High Yield of Aromatics from CH_4 in a Plasma-Followed-by-Catalyst (PFC) Reactor

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The oxygen-free dehydroaromatization of methane is of great scientific importance and industrial benefit for the effective utilization of natural gas and biogas to provide alternative petrochemical feed stocks and CO_x-free hydrogen production for fuel cells.[1] Methane oxygen-free conversion into aromatics and hydrogen is not thermodynamically favorable at low temperatures ($<$773 K); the equilibrium CH_4 conversion at 973 K is ~12%. At this temperature, benzene and naphthalene, in approximately equimolar amounts, are the thermodynamically preferred hydrocarbon products.[2] The thermodynamic limitation is the main barrier for this process. To enhance the conversion of methane into aromatics beyond thermodynamic equilibrium, studies using H_2-permeation membrane catalytic reactors are already underway by several research groups.[3,4] However, preliminary reports on this approach are not very optimistic, and catalyst deactivation was more pronounced in a membrane catalytic reactor than in a fixed-bed reactor because of continuous withdrawal of the coproduced H_2.[3]

Atmospheric nonthermal equilibrium plasma has been used as an efficient method for oxygen-free conversion of methane into C_2 hydrocarbons (mainly acetylene) and H_2 using pulsed corona/streamer discharges, or pulsed spark discharges.[5-10] Only small amounts of C_3-C_5 hydrocarbons and trace amounts of aromatics were usually coproduced. Recently, Heintze and Magureanu reported the conversion of CH_4 into aromatics in pulsed microwave plasma at atmospheric pressure in the presence of a heterogeneous catalyst.[11] In their work, the authors suggested that methane aromatization is very likely catalyzed on coke surfaces and highly unlikely by the trimerization of acetylene. The most abundant aromatic formed was benzene, and ~5% of the maximum benzene yield was obtained. Herein, we show a two-stage plasma-followed-by-catalyst (PFC) reactor for the oxygen-free conversion of methane into aromatic-rich hydrocarbons and coproduced H_2. Methane is converted to acetylene by plasma in the first stage, with the second stage for acetylene trimerization on nickel-loaded HZSM-5 catalyst.

Oxygen-free conversion of methane was performed at atmospheric pressure in a two-stage PFC reactor, as shown in Figure 1. The first stage of the PFC reactor, for generating pulsed spark discharge, was located in the upper part of a quartz tube (i.d. 10 mm) and consisted of a stainless steel wire (2 mm diameter) as the high-voltage electrode and a perforated iron plate (9 mm diameter) as the ground electrode. The distance between the two electrodes was 10 mm. The high-voltage power supply source for generating pulsed spark discharge was described before.[10] The second stage of the PFC reactor was filled with 0.5 g of HZSM-5 or Ni/HZSM-5 pellets of 20-40 mesh. The Ni/HZSM-5 catalysts were prepared by the conventional impregnation method using HZSM-5 ($SiO_2/Al_2O_3 = 25$, Nankai University, China) and aqueous solution of nickel nitrate. The impregnated samples were dried at 393 K for 4 h, calcined at 723 K for 4 h in air, and reduced at 673K for 2 h in hydrogen.

The flow rates for CH_4, H_2, and N_2 were controlled through a mass flow controller. The feed gas mixture of CH_4 (99.99%) and H_2 (99.99%) with a molar ratio of $CH_4/H_2 = 1$ was introduced into the PFC reactor at a flow rate of 9.2 cm^3/min. 2.2 cm^3/min of N_2 (99.99%) was used as an internal standard for analysis and introduced into the effluent gas from the PFC reactor to avoid conversion of N_2 in the plasma.

