acidic sites of ZSM-5 [6–11]. The study of the chemistry of CH_3 and CH_2 species on Mo_2C/Mo(100) surface in UHV conditions confirmed that both radicals can recombine on the Mo_2C surface [12,13]. Further works disclosed the Mo_2C/ZSM-5 is an active catalyst for the aromatization of the other lower alkanes, such as ethane [14], propane [15], n-butane [16–19] and iso-butane [20]. Aromatic compounds, however, were not detected, or only in trace amounts, on unsupported Mo_2C in either case.

As a continuation of our research program in this area we undertook the study of *n*-hexane on Mo_2C – containing catalyst. Surprisingly we found that the aromatization of hexane readily occurs on Mo_2C itself, which forms the subject of the present paper.

2. Experimental

Catalytic reaction was carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube connected to a capillary tube [7,19]. The flow rate was in most cases 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 analysed gas chromatographically using a Hewlett-Packard 4890 gas chromatograph with an HP-Plot Al_2O_3 column and with a Porapak QS + S columns. The conversion of *n*-hexane was calculated taking into account its 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 products.

The gases were of commercial purity (Linde). MoO_3 used for the preparation of Mo_2C was the product of ALFA AESAR. Mo_2C was prepared by the carburization of MoO_3 by C_2H_6/H_2 [21]. 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. Afterwards the sample was cooled down to room temperature under argon. The carbide was passivated in flowing 1% O_2/He at 300 K [22]. 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. Mo_2C/SiO_2 samples have been made in the similar ways by the carburization of MoO_3/SiO_2. The latter material was prepared by impregnating SiO_2 (Aerosil, BET area is 200 m^2/g), with a basic solution of ammonium heptamolybdate to yield 2 or 10 wt% of MoO_3. The suspension was dried at 373 K and calcined at 863 K for 5 h. Mo_2C samples have been characterized by XPS. The binding energies for Mo($3d_{5/2}$) were

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227.8–228.2 and 230.7–231.1 eV, and for C(1 s) 283.8 eV. These values are consistent with those attributed to Mo_2C [7,9,23]. In order to remove the excess carbon deposited on the Mo_2C during the preparation, the catalyst has been reduced before at 873 K in H_2 stream for 60 min.

3. Results and discussion

Figure 1a shows that the reaction of *n*-hexane occurs to a well measurable extent over pure Mo_2C even at 723 K. The main product is benzene, which is formed with a selectivity of 30–35%. It is followed by hexene, and several C_1–C_5 compounds. Toluene was also evolved with 3.7–5.7% selectivity. In addition, the release of CO was registered throughout the measurements. Its formation ceased only at 873 K. This suggests that oxygen remained dissolving in the Mo_2C during the carburization [24], or reacted with Mo in the deactivation process followed the preparation. Raising the temperature increased the conversion of hexane; at 873 K it reached the value of 26%. Benzene was formed with the highest selectivity, ~65%, at 773–823 K. At 873 K, we obtained lower values for the benzene, and higher ones for alkenes. When the reaction was measured in time on stream at 873 K for longer period, a decay both in the conversion of *n*-hexane and the selectivity of benzene was observed. At the same time, the selectivity of hexene, and that of other alkenes increased. This is also illustrated in figure 1a. When the *n*-hexane was contacted with Mo_2C straight at 873 K, the initial conversion was higher than in the previous measurement, but the general picture was the same.

