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PYROLYSIS OF METHANE AND THE ROLE OF SURFACE AREA

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ABSTRACT
   A range of catalysts was screened for activity and product selectivities
in the pyrolysis of methane. Experiments were performed in a flow reactor at
1125 $^\circ$C and atmospheric pressure. It appears that the pyrolysis of methane is
primarily affected by the specific surface area of the catalyst and not by the
particular type of catalyst. The highest yields to gaseous and liquid products
are obtained in an empty reactor tube, whereas high specific surface areas pro-
duce mainly graphitic coke and hydrogen. The results are compared with specific
surface area effects in the catalytic oxidative dimerization of methane.

INTRODUCTION

   The problem of methane activation has received considerable attention during
the last few years. A significant research effort has been spent on the
oxidative dimerization of methane using metal oxides as catalysts [see for
example Refs. 1-13]. In the cofeed process, where methane (natural gas) and
oxygen or air are introduced simultaneously into the reactor, a costly
separation procedure is involved [14]. Pyrolysis of methane would therefore
offer a potential advantage over the oxidative dimerization process, provided
that high yields of useful products can be obtained.

   Within the temperature region 1000-1300 $^\circ$C aromatics production from methane
is thermodynamically allowed [15]. However, coke formation forms a major
problem at these temperatures. Chevron workers [16] recently reported high
aromatics yields (up to 22 % on a carbon basis) from methane under pyrolysis
conditions, using selected materials as catalyst. Surprisingly, they claimed
that in the case of an Al_2O_3 and a BN catalyst coke formation could be
completely suppressed. In order to verify these results we undertook the
present study. In addition, we felt that some of the results of this study,
particularly those on the role of surface area, might add to the understanding
of the mechanism of the oxidative dimerization reaction of methane.

EXPERIMENTAL

   Methane pyrolysis was studied in a flow reactor (a quartz tube, 3 mm i.d.),
at a temperature of 1125 $^\circ$C using methane of atmospheric pressure and contact

times of the order of 0.1 s. The central part of the tube was packed with 30/80 mesh size particles of the catalyst. A range of catalysts was tested, including $-Al_2O_3$'s, γ-Al_2O_3, several metals supported on Al_2O_3's, SiC, SiN, BN and quartz particles. The surface areas of the catalysts, which varied between 0.03 and 130 m^2/g, were measured by the BET method using either Kr (low surface areas) or N_2 (high surface areas) adsorption. After a methane pulse of 5 minutes, the reaction products were analysed by standard GLC techniques. The amount of coke and tar (high molecular weight polycyclic aromatic hydrocarbons) was obtained from mass balance calculations assuming a fixed C/H ratio in the coke/tar fraction, which was determined in a separate experiment. Subsequently, coke was removed from the catalyst by passing an oxygen/nitrogen mixture through the reactor for a period of 20 minutes at 750 ^{0}C.

RESULTS

Since the product selectivities depend on conversion, the selectivities of the main reaction products have been plotted at a fixed conversion level (25 %; see Fig. 1). All selectivity and yield values are given as percentages on a carbon basis. As the reactor was filled with the catalyst on a volume basis, the points are plotted as a function of surface to volume (S/V) ratio rather than as a function of specific surface area. The values range from 3 x 10^2 cm^{-1} (0.03 m^2/g) to 1.3 x 10^6 cm^{-1} (130 m^2/g). The empty reactor tube was also
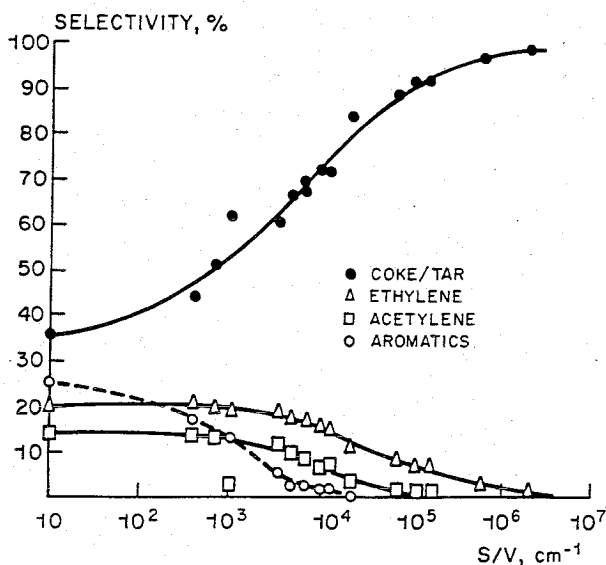

Fig. 1. Selectivity to ethylene, acetylene, light aromatics and coke/tar as a function of surface to volume ratio at 25 % conversion and 1125 ^{0}C. Reactor volume ~1 cm^3.

tested; these results are indicated on the vertical axis (S/V ~ 10). The main
species observed at 1125 ^{o}C are: ethylene, acetylene, light aromatics (i.e.
mainly benzene, with minor amounts of toluene and naphthalene) and coke/tar.
Small amounts of ethane, propene, propane and butene are found in the reaction
mixture as well. The selectivities to all products except coke/tar decrease
with increasing S/V ratio. The dependence on S/V ratio becomes progressively
stronger in the order ethylene, acetylene and aromatics. The selectivity to
coke/tar increases with increasing S/V ratio.