Hydrocarbon products were sampled by a six-way valve heated to 473 K and analyzed on-line by a gas chromatograph (Agilent 1790F) with a flame ionization detector (FID) and using a 2 mm (i.d.) × 3m Porapak-P column with N_2 as the carrier gas. N_2 and CH_4 were analyzed on-line by another gas chromatograph (Agilent 1790T) with a thermoconductive de-

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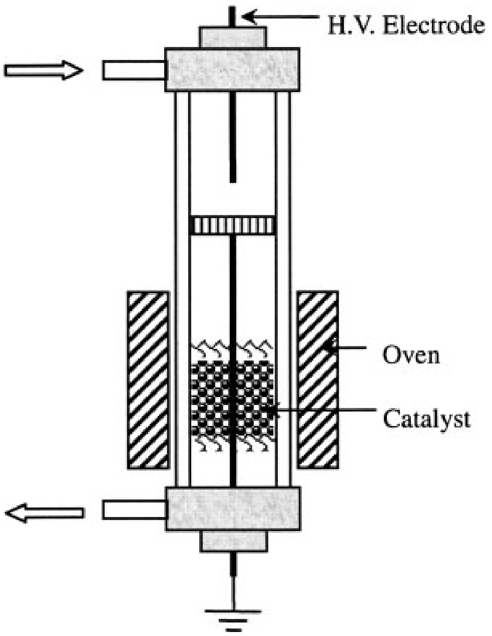

Figure 1. Two-stage PFC reactor.

tector (TCD) using a 2 mm (i.d.) × 1m carbon molecular sieve 601 column and H_2 as the carrier gas. H_2 in the effluent gas was analyzed on-line by one more gas chromatograph with a TCD using 2 mm (i.d.) × 1m carbon molecular sieve 601 column and N_2 as the carrier gas. To avoid electromagnetic noise from the pulsed discharges, the three on-line gas chromatographs were placed in a shielded room.

According to the mass balance for carbon and hydrogen, the conversion of methane (X_{CH4}), the yields of individual hydrocarbon products (Y_{CxHy}), and the total hydrocarbon yield (Y_{HCs}) were evaluated using an internal standard analyzing method[12] according to the following equations:

X_{CH4} (%) = (moles of CH_4 consumed/moles of CH_4 introduced) × 100

Y_{CxHy} (%) = x (moles of C_xH_y produced/moles of CH_4 introduced) × 100

Y_{HCs} (%) = ΣY_{CxHy}

Here, x and y represent carbon-atom number and hydrogen-atom number in a molecule of hydrocarbon product, respectively.

Hydrogen yield was calculated using the external standard analyzing method from the following equation:

Y_{H2} (%) = 0.5 (moles of H_2 produced/moles of CH_4 introduced) × 100

The yield of coke, given by 100%-ΣY_{CxHy}, includes undetected heavy aromatics and carbonaceous deposition on the wall of the PFC reactor, the electrode surfaces, and the catalysts.

The energy density, calculated by discharge power per feed flow, is 1400 kJ/mol at this experimental condition. The energy cost for methane conversion, defined as energy consumed per molecule of methane converted, was given in eV/molecule.

Preliminary control experiments under plasma alone (9.6 W of discharge power, pulsed spark discharge) using 9.2 cm^3/min of the feed gas with a molar ratio of CH_4/H_2 = 1 confirmed that methane conversion and product yields remained relatively constant for over 10 h. Then, the conversions of methane were compared in the following cases: (A) in the plasma reactor without any catalysts; and (B) in the two-stage PFC reactor using nonloaded HZSM-5 or nickel-loaded HZSM-5 catalysts. As shown in Figure 2, the plasma alone case gives 78.2% of methane conversion at 1400kJ/mol of energy density and, thus, the energy cost for methane conversion was 37 eV/molecule. Acetylene (yield 68.8%) and hydrogen (yield 62.6%) were the dominant products, with only extremely small amounts of aromatic product (1.0% of benzene yield). With a feed gas ratio of CH_4/H_2 = 1, the results of methane conversion in the plasma alone, the molar ratio of $C_2H_2/H_2/CH_4$ in the effluent gas can be calculated approximately at 1.6/10/1. In all the PFC runs presented in this article, the experimental conditions of the first stage (plasma part) are the same as those of the plasma alone