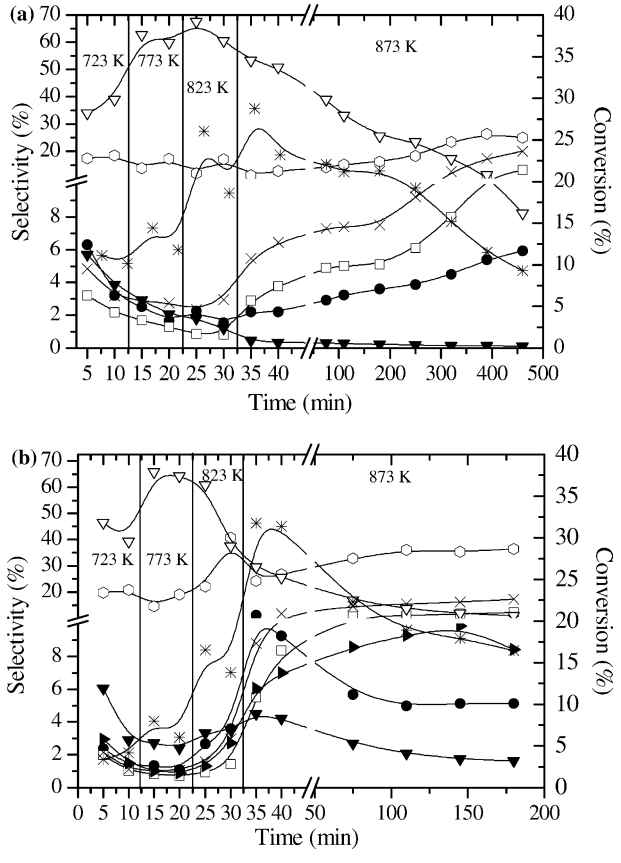

Figure 1. Reaction of *n*-hexane over Mo_2C (a) and 10% Mo_2C/SiO_2 (b) catalyst at different temperatures (● methane; □ ethylene; × propylene; ◀ butene; ⬡ hexene; ∇ benzene; ▼ toluene; ✳ conversion).

This behavior of unsupported Mo_2C is rather surprising as in the reactions of all other C_1–C_5 alkanes it catalyzed only the dehydrogenation and/or the cracking process; aromatic compounds were produced only in traces even at 873–973 K. The formation of aromatics required the presence of another solids, namely ZSM-5 (or SiO_2), which contain acidic sites for the oligomerization and aromatization process of alkenes produced in the dehydrogenation reactions.

From the results presented in figure 1a, one may infer that beside the dehydrogenation reaction

$$C_6H_{14} = C_6H_{12} + H_2 \quad (1)$$

Mo_2C is able to promote the cyclization of the hexene formed

$$C_6H_{12} = C_6H_6 + 3H_2 \quad (2)$$

Mo_2C exhibited a high activity towards the reaction of hexane when it was deposited in a small amount (2–10%) on silica support. Benzene formed with a selectivity of 40–45% even at 723 K: its maximum value, ~65%, was attained again at 773–823 K. The conversion was ~34% at 872 K which, together with the selectivity of benzene, gradually decreased in time on stream at 873 K (figure 1b). The formation of other products showed the same trend as in the case of pure Mo_2C. The selectivity of hexene was somewhat higher at all temperatures. As no reliable method available for the determination of the dispersion of Mo_2C, we calculated the rate of formation of the major products and related to the number of Mo_2C molecules in the catalysts. In this way, we obtained, a very high 'specific' rate for the Mo_2C/SiO_2 sample (table 1).

The simple explanation of the higher activity of the Mo_2C on silica could be attributed to its higher dispersion. If we accept that the formation of benzene occurs through the two consecutive steps (equation 1 and 2), the enhanced rate of benzene formation could be the consequence of the higher concentration of hexene formed. The same phenomenon was experienced in the aromatization of C_1–C_4 alkanes Mo_2C/SiO_2 catalysts [18–20]. In the explanation of the catalytic performance of Mo_2C on SiO_2 the following points should be considered: (i) the preparation of Mo_2C on SiO_2 surface does not create Bronstead sites, (ii) it leads, however, to the formation of stronger Lewis acid sites on the silica. Accordingly, we may come to the conclusion that these Lewis sites or more precisely the Mo_2C particles

Table 1
Rate of reactant consumption and formation of some products

Catalyst/Reactant	Temperature (K)	Formation rate (μmol/$mol_{Mo\text{-}carbide}$sec)		
		Benzene	Hexene	Reactant consumption
Mo_2C/*n*-hexane	823	14.41	2.55	60.54
	873	20.86	4.45	66.79
10% Mo_2C/*n*-hexane	823	71.45	25.97	157.14
	873	55.94	45.64	301.36
Mo_2C/1-hexene	823	23.25	–	108.31
	873	19.66	–	149.18
10% Mo_2C/1-hexene	823	217.24	–	552.43
	873	149.14	–	779.08

interacting with these acid sites are also contributing to the enhanced dehydro-aromatization of hexane.

