Aromatization of *n*-butane over supported Mo_2C catalysts

F. Solymosi *, R. Németh, and A. Széchenyi

Institute of Solid State and Radiochemistry, University of Szeged, and Reaction Kinetics Research Group of the Hungarian Academy of Sciences[†]
P.O. Box 168, H-6701 Szeged, Hungary

Received 12 March 2002; accepted 13 May 2002

Similarly to the case of methane, ethane and propane, Mo_2C deposited on ZSM-5 significantly enhanced the aromatization of *n*-butane observed on ZSM-5 (SiO_2/Al_2O_3 ratio of 80) alone. The catalytic performance of Mo_2C/ZSM-5 sensitively depended on its preparation and pretreatment. The selectivity of aromatics measured for pure ZSM-5 increased from 11–13% to 28–34% at the conversion level of 60–65%. The formation of aromatics was also observed over Mo_2C/SiO_2.

KEY WORDS: aromatization of *n*-butane; Mo_2C/ZSM-5 catalyst; Mo_2C/SiO_2 catalyst; cracking and dehydrogenation of butane; preparation of Mo_2C.

1. Introduction

Since it had been demonstrated that MoO_3 on ZSM-5, effective in the direct aromatization of methane [1–3], has been converted into Mo_2C during the reaction, and Mo_2C and not MoO_3 is the key component of the catalyst [4–7], increased attention has been devoted to its properties. In our laboratory we continued our work in two directions: (i) elaborating the effect of Mo_2C on the aromatization of the hydrocarbons, ethane [8,9], ethylene [10] and propane [11] and (ii) studying the chemistry of hydrocarbon fragments, the primary products of the activation of the above compounds, on Mo_2C/Mo(100) in UHV by several spectroscopic methods [12,13]. Other laboratories dealt with the interaction of MoO_3 and Mo_2C with ZSM-5, with their location in the zeolite, and with structural and other properties of Mo_2C [14–20].

In the continuation of our research program, in the present paper we report on the effect of Mo_2C on the reactions of *n*-butane over ZSM-5. In addition, we test whether the aromatization of *n*-butane also occurs on Mo_2C/SiO_2, which was also active in the conversion of methane into benzene.

2. Experimental

The gases used were of commercial purity (Linde). NH_4-ZSM-5 was a commercial product (Zeolite International), which was calcined to produce H-ZSM-5 in air at 863 K for 5 h. The surface area of the sample was 425 m^2/g. SiO_2 was Cab-O-Sil, area: 200 m^2/g.

MoO_3-containing catalysts were prepared by impregnating H-ZSM-5 or SiO_2 with a basic solution of ammonium heptamolybdate 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 carburization of calcined MoO_3/ZSM-5 or MoO_3/SiO_2 with 20% CH_4/H_2 mixture flowing at 300 ml/min [21]. Preparation temperature was increased rapidly from 300 K to 773 K, then at 3 K/min from 773 to 1023 K and maintained at 1023 K for 3 h. Mo_2C was also prepared by the reaction of MoO_3 with ethane. This process takes place at lower temperatures than with methane and presumably produces Mo_2C of higher dispersity, as indicated by the enhanced surface area of pure Mo_2C prepared in this way [9,22]. In this case the supported MoO_3 samples were heated in the flow of 10% C_2H_6/H_2 from room temperature to 900 K at a heating rate of 0.8 K/min. After preparation the catalysts were cooled down to room temperature under argon. Before exposure to the atmosphere, the carbides were passivated in flowing 1%O_2/Ar at 300 K, as suggested by Lee *et al.* [21].

The samples were characterized by XPS measurements. Before measurements, the samples were treated with H_2 at 873 K for 30 min to remove the excess carbon. The binding energies for Mo($3d_{5/2}$) and Mo($3d_{3/2}$) were 227.8–228.2 and 230.7–231.1 eV, and for C(1s) 283.8 eV. These values are consistent with those attributed to Mo_2C [6,7,23]. Catalytic reactions were carried out at 1 atm of pressure in a fixed-bed, continuous flow reactor consisting of a quartz tube (7 mm i.d.) connected to a capillary tube. The flow rate was 12 ml/min. The carrier gas was Ar. The butane content was 12.5%. Generally 0.3 g of loosely compressed catalyst sample was used. Reaction products were

---

* To whom correspondence should be addressed.
E-mail: fsolym@chem.u-szeged.hu

[†] This laboratory is a part of the Center for Catalysis, Surface and Material Science at the University of Szeged.