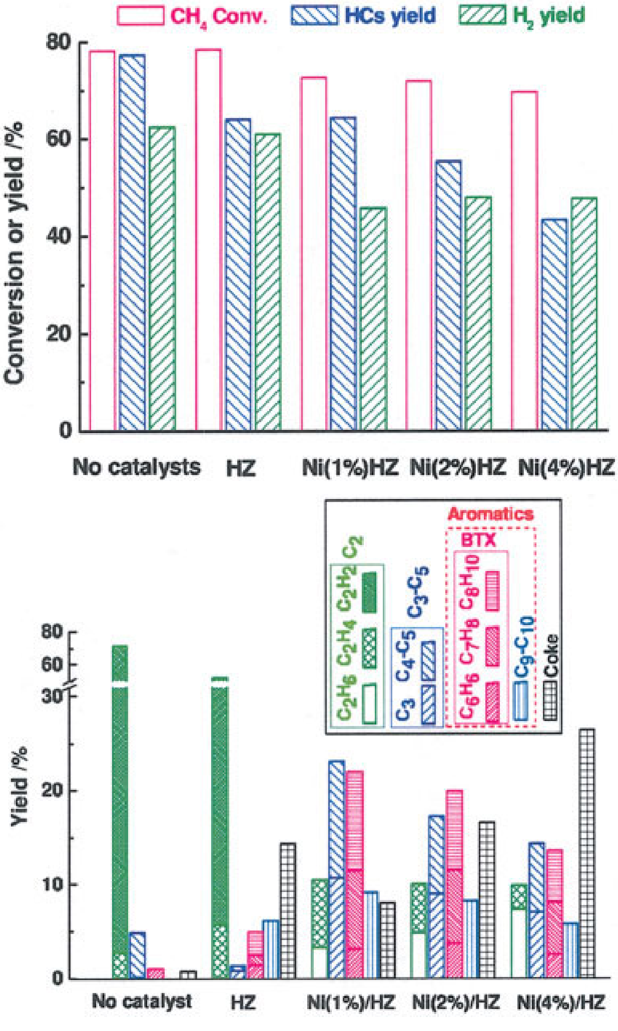

Figure 2. Comparison of methane conversion and product yields in the plasma reactor alone, and in the PFC reactor using Ni/HZSM-5 catalysts of different Ni loadings.

Total flow rate: 9.2 cm^3/min, CH_4/H_2 = 1, discharge power: 9.6 W, catalyst temperature: 673 K. Data taken time: 300 min for the plasma alone reactor and the PFC reactor using Ni/HZSM-5 catalysts, 20 min for the PFC reactor using HZSM-5 catalysts. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

case. In other words, the component content of the gas into the second stage (catalyst bed) in all the PFC runs can be assumed to be almost the same as that in the plasma alone run.

In the PFC reactor, using nonloaded HZSM-5 as catalyst, it was found that the generation of coke (C_{11+} aromatics can presumably act as precursors to coke formation) resulted in the rapid deactivation of the catalyst. This is in agreement with relevant literature[13,14] on C_2H_2 conversion. The data given in Figure 2 for the PFC reactor using HZSM-5 catalyst shows that acetylene yield jumped to 46.1% after only 20 min on-stream time at 673 K, implying that the catalytic activity of HZSM-5 for acetylene conversion decreased rapidly to a lower level.[14] In contrast, it can also be more clearly seen from Figure 2 that, for the PFC reactor using nickel-loaded HZSM-5 catalyst, no acetylene was detected in the products from the PFC reactor (that is, acetylene produced in the first stage was 100% converted in the second stage) during several hours of onstream time and, thus, the data were taken at 300 min onstream time. Thereby, Ni/HZSM-5 catalyst showed a better performance than that of the nonloaded HZSM-5 for C_2H_2 conversion, which is consistent with work reported in the literature.[15] Moreover, significant amounts of aromatics were produced in the PFC reactor using Ni/HZSM-5 catalyst. BTX, that is, benzene (B), toluene (T), and xylene (X, some styrene and ethylbenzene), are the major aromatic products. BTX yield ($Y_{BTX} = Y_{C6H6} + Y_{C7H8} + Y_{C8H10}$) accounts for approximately 70% of aromatics yield ($Y_{aromatics} = Y_{BTX} + Y_{C9\text{-}C10}$), which remains constant under different Ni content conditions. Figure 2 also shows that methane conversion, as well as H_2 yield, decreased when HZSM-5 was loaded with Ni, which probably results from the hydrogenolysis function of Ni. Increasing Ni content from 1 wt% to 4 wt%, the total hydrocarbon yield, aromatics yield, and BTX yield significantly decreased, and the coke yield accordingly increased.

