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# Methane Conversion over Vacuum Carbon Black: Influence of Hydrogen

S.D. Kushch*, V.E. Muradyan, N.S. Kuyunko
Institute of Problem of Chemical Physics Russian Academy of Sciences
18 Institutsky prospect, Chernogolovka, Moscow Region, Russian Federation, 142432

## Abstract

Methane pyrolysis over vacuum carbon black has been studied in the temperature range 550–1000°C. The methane conversion degree and selectivity with respect to ethene and propene do not depend on the initial concentration of methane *i.e.* the process order with respect to methane is first. The selectivity with respect to pyrolytic carbon is antibate to the methane initial concentration.

Hydrogen introduced to methane inhibits formation of pyrolytic carbon and aromatics especially in methane pyrolysis. The methane conversion degree in pyrolysis of methane/hydrogen mixture is inversely proportional to the initial concentration of hydrogen while the selectivity with respect to ethene being symbate to the one. A hypothesis on the reason of inhibition of pyrolytic carbon formation by hydrogen is proposed.

Methane pyrolysis is a homogeneous-heterogeneous reaction up to 850°C, but homogeneous reaction is prevalent at the temperature range of maximal selectivity with respect to alkenes.

## Introduction

Methane pyrolysis over catalysts based on carbon materials has been studied earlier [1–8]. We have reported methane dehydrogenation and aromatization over catalysts based on carbon materials. Also we have noted that catalysts based on fullerene materials are more active than other ones based on carbon materials having planar basic structure elements [9, 10]. In contrast to inert gas additions hydrogen additions to feed promoted a coking decrease and an increase of alkene yields [8, 9]. In this paper we report kinetic data on pyrolysis of $CH_4$/Ar and $CH_4$/Ar/$H_2$ mixtures over a catalyst based on vacuum carbon black.

## Experimental

A mixed catalyst containing 0.1 g (3.3 %) of carbon material named as vacuum carbon black [10] and 2.9 g of crushed (particles size of 0.25-0.5 mm) quartz has been used. Argon was used as an inert gas. Binary $CH_4$/Ar mixtures were used as a pyrolysis feed. The influence of hydrogen on methane pyrolysis has been studied in pyrolysis of ternary $CH_4$/Ar/$H_2$ mixtures with the constant methane concentration (33.3 % mol.) at various contents of Ar and $H_2$. The basic invariable details of the experiments have been reported earlier [9].

## Results and discussion

A composition of products of methane pyrolysis in the $CH_4$/Ar mixtures does not differ from that in the case of methane alone [10]. These products are alkanes $C_3$–$C_4$ and alkenes $C_2$–$C_4$ (ethene and propene are prevalent), ethyne, benzene, toluene, xylenes and condensed aromatics (with naphthalene prevalence) and pyrolytic carbon, along with stoichiometric amounts of hydrogen [9, 10]. The methane conversion degree does not depend on its initial concentration in the mixture (Fig. 1) that points to the first order of the process with respect to methane. The selectivity with respect to ethene, propene and benzene do not depend on the methane concentration in the initial mixture (Fig. 2), *i.e.* formation of ethene and propene is a first-order process with respect to methane. The initial methane concentration dependence of the selectivity with respect to pyrolytic carbon is antibate (Fig. 2). Ethane is absent in the reaction

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*corresponding authors. E-mail: ksd@icp.ac.ru products that evidences the absence of methyl radicals recombination as the basic way of ethane formation. Ethene formation proceeds probably by ethyl radical dehydrogenation. Propene in the pyrolysis products occurs at higher reaction temperatures, than ethene. The ethene/propene ratio does not depend on the composition of initial mixture that points to propene formation from ethene, as it was noted for pyrolysis of methane alone [9, 10].

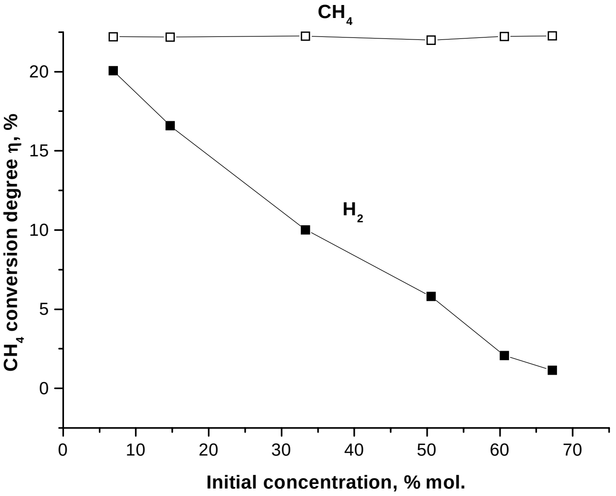

Fig. 1. Influence of initial concentration of methane ($CH_4$) or hydrogen ($H_2$) to methane conversion degree η in pyrolysis (1000°C, 1000 $h^{-1}$) of mixtures $CH_4$/Ar or 33.3 % mol. $CH_4$/Ar/$H_2$ over vacuum carbon black.

