Catalysis Letters 39 (1996) 157–161

Conversion of methane to benzene over Mo_2C and Mo_2C/ZSM-5 catalysts

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Received 24 November 1995; accepted 22 February 1996

The activation and dehydrogenation of CH_4 on Mo_2C and Mo_2C/ZSM-5 have been investigated under non-oxidizing conditions. Unsupported Mo_2C exhibited very little activity towards methane decomposition at 973 K. The main reaction pathway was the decomposition of methane to give hydrogen and carbon with a trace amount of ethane. Mixing Mo_2C with ZSM-5 support somewhat enhanced its catalytic activity, but did not change the products of the reaction. A dramatic change in the product formation occurred on partially oxidized Mo_2C/ZSM-5 catalyst; besides some hydrocarbons benzene was produced with a selectivity of 70–80% at a conversion of 5–7%. Carburization of highly dispersed MoO_3 on ZSM-5 also led to a very active catalyst: the conversion of methane at the steady state was 5–6% and the selectivity of benzene formation was 85%.

Keywords: methane conversion to benzene; decomposition of methane; Mo_2C catalyst; Mo_2C/ZSM-5 catalyst; oxidation of Mo_2C; MoO_3/ZSM-5 catalyst

1. Introduction

Recently many attempts have been made to activate methane under non-oxidative conditions and to convert it into higher hydrocarbons and aromatic compounds. In the case of supported Pt metal catalysts the dehydrogenation of methane occurred readily yielding a small amount of ethane in addition to the main products, H_2 and surface carbon [1–9]. The subsequent hydrogenation of the most reactive carbon gave several higher hydrocarbons and even benzene [1–9].

Similar studies on MoO_3/ZSM-5 catalysts produced more attractive results: it appeared that methane can be directly transformed to aromatic products [10–13]. Wang et al. [10] reported 100% selectivity of benzene formation at 7.2% conversion. 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 [11,12]. After a rather long induction period, this reaction occurred also on MoO_3/SiO_2 (the highest selectivity to benzene was 56% at a methane conversion of 3.2%) [11]. 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) than on MoO_3/ZSM-5, but still with high selectivity (60–67%) of benzene formation [12].

As the reduction of Mo^{6+} to Mo^{4+} proceeded during the induction period, Mo^{4+} or its compounds were considered as key species in the methane conversion [11]. Taking into account the large amount of carbon deposited on the catalyst in the course of the high temperature methane reaction, Mo_2C is a good candidate for the active compound. Recently Lunsford et al. [13] 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].

In the present paper the interaction of CH_4 is investigated with unsupported and supported Mo_2C under the same conditions as reported in our previous studies [11,12].

2. Experimental

The reactor and the analysis of the products were described previously [11]. Briefly, reactions were carried out in a fixed bed, continuous flow reactor consisting of a quartz tube (20 mm i.d.) connected to a capillary tube. Undiluted CH_4 was used. The flow rate was 12 ml/min. The selectivity values of product formation represent the fraction of methane that has been converted to specific products taking into account the number of carbon atoms in the molecules.

Mo_2C was the product of Aldrich, its surface area is 1.1 m^2/g. The sample was characterized by X-ray photoelectron spectroscopy. Binding energies were normalized to the Fermi level of Mo. The XPS peaks for Mo(3d) and C(1s) were located at 228.9 and 283.8 eV, respectively.

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A mixture of Mo_2C and ZSM-5 was prepared by the slurry method. ZSM-5 was suspended in triply distilled water and the fine powder of Mo_2C was added slowly to a stirred slurry of ZSM-5. Water was evaporated while the slurry was stirred. The solid was homogenized and further dried at 403 K. The homogenized powders were slightly pressed into wafers and calcined in situ. Supported Mo_2C was prepared according to the method of Lee et al. [14]. Starting material in this case was 2 wt% MoO_3/ZSM-5 which was obtained by impregnating the H-ZSM-5 (Si/Al = 55.0) zeolite with a basic solution of ammonium paramolybdate [11].

3. Results and discussion

3.1. Reactions of methane on unsupported Mo_2C

As shown in fig. 1 methane interacts with Mo_2C at 973 K. The reaction starts with a maximum rate, the conversion is, however, very low (0.16%), which further decreases in time. The main gaseous product is H_2. Ethane is formed only in a very small amount. No change in the products occurred after several hours of reaction. Variation of the temperature, in the range of 873–1073 K, resulted in the same picture.

One possible reason for the low reactivity of Mo_2C is that during its preparation excess carbon was deposited on the surface of Mo_2C, which poisoned its surface. When treating the Mo_2C with hydrogen, methane evolved, which supports the presence of carbon contamination. This carbon species was removed by isothermal H_2-treatment at 873 K, where bulk carbon was found to be unreactive [14–16].