Figure 3 shows the conversion results for methane in the PFC reactor using Ni(1 wt%)/HZSM-5 catalyst at 100 min onstream time, plotted as a function of catalyst temperature. From 573K to 723K, CH_4 conversion changed slightly in the range of 72-76% and 100% of C_2H_2 conversion over Ni/HZSM-5 catalyst was always obtained. The yield of BTX exhibits a clear dependence on catalyst temperature, with a maximum yield achieved at a catalyst temperature of 673 K. It can be observed that the selectivities for BTX plus C_4-C_5 remained nearly constant in the temperature range of 573-673K. For example, BTX selectivity and C_4-C_5 selectivity were 14.2% and 31.9% at 573K and 34.7% and 10.7% at 673K, respectively. As a result, the total selectivity of BTX plus C_4-C_5 was 46.1% at 573K and 45.4% at 673K. Thereby, it can be inferred that C_4-C_5 species play an intermediate role in the formation of BTX from acetylene. At temperature $>$ 673K, there was a sudden increase in H_2 yield and coke yield. This suggests that hydrocarbon products may undergo decomposition to hydrogen and carbon, resulting from the nickel sites of Ni/HZSM-5 catalyst.[16] For the PFC reactor using Ni(1 wt%)/HZSM-5, 62% of HCs yield, 32% of aromatics yield, 25% of BTX yield, and 44% H_2 yield with 72% of methane conversion have been achieved at 1400kJ/mol of energy density and 673 K of catalyst temperature.

Figure 4 shows variations in CH_4 conversion and product yields vs. onstream time in the PFC reactor using Ni(2 wt%)/HZSM-5 catalyst at 673 K. The conversion of CH_4 did not change over an onstream time of 9 h, while H_2 yield and coke yield gradually increased with onstream time. Aromatics yield and BTX yield were very stable during 5 h of onstream time. With the present catalyst, deactivation to some extent resulted in <100% C_2H_2 conversion after onstream time of 9 h.