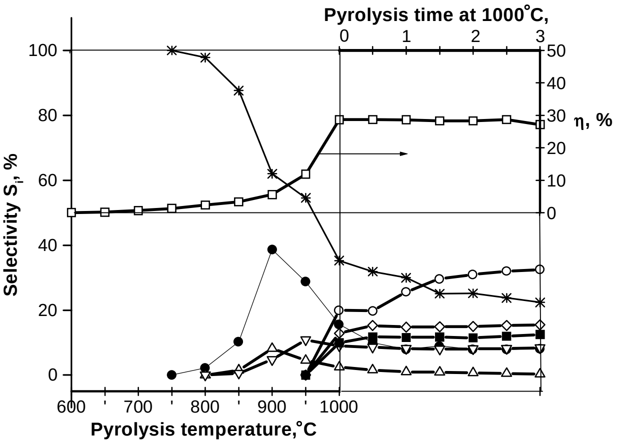

Fig. 2. Dependence of methane conversion degree η and selectivity with respect to products $S_i$ in pyrolysis of mixture 33.3 % mol. $CH_4$/Ar vs temperature pyrolysis and pyrolysis time at 1000°C over vacuum carbon black. □-η, selectivity with respect to: ethene (•), propane (△), propene(▽), benzene (○), toluene (◊), condensed aromatics (■) and pyrolytic carbon (∗).

The product composition of pyrolysis of the ternary $CH_4$/Ar/$H_2$ mixture strongly differs from the one of the binary $CH_4$/Ar mixtures. The methane conversion degree doesn't depend on the initial methane concentration. The methane conversion degree in the ternary 33.3 % mol. $CH_4$/Ar/$H_2$ mixtures pyrolysis is inversely proportional to the hydrogen initial concentration ($[H_2]_0$) (Fig. 1). The selectivity with respect to ethene is symbate to $[H_2]_0$ but the selectivity with respect to propene is practically constant. The maximal selectivity with respect to alkenes in the studied temperature range are observed at 1000°C (Fig. 3) as well as in the case of conversion of methane alone [10]. The hydrogen influence is highest on the selectivity with respect to total aromatics (Σ Aromatics is equal to sum of the selectivity with respect to benzene, toluene and condensed aromatics, i.e. Σ Aromatics = $S_{benzene}+S_{MePh}+S_{CAr}$), which, as we specified [9, 10], are pyrolytic carbon precursors. Hydrogen influence on the selectivity with respect to pyrolytic carbon is smaller than the one on the selectivity with respect to total aromatics. Σ Aromatics decreases practically to zero (Fig. 3) at hydrogen initial concentration about 14 % mol., but the selectivity with respect to pyrolytic carbon decreases to zero at hydrogen initial concentration 66.7 %.

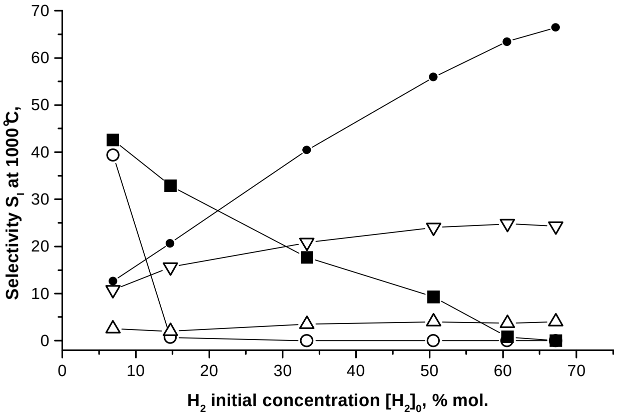

Fig. 3. Influence of initial hydrogen concentration in the feed mixture $[H_2]_0$ to selectivity ($S_i$) with respect to ethene (•), propane (△), propene(▽), total (equal to sum $S_{benzene}$+ + $S_{MePh}$ + $S_{CAr}$) aromatics (○) and pyrolytic carbon (■) in pyrolysis of feed mixture 33.3 % mol. $CH_4$/$H_2$/Ar at 1000°C over vacuum carbon black.

The catalyst based on vacuum carbon black as well as the catalyst based on fullerene black [10], transformed in $CH_4$/Ar mixture pyrolysis by coke and its precursors formation, stops to form propane, pyrolytic carbon and its precursors when $CH_4$/Ar mixture to according $CH_4$/Ar/$H_2$ one was exchanges. The reason for such reversible inhibition, along with blocking of the catalyst active centers by hydrogen, can be hydrogenation of pyrolytic carbon formed and not still graphitized and/or heterogeneous process small contribution.