1011-372X/02/1000-0213/0 © 2002 Plenum Publishing Corporation

analyzed gas chromatographically using a Hewlett-Packard 5890 gas chromatograph and an HP-PLOT Al_2O_3 column.

3. Results and discussion

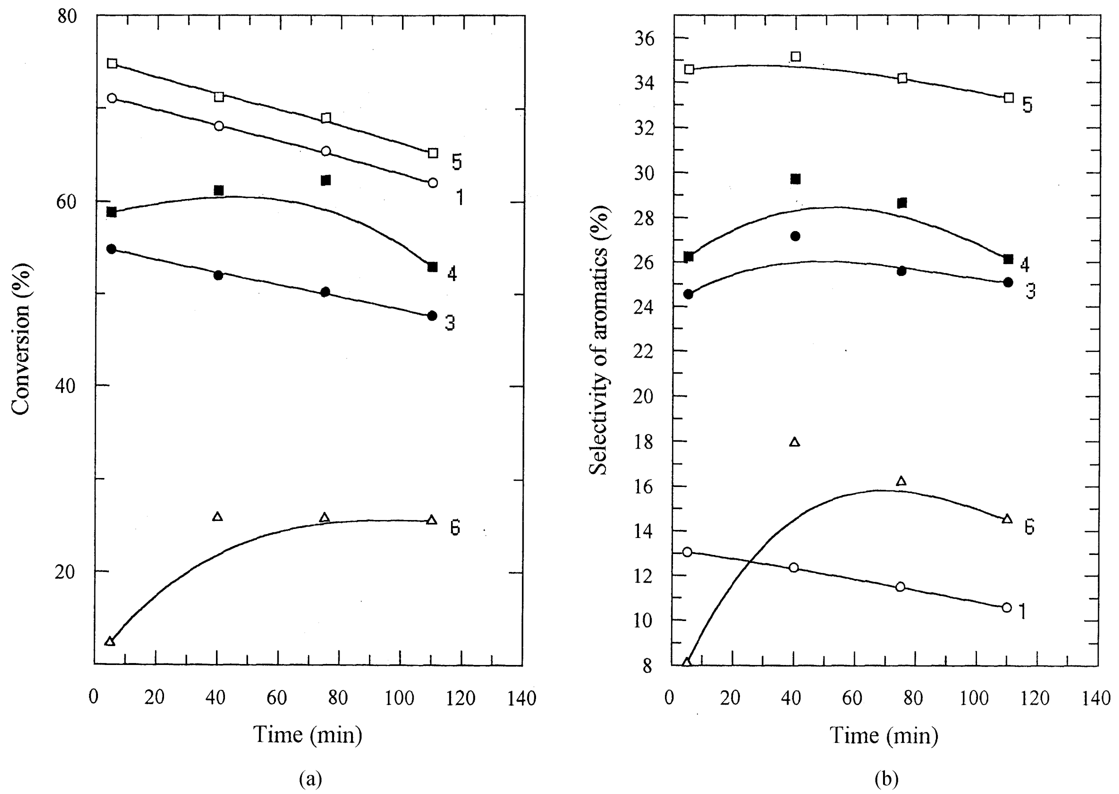
3.1. Reactions of n-butane on H-ZSM-5 and SiO_2

First the catalytic behavior of different ZSM-5 samples was tested. Reaction was measurable above 700 K. In harmony with the literature data [24], the product distribution sensitively depended on the composition of ZSM-5. As a support for Mo_2C we chose ZSM-5 with an SiO_2/Al_2O_3 ratio of 80. The initial conversion of butane on this sample was 60–65%. There was no or only a slight decay in the conversion and in the rate of formation of various products. Whereas the cracking of butane was the dominant reaction pathway, yielding propane, propene, ethylene, ethane and methane in decreasing amounts, the production of aromatics (benzene, toluene and xylenes) occurred on all samples. The selectivity of aromatics varied between 11.0 and 13.0% during the measurement (figure 1). The yield of aromatics was about 7.5% (table 1). At higher temperature, at 873 K, the conversion exceeded even 70%, and the selectivity of aromatics attained a value of 15–16%.

The catalytic effect of silica was also tested. It exhibited very low reactivity, the decomposition of *n*-butane at 823 K was less than 1.5%, which reached ~3–4% at 923 K, yielding the same cracking products observed for ZSM-5 without any sign of aromatics.