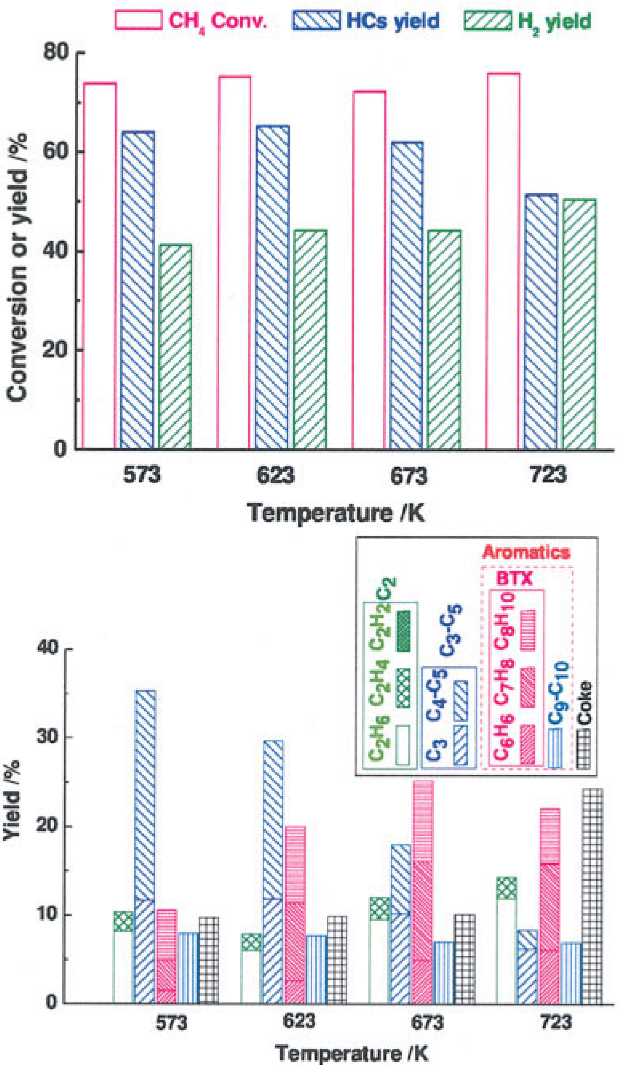

Figure 3. Effect of catalyst temperature on methane conversion and product yields in the PFC reactor using Ni(1%)/HZSM-5 catalysts.

Total flow rate: 9.2 cm^3/min, $CH_4/H_2 = 1$, discharge power: 9.6 W. Data taken time: 100 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In conclusion, we have shown that high yields of aromatic-rich hydrocarbons and CO_x-free hydrogen are simultaneously obtained from oxygen-free conversion of methane in a two-stage PFC reactor composed of pulsed spark discharge plasma and Ni/HZSM-5 catalyst at atmospheric pressure and 673 K of catalyst temperature. BTX are the major aromatic products. This study shows very encouraging progress in overcoming the thermodynamic barrier for oxygen-free conversion of methane into aromatics and hydrogen.

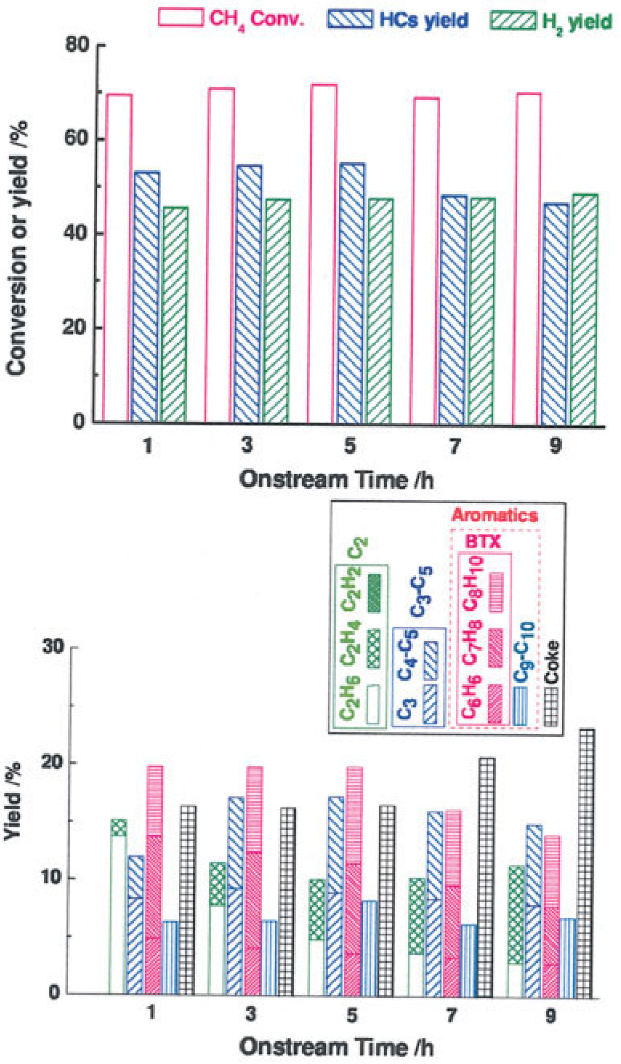

Figure 4. Variations in methane conversion and product yields vs. onstream time in the PFC reactor using Ni(2%)/HZSM-5 catalysts.

Total flow rate: 9.2 cm^3/min, CH$_4$/H$_2$ = 1, discharge power: 9.6 W, catalyst temperature: 673 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Acknowledgments

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