Dehydrogenation–Aromatisation of Methane on Amorphous-like Carbons

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Amorphous-like carbon compounds prepared by direct pyrolysis of organic precursors such as tri-*n*-propylphosphine were found to enhance the dehydro-aromatisation reaction of methane and a high yield of benzene was obtained.

There has been increasing recent interest in methane conversion into liquid products,[1] metal oxide catalysts mostly being used under oxidation conditions. However, these are not always favourable systems for benzene production from CH_4, because CO_x and pyrolytic carbon formation can predominate owing to the acidic and/or basic properties of these catalysts in the presence of oxygen. In fact, the benzene yield is extremely low,[2] although under non-oxidizing conditions, recently, the aromatization of methane was briefly reported using modified ZSM-5 catalysts, but the yield was still not high.[3]

The dehydrogenation–aromatisation of methane into benzene has now been examined using carbon compounds produced by direct pyrolysis or organic monomers such as cyclohexane. The bulk carbon and/or carbon surface might be expected to promote formation of radicals from methane, enhancing their coupling and aromatization.

The carbon compounds used here were produced at 1223–1373 K according to procedures previously reported.[4] Organic precursors such as cyclohexane, di-*n*-propylamine and tri-*n*-propylphosphine were employed. The carbon products obtained were insoluble but air-stable materials. X-Ray diffraction analysis of them showed little evidence of a distinct crystalline phase with weak C(002) and/or C(101) bands at $2\theta = 25°$ ($d = 0.345$–0.361 nm) and 42° ($d = 0.205$–0.212 nm). The saturation magnetization values of these carbons, measured by a vibrating sample magnetometer (VSM), were *ca.* 0.21–5.4×10^{-7} Wb m kg^{-1}. The electrical conductivities, measured by a dc four-probe method using silver paste as electrodes, were *ca.* 900–1500 S cm^{-1} at room temperature, lower than for graphite itself.[5] XPS spectra, recorded on a PHI-5500 spectrometer using monochromatized radiation (1486.6 eV), showed carbon 1s (284.2–284.4 eV) absorptions with a full width at half maximum of 0.65–0.80 eV. These findings are consistent with an incompletely graphitized structure.[6]

The carbon powder sample (0.05 g) with quartz sand (2 g) as a diluent was placed in a quartz reaction tube (15 mm diameter). An IR image furnace was used for heating. The carbon was pretreated in helium at 1373 K for 50 min. The tube was cooled to room temperature, and a helium–methane mixture [8% CH_4 (*v*/*v*); 40 ml min^{-1}] was introduced and the temperature was raised again (4 °C min^{-1}) to the appropriate temperature. The products were analysed by gas chromatography after 2 h on-stream at each temperature, with the carbon samples being weighed before and after the reaction.

Methane was pyrolysed on carbon compounds at 1073–1373 K and aromatic and higher hydrocarbons were obtained with total selectivities as high as *ca.* 80%; Benzene was the major product with a selectivity of *ca.* 50–60%, and C_2 and pyrolytic carbon (PC) followed with selectivities of around 20–30% and 15–20%, respectively, (Table 1). Small amounts of other hydrocarbons such as propene, naphthalene, acenaphthylene and anthracene were also detected as by-products. A maximum benzene yield of 23% was achieved at 1323 K, when tri-*n*-propylphosphine-based carbon (NPP) was used (run 3). The use of α-graphite (AGR), fullerene (C_{60}) and quartz sand (QS) resulted in a lower yield of benzene with predominant formation of PC (runs 8, 9, 11). Temperatures above 1350 K favour PC formation, and so decrease the selectivity for benzene (Fig. 1).

The reaction mechanism and the role of the organic monomer-based carbon in the present dehydrogenation–aromatisation reaction are still not clear. However, the following thermodynamic points may be relevant in the temperature range employed: (*i*) PC formation predominates over hydrocarbons such as benzene and C_2 and (*ii*) above 1250 K, benzene formation is more favoured than C_2 production, while at lower temperature C_2 should prevail.[7] This is true for AGR, C_{60} and QS (Table 1). Carbons such as NPP, however, showed unusually high selectivities for these hydrocarbons. It is unlikely that the hydrocarbons could come from a degradation of the initially introduced carbon itself, because the gain in the carbon weight after the reaction is in reasonable agreement with the amount of PC estimated from the PC selectivity (Table 1), reaction time and CH_4 flow rate. Under the conditions employed, therefore, the pyrolysis of methane could occur on the bulk and/or surface carbon, as well as in the gas phase. Unlike graphite itself, these carbons contain an amorphous-like structure consisting of sp^2 and sp^3 carbons.[4] There is a good correlation between the benzene yield and

Table 1 Conversion and product distribution in dehydrogenation–aromatisation of methane at 1323 K

Starting material for carbon	Methane conv. (%)	Product distribution (mol %) Benzene	C_2[a]	PC[b]
1 Cyclohexane	30.9	54.7	29.4	13.8
2 Di-*n*-propylamine	41.9	38.6	18.8	40.7
3 Tri-*n*-propylphosphine	40.5	55.8	24.0	18.6
4 Triphenylphosphine	35.8	54.1	24.3	19.4
5 Di-*n*-propyl sulfide	33.9	32.5	24.1	40.9
6 Triethylborane	51.9	25.6	18.5	54.4
7 Dimethyl selenide	44.2	20.6	16.1	61.9
8 α-Graphite	26.3	10.7	23.2	63.1
9 Fullerene (C_{60})	50.2	8.98	12.4	78.0
10 Activated carbon	16.9	42.0	30.8	20.3
11 Quartz sand	13.5	12.2	18.3	62.9

[a] C_2 = ethane + ethene + ethyne. [b] The carbon produced by pyrolysis of CH_4 during reaction.

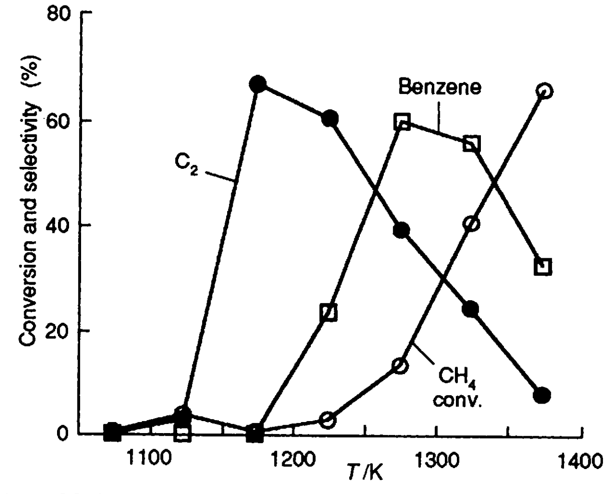

Fig. 1 Methane conversion and product selectivities in the dehydrogenation–aromatisation reaction on the carbon obtained from tri-*n*-propylphosphine

amorphous/graphite ratio (*P*), calculated from the *d*(002) value according to the Franklin equation.[8] Taking these findings into consideration, the amorphous-like structure, possibly, could accelerate the dehydrogenation–aromatisation of methane.

The reaction may possibly be initiated by the radical fission of methane either adsorbed on the carbon or in the gas phase to form methyl radicals, followed by their dimerization into C_2 species and then aromatization. In this temperature range, C_2 formation might precede benzene formation (Fig. 1). When ethene or ethane was passed over the carbon at the same flow rate as that of methane,benzene was formed even at 1023 K. These results are consistent with the view that these C_2 species are intermediates of the benzene formation.

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