The formation of ethene and propene only as pyrolysis products is observed over vacuum carbon black at the molar ratio $[CH_4]_0/[H_2]_0 \approx 2$ and $\eta$ = 2.1 % (Figs. 1, 3). Over fullerene black this effect was observed at the molar ratio $[CH_4]_0/[H_2]_0 = 1$ and $\eta$ = 5 % [9]. In contrast to vacuum carbon black fullerene black is subjected to non-catalytic destructive hydrogenolysis [11]. These facts substantiate our hypothesis on hydrogenation of pyrolytic carbon generated on an active component of the catalyst and catalyst active centers blocking as a reasons of inhibition of pyrolytic carbon formation in methane pyrolysis. These reasons seem to be not consistent with the earlier proposed hypothesis [9, 10] on a defining role of the curvature of basic structure elements for C–H bond activation. However, the contradiction is absent, as reactivity, the capacity to hydrogenolysis for example, in the case of fullerene black relates to the presence of curved and therefore non-conjugated and active multiple bonds. The capacity to be subjected to non-catalytic hydrogenolysis (under standardized conditions) is observed by experiment. However, the radius of curvature measure is difficult (especially if there are several parts in the active component of the catalyst). The thermogravimetry in air is the second test of material to reactivity. So, fullerene black [9] is characterized by the oxidation point equal to 270°C, the temperature of maximal rate of weight loss at 508°C and it does not contain graphitized particles. These characteristics for vacuum carbon black are higher (300 and 670°C) and the content of graphitized particles exceeds 32 % wt.

In pyrolysis of mixtures $CH_4$/Ar over vacuum carbon black (Figs. 1-2) the maximal ethene yield is independent on the initial mixture composition. It is determined only by pyrolysis temperature and comprises 5 % per passed methane. In pyrolysis of mixtures $CH_4/H_2$ over fullerene black this maximal ethene yield is similar, but coke is not formed [9]. Over vacuum black in the case of mixtures $CH_4/Ar/H_2$ the ethene yield is lower (Figs. 1 and 3). The similar maximal ethene yield was observed in oxidative methane coupling (for example [1]).

The nature of pyrolysis process has been studied in the presence of different amounts of vacuum carbon black as an active component with the total mass of mixed catalyst being constant. The methane conversion degree data over mixed catalysts based on vacuum carbon black with the content 3.3 and 13.2 % wt. (Cat 1 and Cat 2 respectively) is given in Fig. 4.

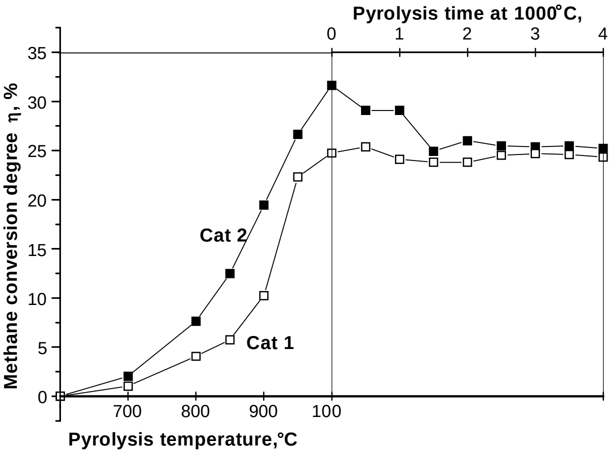

Fig. 4. Methane conversion degree vs pyrolysis temperature and reaction time at 1000°C in methane pyrolysis over catalysts containing 13.2 (Cat 2) and 3.3 % wt. (Cat 1) of vacuum carbon black.

These data show that the Cat 2 having surface 4 times more than that of the Cat 1, is more active than the Cat 1. The difference in the methane conversion degree over the catalysts Cat 2 and Cat 1 is quite visible at temperatures up to 900°C. It decreases at 950–1000°C and becomes insignificant at 1000°C. The methane conversion degree over the Cat 2 in the studied temperature range does not exceed that over Cat 1 by 4 times, *i.e.* $\eta$ is not proportional to the catalyst surface that points to homogeneous-heterogeneous nature of methane conversion. The contribution of heterogeneous part of the reaction depending on the value of initial catalyst surface decreases with the rise of reaction temperature and does not exceed 60 % at 700°C according to calculation. Pyrolytic carbon deposited on the catalyst surface deactivates the catalyst: initially high methane conversion degree over the Cat 2 decreases and reaches the constant value, close to the value $\eta$ for the Cat 1 because of close values of specific surface area for the Cat 1 and Cat 2 at this time (Fig. 4). Indeed, the specific surfaces area for both Cat 1 and Cat 2 is equal to 1.6–1.7 $m^2$/g after 4 h of pyrolysis at 1000°C. An estimation of Figs. 4, 2 data performed according with ref. [13] shows that such effect takes place after a deposition of monolayer of pyrolytic carbon.

## Conclusion

The results of methane conversion over vacuum black in mixtures with hydrogen are consistent with the data of homogeneous methane pyrolysis at the temperature of 1000°C (see for example [12,14]) that confirms the observed insignificant contribution of heterogeneous reactions at this temperature. The maximum selectivity with respect to alkenes in ternary $CH_4/Ar/H_2$ mixtures pyrolysis over catalyst based on fullerene black subjected to non-catalytic hydrogenolysis, is observed at methane/hydrogen molar ratio equal to 1. In the case of vacuum carbon black that doesn’t undergo to hydrogenolysis, the maximum selectivity is achieved only at the ratio 2.0. These differences also point to the catalyst effect in this predominantly homogeneous process. At temperatures up to 700°C when the surface reactions prevail, the maximum yield of alkenes does not exceed 0.5 %.

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