In order to obtain more informations on the reaction pathways of the aromatization the reaction of 1-hexene has been examined over Mo_2C catalysts under the same experimental conditions. As shown in figure 2, hexene exhibited a higher reactivity compared to hexane. The conversion was 35% at 723 K, which increased to 62–63% at 873 K. The selectivity of benzene was very high, 53–75% in the temperature range at 723–823 K. It started diminishing at 823–873 K with the increase in the selectivity of other products. An interesting feature is the formation of hexane at 723 K, its selectivity decreased with the rise of the temperature.

The results obtained for the reaction of both hexane and hexene revealed the occurrence of significant deactivation of the catalyst, particularly at 873 K. This is very likely due to the deposition of some kind of carbonaceous compound on the active sites of the Mo_2C. The amount and the reactivity of this deposite on the Mo_2C have been determined by TPR measurements using hydrogen. As seen in figure 3a, the excess carbon formed on Mo_2C during the carburization exhibited rather low reactivity towards hydrogen. Its hydrogenation resulting in methane started above 650 K; the Tp value is 798 K. In addition, minor amounts of C_2H_6 and C_2H_4 were also released. If the experiment was repeated with the hydrogenated sample only a tiny amount of CH_4 (1–2% of the previous value) was still produced. Similar TPR measurements with the catalysts used for hexane conversion at 873 K for 15 min and for 180 min gave identical TPR curves with somewhat higher Tp values (figure 3b, c). The amount of carbon reacted with H_2 was 0.199 mgC/g catalyst after 15 min and 0.614 mgC/g catalyst after 180 min of reaction.

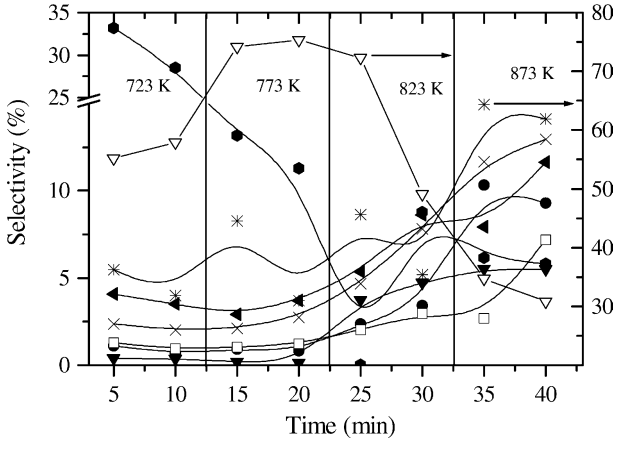

Figure 2. Reaction of 1-hexene over 10% Mo_2C/SiO_2 catalyst at different temperatures (● methane; □ ethylene; × propylene; ◀ butene; ⬢ hexane; ▽ benzene; ▼ toluene; ✳ conversion).

In the subsequent experiment we examined the interaction of *n*-hexane with MoO_3/SiO_2 and determined the product distribution. This experiment was initiated by the findings that molybdenum oxycarbide is an active catalyst for *n*-hexane isomerization using a H_2 /hexane gas mixture with a ratio of 150, while pure Mo_2C was found to be inactive [25]. In the absence of hydrogen we found only a very slight indication for the isomerization of *n*-hexane under the experimental conditions used. At 773 K, the initial conversion was below ~1%. At 873 K, however, the reaction of hexane set in even after 5 min yielding CO, hexene, benzene, toluene and methane. The rate of formation of these products reached a maximum at 20–30 min, then decreased. At the same time the rate for hexene showed a minimum (figure 4). The conversion at the maximum attained a value of 40%.

The observed maximum in the rate of formation of benzene can be attributed to the effect of several factors advantageous for the activation and aromatization of *n*-hexane: (i) the partial reduction of MoO_3, (ii) the formation of Mo oxycarbide, and (iii) the presence of Mo–O species. In order to clarify the role of Mo oxycarbide or Mo–O species in the reaction of hexane, Mo_2C, free of Mo–O species, was prepared *in situ*, in the catalytic reactor. The sample was used at once after preparation without any oxygen treatment at room temperature. We obtained practically the same results as before (figure 1) suggesting that Mo oxycarbide is not required for the dehydrogenation and aromatization of hexane.