3.2. Reactions of n-butane on supported Mo_2C

As ZSM-5 itself exhibited relatively high activity, a great improvement of its catalytic performance with Mo_2C addition was not expected. Nevertheless, depending on the preparation and pretreatment of Mo_2C/ZSM-5, the conversion of *n*-butane approached or even exceeded the value measured for pure ZSM-5. The aromatic compounds, however, unambiguously formed with higher selectivities. The Mo_2C samples prepared by carburization of MoO_3 with CH_4/H_2 mixture always exhibited less reactivity and only slight improvement of the production of aromatics. Elimination of excess carbon of Mo_2C with H_2 at 873 K before the catalytic reaction caused an increase in the conversion of *n*-butane, but decreased the selectivity of the formation of aromatics. Better catalytic performance was shown by the Mo_2C/ZSM-5 sample obtained by the carburization of MoO_3 with ethane. In this case the selectivity of aromatics increased from 11.5% to 28–34%, practically at the same high conversion determined for pure ZSM-5. The aromatic distribution was as follows: 16.0% C_6H_6, 18.0% C_7H_8, 0.5% C_8H_{10}. The favorable effect of Mo_2C appeared more dramatically in the value of the yield of aromatics (table 1).



(a) (b)

Figure 1. Conversion of *n*-butane (a) and the selectivity of aromatics (b) on different Mo_2C catalyst in time on stream at 823 K. 1: H-ZSM-5; 2–5: Mo_2C/ZSM-5; 6,7: Mo_2C/SiO_2. For pretreatment see table 1.

Table 1
Characteristic data for the reaction of *n*-butane at 823 K

No.	Catalyst	Conversion (%)	Selectivity (%)							Yield of aromatics
			Methane	Ethane	Ethylene	Propane	Propene	Butenes	Aromatics	
1	H-ZSM-5	65.4	8.8	14.3	14.7	27.5	15.5	5.0	11.5	7.5
2	Mo_2C/ZSM-5	33.7	8.5	13.3	12.2	8.3	18.6	12.2	24.3	8.2
3	Mo_2C/ZSM-5	50.2	9.4	12.2	12.8	12.5	17.3	8.0	25.6	12.8
4	Mo_2C/ZSM-5	62.3	10.7	12.0	13.0	8.9	16.4	8.3	28.6	17.8
5	Mo_2C/ZSM-5	68.9	13.5	11.7	12.3	8.2	13.9	4.8	34.5	23.6
6	Mo_2C/SiO_2	25.8	6.2	2.3	19.7	0.4	13.5	40.0	16.2	4.2
7	Mo_2C/SiO_2	15.0	1.8	0.5	7.0	0.2	10.0	67.0	8.0	1.5

Note: Data taken at 79 min on stream. All Mo_2C samples have been prepared by using C_2H_6/H_2 except the catalysts No. 2 and 7, when CH_4/H_2 was used. Samples No. 3 and 4 have been treated with H_2 stream at 873 K for 60 min in the reactor before the catalytic run. Catalyst No. 5 has been prepared *in situ* before the catalytic run. The weight of the catalyst was 0.5 g.

In the case of the reaction of methane we found that not only the Mo_2C/ZSM-5 but also the Mo_2C/SiO_2 catalyzed the conversion of methane into benzene [3,6]. The catalytic behavior of Mo_2C/SiO_2 prepared by two methods was tested in the present case, too. Some results obtained are shown in figure 1. The conversion underwent very little change in time on stream. Whereas the main reaction pathway was the dehydrogenation and cracking of *n*-butane, aromatic compounds were also produced with a selectivity of ~8–16% (table 1). An increase in the Mo_2C content exerted no significant influence on the data obtained.