Exposing the catalyst, free of contamination of non-carbidic carbon, to methane flow at 973 K, we obtained somewhat higher initial activity, but the general behavior remained the same (fig. 1). Examination of the catalyst surface after methane decomposition for 2 h showed the formation of excess carbon on the surface of Mo_2C catalyst. This carbon exhibited very low reactivity. Whereas on supported Pt metal catalysts, the hydrogenation of the most reactive carbon produced by methane decomposition gave C_4–C_6 compounds [1–9], in the present case we obtained only methane. According to the TPR profile, the excess carbon formed in the high temperature decomposition of methane on Mo_2C is hydrogenated only above 800 K.

In the next experiment the catalytic performance of Mo_2C mixed with ZSM-5 was examined. It is known that ZSM-5 is a very active catalyst in the oligomerization and aromatization of ethylene [17,18]. As shown in fig. 1, the use of Mo_2C/ZSM-5 still resulted in very little activity in the methane decomposition and caused no change in the product distribution. (This sample contained an amount of Mo which corresponds to 2 wt% MoO_3.) Increasing the amount of Mo_2C to 30%, the initial conversion of CH_4 was still below 0.5% at 973 K.

The absence of a larger production of hydrocarbons suggests that methane decomposes completely to carbon

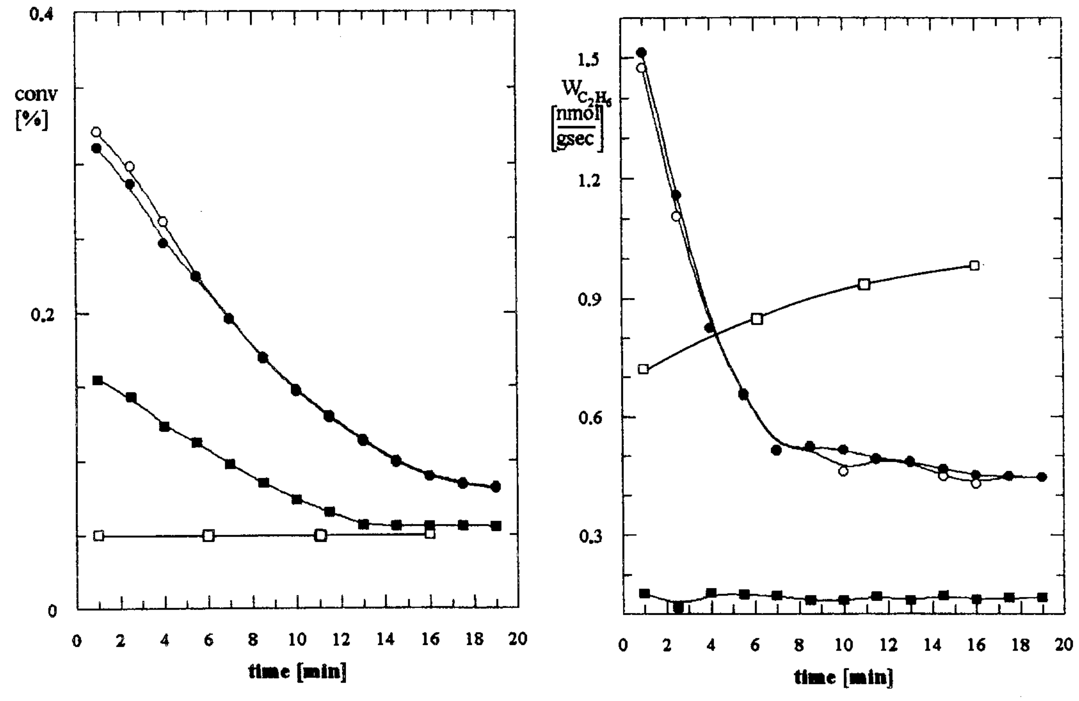

Fig. 1. Decomposition of methane on different Mo_2C samples at 973 K. (■) Mo_2C as received, (○, ●) Mo_2C treated with H_2 at 873 K, (□) 1.4 wt% Mo_2C/ZSM-5 treated with H_2 at 873 K. Mo_2C was the product of Aldrich Co.

on Mo_2C under the reaction conditions. The formation of a small amount of ethane indicates that the primary product, CH_3, of the dissociation of CH_4,

$$CH_4 \rightleftharpoons CH_3 + H\,,$$

may have a sufficient lifetime to recombine into ethane,

$$2CH_3 \rightleftharpoons C_2H_6\,.$$

Due to the high reaction temperature, this reaction very likely occurs in the gas phase, similarly as during the oxidative coupling of CH_4. The presence of ZSM-5 could not lead to a more active catalyst and did not alter the reaction pathways of methane on this Mo_2C. In other words, it could not promote coupling of the CH_x fragments, CH_3 and CH_2, possibly formed in the decomposition of CH_3 species, to ethane and ethylene. One of the reasons of the lack of improvement of the catalytic performance of Mo_2C mixed with ZSM-5 is the low dispersion of Mo_2C, and/or blocking of some of the channels in the ZSM-5.