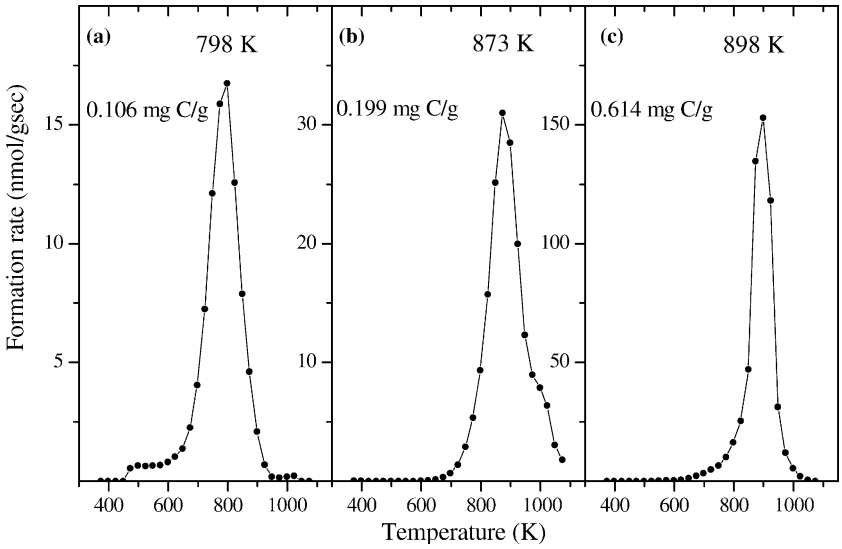

Figure 3. TPR spectra of Mo_2C (a) after preparation, (b) after reaction of *n*-hexane at 873 K for 15 min, and (c) for 180 min.

4. Conclusions

In contrast to the reaction of C_1–C_5 alkanes, Mo_2C effectively catalyses the dehydro-aromatization of *n*-hexane into benzene above 773 K. The aromatization of 1-hexene formed in the dehydrogenation process of *n*-hexane also proceeds with high rates on Mo_2C indicating the capability of Mo_2C in the cyclization of C_6 compounds. The catalytic performance of Mo_2C was enhanced by depositing it on silica surface. Although the presence of Mo oxycarbide is not disadvantageous for the activation and aromatization of *n*-hexane and 1-hexene, its presence is not required for these processes.

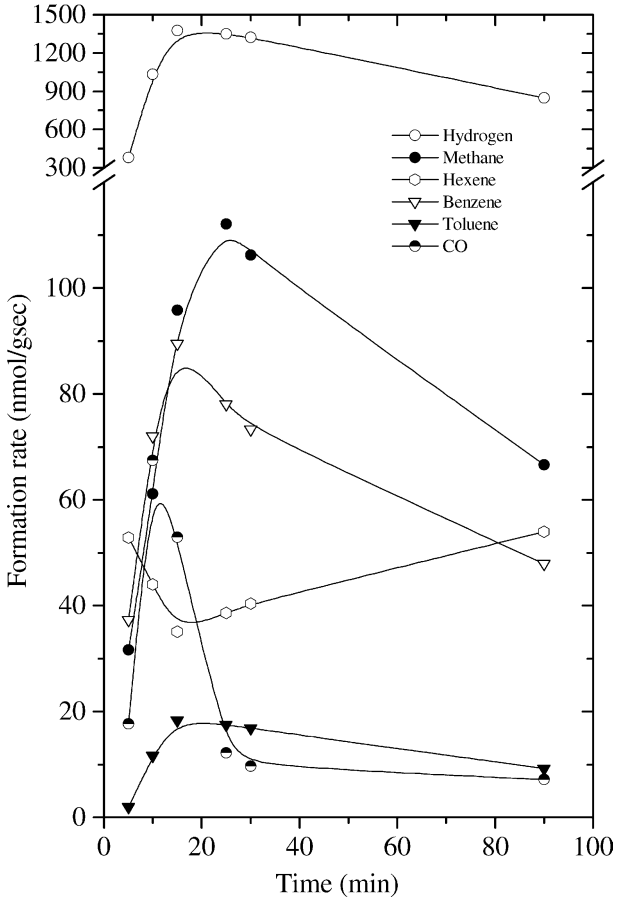

Figure 4. Reaction of *n*-hexane on 2% MoO_3/SiO_2 at 873 K.

Acknowledgments

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