These results clearly demonstrate that similarly to the case of the reaction of methane, ethane and propane [4–11], the deposition of Mo_2C on ZSM-5 alters the reaction route of *n*-butane and the aromatization comes into prominence. This promotion occurs in spite of the finding that the deposition of Mo_2C lowers the number of Brønsted-acid sites of ZSM-5 [15,16] responsible for the conversion of unsaturated compounds into aromatics. It is very likely that this disadvantage is overcompensated by the enhanced activation of the C–H bond by Mo_2C. During the preparation of this work a paper was published by Yuan *et al.* [24], which also showed that the production of aromatics is significantly promoted by the loading of Mo_2C on HZSM-5. They found that α-Mo_2C/ZSM-5 exhibits better aromatization performance than β-Mo_2C/HZSM-5. The important role of Mo_2C in the conversion of *n*-butane into other compounds is clearly demonstrated by the results obtained when Mo_2C was dispersed on almost inactive SiO_2 (figure 1). On Mo_2C/SiO_2 not only were the cracking and dehydrogenation of *n*-butane catalyzed, but also the aromatization reaction was promoted. Note that the effect of Mo_2C/SiO_2 was not reported by Yuan *et al.* [24]. We may assume that the deposition of Mo_2C created some active acidic sites on SiO_2 or at the Mo_2C/SiO_2 interface which facilitated the coupling of reactive hydrocarbon species formed.

4. Conclusions

1. The deposition of highly dispersed Mo_2C on ZSM-5 greatly improved the conversion of *n*-butane into aromatic compounds observed for pure ZSM-5 alone.
2. Mo_2C on almost inert SiO_2 also catalyzed the reaction of *n*-butane and the formation of aromatics.
3. The primary role of Mo_2C possibly is the activation of the propane molecule and the production of reactive C_xH_y species.

Acknowledgments

This work was supported by the Hungarian Academy of Sciences and by Grant OTKA T38233.

References

[1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.
[2] Y. Xu, L. Wang, M. Xie and X. Gou, Catal. Lett. 30 (1995) 135.
[3] F. Solymosi, A. Erdöhelyi and A. Szöke, Catal. Lett. 32 (1995) 43.
[4] D.W. Wang, J.H. Lunsford and M.P. Rosynek, Topics Catal. 3(4) (1996) 299.
[5] F. Solymosi and A. Szöke, Catal. Lett. 39 (1996) 157.
[6] F. Solymosi, J. Cserényi, A. Szöke, T. Bánsági and A. Oszkó, J. Catal. 165 (1997) 150.
[7] D.W. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.
[8] F. Solymosi and A. Szöke, Appl. Catal. A166 (1998) 225.
[9] F. Solymosi and R. Németh, Catal. Lett. 62 (1999) 197.
[10] F. Solymosi and A. Szöke, Stud. Surf. Sci. Catal. 119 (1998) 355.
[11] F. Solymosi, R. Németh, L. Óvári and L. Egri, J. Catal. 195 (2000) 316.
[12] F. Solymosi, L. Bugyi and A. Oszkó, Catal. Lett. 57 (1999) 103.
[13] F. Solymosi, L. Bugyi, A. Oszkó and I. Horváth, J. Catal. 185 (1999) 160.
[14] R.W. Borry III, E.C. Lu, K. Young-ho and E. Iglesia, Stud. Surf. Sci. Catal. 119 (1998) 403.
[15] J.-Z. Zhang, M.A. Long and R.F. Howe, Catal. Today 44 (1998) 293.
[16] S.L. Liu, L. Wang, R. Ohnishi and M. Ichikawa, J. Catal. 181 (1999) 175.

[17] S.B. Derouane-Abd Hamid, J.R. Anderson, I. Schmidt, C. Bouchy, C.J.H. Jacobsen and E.G. Derouane, Catal. Today 63 (2000) 461.

[18] Y.-Y. Shu, D. Ma, L.-L. Su, L.-Y. Xu, Y.-D. Xu and X.-H. Bao, Stud. Surf. Sci. Catal. 136 (2001) 27.

[19] R. Ohnishi, L. Xu, K. Issoh, K. and M. Ichikawa, Stud. Surf. Sci. Catal. 136 (2001) 393.

[20] F. Solymosi, A. Oszkó, T. Bánsági and P. Tolmacsov, J. Phys. Chem. in press.

[21] J.S. Lee, S.T. Oyama and M. Boudart, J. Catal. 106 (1987) 125.

[22] A.J. Brungs, A.P.E. York, J.B. Claridge, C. Márquez-Alvarez and M.L.H. Green, Catal. Lett. 70 (2000) 117.

[23] K. Oshikawa, M. Nagai and S. Omi, J. Phys. Chem. B 105 (2001) 9124.

[24] S. Yuan, S.B. Derouane-Abd Hamid, Y. Li, P. Ying, Q. Xin, E.G. Derouane and C. Li, J. Mol. Catal. A: Chem. 3519 (2002) 1.