To overcome this problem, Mo_2C was produced by the carburization of 2% MoO_3/ZSM-5 following the method of Lee et al. [14] (fig. 2). In this case we experienced a dramatic change in the conversion of methane and also in the product distribution. The conversion of methane on Mo_2C/ZSM-5 is as high as measured for MoO_3/ZSM-5, and qualitatively the same products were formed. There are, however, important differences. The induction period is practically missing; the reaction starts with the highest rate. Although a decay in the conversion occurs in this case too, the conversion at the steady state is higher (5–6%) compared to that obtained for 2 wt% MoO_3/ZSM-5 under the same conditions [11,12]. The selectivity to benzene is also higher, ~ 85.0%, on Mo_2C/ZSM-5, and remained constant after 30 min.

The fact that CO was also identified among the products suggests that the carburization of highly dispersed MoO_3 was not complete during the preparation of Mo_2C on ZSM-5. Accordingly, we may count with the presence of some kind of molybdenum oxide.

3.2. Effects of partial oxidation of Mo_2C

In order to explore the influence of molybdenum oxides, in the subsequent experiments we examined the effect of the oxidation of 2 wt% Mo_2C (Aldrich) mixed with ZSM-5 support. In a separate thermogravimetic study we found that the oxidation of this Mo_2C to MoO_3 proceeds at a measurable rate at 773 K [19]. Based on this finding, the oxidation of Mo_2C was performed in situ to different extents and the catalytic behavior of the solid so formed was tested. Note that this sample exhibited very little activity towards methane decomposition before the oxidation (fig. 1). As we wanted to explore the product formation in the initial phase of the interaction of methane with the partially oxidized catalyst, the methane flow through the catalyst bed was stopped during the analysis of outlet gases. The initial products were CO, CO_2 and H_2O, which diminished to a very low level

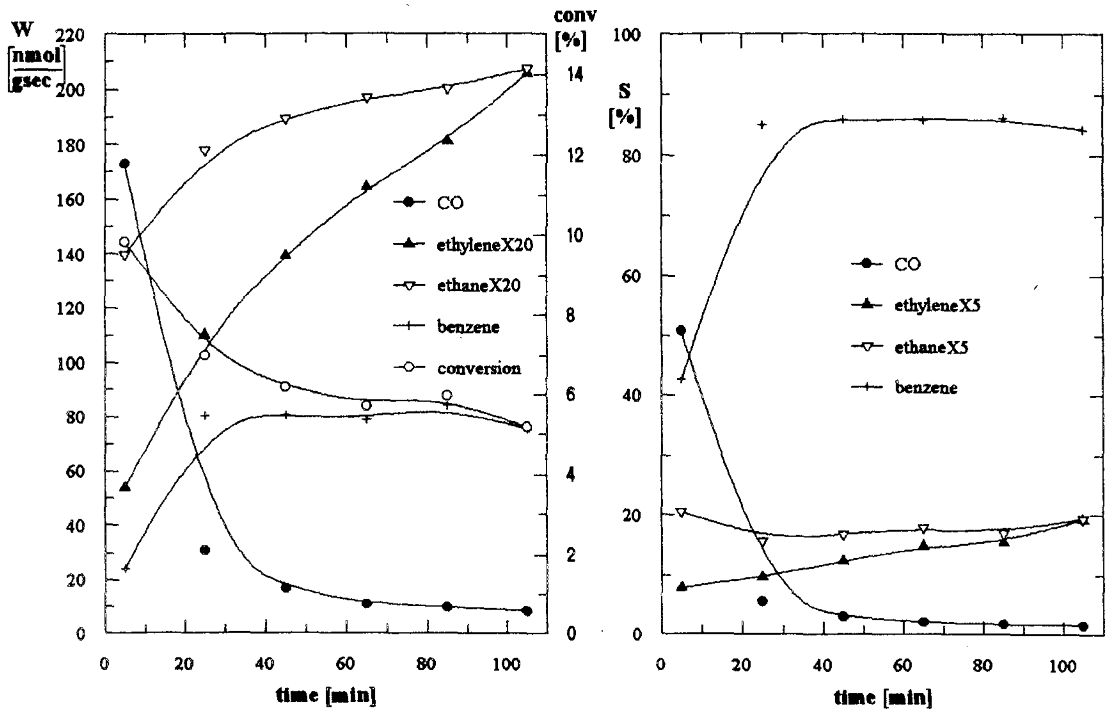

Fig. 2. Conversion of methane, rates and selectivities of the formation of various products on Mo_2C/ZSM-5 at 973 K. Mo_2C on ZSM-5 was prepared by carburization of 2% MoO_3/ZSM-5 by the method of Lee et al. [14].