Figure 2 shows the conversion of methane and the yields of ethylene,
acetylene and light aromatics as a function of the S/V ratio at a constant GHSV
of 4000 h^{-1}. The conversion is weakly dependent on the S/V ratio: it increases
only by a factor of 10-20 when the S/V ratio is increased by four orders of
magnitude. The maxima in the yield curves are caused by the interplay between
the increasing conversion and decreasing selectivities with increasing S/V
ratio. It should be stressed that these yield curves are only valid for the
particular space velocity chosen; different maximum yields are obtained at
other combinations of space velocity and S/V ratio.
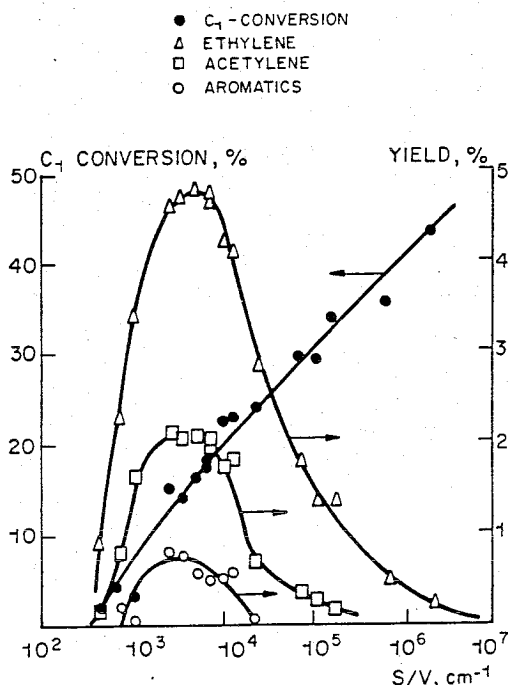

Fig. 2. Methane conversion and yields of ethylene, acetylene and light
aromatics as a function of surface area at constant GHSV (4000 h^{-1}) and
1125 ^{o}C (arrows indicate the correct scale). Reactor volume ~1 cm^{3}.

DISCUSSION

From the above, it appears that the pyrolysis of methane is primarily affected by the S/V ratio, i.e. the specific surface area of the catalyst (since the volume of the reactor is constant) and hardly, if at all, by the particular type of catalyst.

It is well known that the reactor wall or other surfaces might have a pronounced effect on both the initiation and termination steps of chain reactions involving free radicals [17,18]. The dependence of the conversion on surface area in the high temperature pyrolysis of methane may be explained in a similar way: dislocations or other radical sites at the surface might facilitate hydrogen abstraction from the methane molecule. This effect should be proportional to the surface area. Since the methane decomposition is autocatalytic [19], the surface may also assist in the termination of the reaction sequence by capturing the species responsible for the autocatalytic effect from the gas phase. These opposite effects might result in a very complex surface area dependence of the conversion. The results shown in Fig. 2 are tentatively ascribed to these phenomena.

The results of Fig. 1 can then be explained as follows: since the formation of ethylene, acetylene and aromatics is consecutive [19], capturing species from the gas phase by the surface will result in a progressively stronger surface area dependence of the selectivities to these products in the same order. In particular the aromatics selectivity is highly surface dependent and drops to zero rapidly with increasing surface area. The captured species may eventually be converted into coke, which would explain the increasing selectivity to coke with increasing surface area.

It appears that the highest selectivity to gaseous (ethylene, acetylene) and liquid products (aromatics) is obtained with a reactor in which the S/V ratio is minimized (i.e. an empty tube). On the other hand, high S/V ratios are advantageous for producing graphitic coke and hydrogen.

It is interesting to note that Iwamatsu et al. [20], who studied the dependence of the C_2 yield on the specific surface area of promoted MgO catalysts in the oxidative dimerization of methane, arrived at a similar conclusion: they found that a low surface area was the key factor in obtaining high C_2 yields. They concluded that the rate of methyl radical formation should be higher over catalysts with a high surface area, but the rate of radical collision with the surface should also be higher, so that there should be an optimum surface area of the catalyst for maximum probability of radical coupling.

For low S/V ratios the $C_2^=$ selectivity is hardly surface-dependent (Fig. 1). As the conversion does increase in this region (at a fixed GHSV; Fig. 2) this implies that the Space Time Yield (STY) of $C_2^=$ obtained from thermal cracking of methane can be optimized by choosing an appropiate S/V ratio.

CONCLUSIONS

The conversion and product selectivities in the pyrolysis of methane at 1125 °C are mainly governed by the specific surface area of the catalyst and not by the particular type of catalyst. The highest yields to gaseous (e.g. ethylene and acetylene) and liquid products (aromatics) are obtained with an empty reactor tube. On the other hand, high specific surface areas will produce graphitic coke and hydrogen.

Similar surface area effects are probably also important in the oxidative dimerization of methane over metal oxides.

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