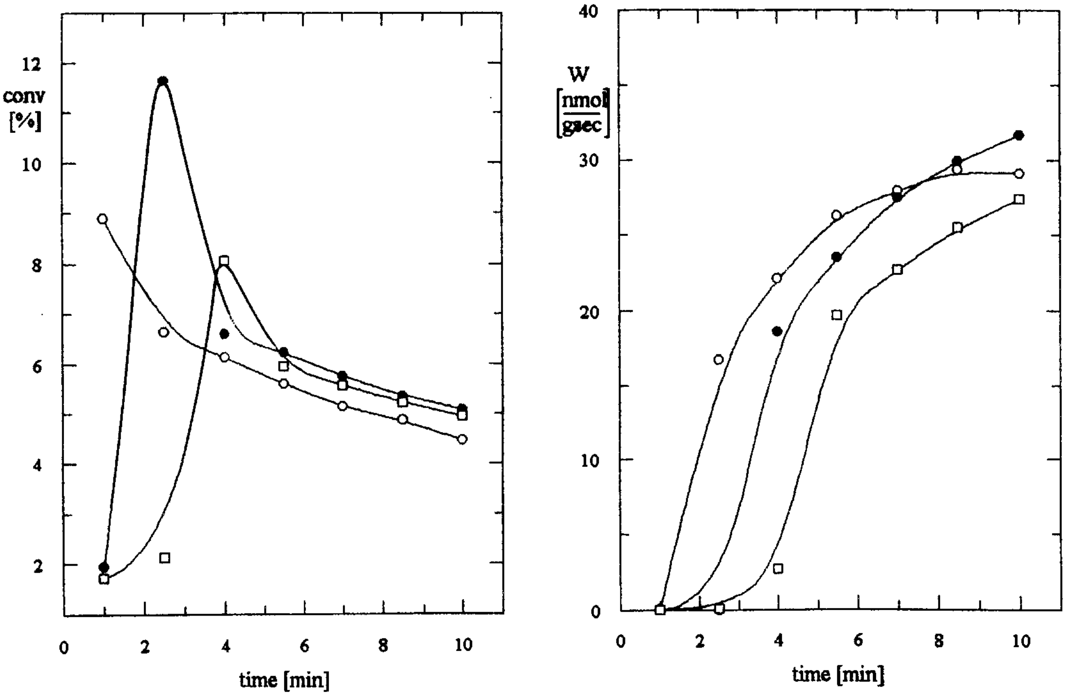

Fig. 3. Effect of the extent of oxidation of 1.4 wt% Mo_2C/ZSM-5 at 773 K (Mo_2C/ZSM-5 was prepared by mixing Mo_2C (Aldrich) with ZSM-5) on the initial phase of methane conversion and on the rate of benzene formation at 973 K. The extent of oxidation of Mo_2C: (○) 15%, (●) 30%, (□) 50%. In these experiments the methane flow was stopped during the analysis of the reaction products.

after 10 min. At the same time, the formation of various hydrocarbons including benzene became prominent. In fig. 3 are plotted the conversion of methane and the rate of benzene formation allowing the oxidation of 1.4 wt% Mo_2C/ZSM-5 to different extents. The conversion of methane started with a maximum value on the sample oxidized to 15%. Following a more extensive oxidation, the development of a more active catalyst required a longer contact of CH_4 with the catalyst. This feature was also exhibited in the rate of benzene formation. The initial rate was high on the Mo_2C oxidized to 15%. A much lower rate (0.1 μmol at 2.5 min and 2.65 μmol at 4 min) was measured on the catalyst oxidized to 50%, although the conversion of methane was 8% in the latter case. All these results suggest that, besides Mo_2C, the presence of some other Mo compounds, perhaps the oxygen deficient MoO_2, is also necessary for the activation of methane and for the promotion of the formation of ethylene from CH_x fragments.

4. Conclusions

(i) Commercial Mo_2C alone and Mo_2C mixed with ZSM-5 are rather inactive catalysts in the high temperature decomposition of methane.

(ii) Partial oxidation of this inactive Mo_2C/ZSM-5 led to a more active catalyst; the extent of the oxidation influenced the initial conversion of methane and the rate of the benzene production.

(iii) Deposition of Mo_2C in finely divided state on ZSM-5 exhibited a high catalytic activity towards methane decomposition: the selectivity to benzene approached 85% at the methane conversion of 5–6%.

(iv) It is assumed that Mo_2C–MoO_2 with an oxygen deficiency represent the active catalytic sites for methane activation and for the formation of ethylene from CH_x fragments, which is transformed into benzene on the acidic sites of the zeolite.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences through the Grant OTKA T 014921.

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