Remarkable non-oxidative conversion of methane to naphthalene and benzene on Co and Fe modified Mo/HZSM-5 catalysts

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Remarkable production of naphthalene and benzene is found in the dehydrocondensation of methane under non-oxidative conditions on Co- and Fe-modified Mo/HZSM-5 catalysts at 973 K and 1 atm pressure of methane.

Recently there is an increasing interest to activate methane under non-oxidative conditions and convert it to higher hydrocarbons and aromatic compounds as alternative feed-stocks for the petrochemical industry.[1,2] Some supported Pt and Ru catalysts yield C_2–C_5 hydrocarbons and even benzene in the low-temperature homologation of methane[3–5] but continuous catalytic reaction does not proceed. It has been previously reported that on Mo-supported ZSM-5 zeolite catalysts, a considerable amount of benzene was produced at 973 K in 60–70% selectivity in the gas-phase products at lower methane conversion while only benzene and toluene have been observed as the aromatic products.[6,7] Nevertheless, methane conversion was drastically decreased owing to irreversible coke formation on the catalysts.

Here, we describe that Fe- and Co-modified Mo/HZSM-5 catalysts exhibit remarkable production of naphthalene and benzene as the major aromatic products together with a small amount of their derivatives such as toluene, xylene and methylnaphthalene in the dehydrocondensation of methane at 973 K and 1 atm pressure. Furthermore, it was found that the addition of cobalt and iron to Mo/HZSM-5 catalyst markedly improved the yield of naphthalene and benzene along with effective reduction of coke formation.

The Mo/HZSM-5 and Fe/Co-modified Mo/HZSM-5 catalysts were prepared by the conventional impregnation (incipient wetness) of NH_4ZSM-5 (Si/Al = 79, Toso Co.) with $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (Kanto Chem. Co.), $Co(NO_3)_2\cdot6H_2O$ (Wako Pure Chem. Ind. Ltd.) or $Fe(NO_3)_3\cdot6H_2O$ (Wako) aqueous solutions. After the impregnated samples were dried at 393 K and calcined at 773 K in air, catalytic tests were carried out under atmospheric pressure of methane in a continuous flow microreactor system equipped with a quartz tube (8 mm id) packed with 0.3 g of catalyst pellets of 20–42 mesh. After flushing with He at 973 K for 40 min, a feed gas mixture (99.99% purity, Sumitomo Seika Co.) of 98% CH_4 with 2% Ar as internal standard for analysis was introduced into the fixed-bed reactor at a flow rate of 7.5 ml min^{-1} [space velocity = 1500 ml (g cat. h)$^{-1}$, contact time = 3.8 s] through a mass flow controller (Brooks 5850E).

Hydrocarbon products including C_2–C_4 alkanes (and/or alkenes) and condensable C_6–C_{12} aromatics such as benzene, toluene, xylene, naphthalene and methylnaphthalenes were removed by a six-way sampling valve heating at 500 K and analyzed by on-line gas chromatography (Shimadzu GC-14A) equipped with a flame ionization detector (FID) using a 4 mm × 1 m Porapak-P column. Another GC (Shimadzu GC-8A) with a thermoconductive detector (TCD) was employed for on-line product analysis of H_2, Ar, CO, CH_4 and CO_2 using a 4 mm × 2 m activated carbon column. All products were identified by using GC–MS (Perkin-Elmer, Auto System GC, 910 Q-Mass).

Using an internal standard analyzing method, conversion of methane, selectivities of hydrocarbon products and coke formed

on the catalyst were evaluated according to the mass balance for carbon and hydrogen. The total gas flow rate at the outlet of the reactor (F^{outlet}) can be calibrated by eqn. (1). The methane

$$F^{inlet} X_{Ar}^{inlet} = F^{outlet} X_{Ar}^{outlet} \qquad (1)$$

conversion (Conv.) and selectivity ($S_{product}^{carbon}$) of hydrocarbon products in gas phase on carbon base were calculated from eqns. (2) and (3). The selectivity of coke including undetected heavy

$$\text{Conv.} = \frac{F^{inlet} X_{methane}^{inlet} - F^{outlet} X_{methane}^{outlet}}{F^{inlet} X_{methane}^{inlet}}$$

$$= 1 - \frac{X_{methane}^{outlet} X_{Ar}^{inlet}}{X_{methane}^{inlet} X_{Ar}^{outlet}} \qquad (2)$$

$$S_{product}^{carbon} = \frac{F^{outlet} X_{product}^{outlet} N_{product}^{carbon}}{F^{inlet} X_{methane}^{inlet} - F^{outlet} X_{methane}^{outlet}}$$

$$= \frac{X_{Ar}^{inlet} X_{product}^{outlet} N_{product}^{carbon}}{X_{Ar}^{outlet} X_{methane}^{inlet} - X_{Ar}^{inlet} X_{methane}^{outlet}} \qquad (3)$$
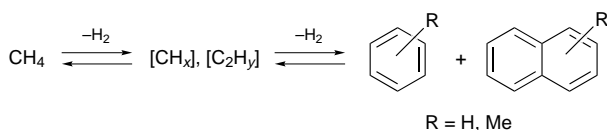
aromatics, amorphous carbon and graphitic carbon on the catalysts is given by $1 - \Sigma S_{product}^{carbon}$. Here, F, X and N^{carbon} represent total gas flow rate, mole fraction and carbon number in a molecule, respectively.

The non-oxidative conversion of methane was conducted by flowing methane on the catalyst in the fixed bed at 973 K. C_2-hydrocarbons and aromatic compounds were continuously obtained with a considerable evolution of hydrogen on the Mo/HZSM-5 and Co/Fe-modified Mo/HZSM-5 catalysts. The major aromatic compounds produced in the reaction are benzene and naphthalene with other aromatics produced only in trace amounts. Fig. 1 shows the conversion of methane and the selectivity of hydrocarbon products such as benzene and naphthalene with time on stream of the reaction at 973 K. The selectivity of hydrocarbon products in the gas phase increases and reaches a value of 68% on carbon basis and then keeps constant, while the selectivity of coke was *ca.* 32% on the Mo/HZSM-5 catalyst. The conversion of methane decreases rapidly from 12 to 8% at the initial stage of the reaction in forming a large amount of hydrogen and CO where MoO_3 supported on HZSM-5 was converted to reduced Mo species and Mo_2C.[2,8] Methane conversion shows a moderate decrease (6–8%) upon prolonged reaction time (30 h) to give a stable selectivity of the hydrocarbon products including C_2–C_4 compounds and aromatics such as benzene and naphthalene. The thermodynamic equilibrium conversion of methane for $6CH_4 = C_6H_6 + 9H_2$ is calculated as 11.8% at 973 K and 1 atm of methane. The constant selectivity of hydrocarbon products (68%) and coke (32%) in the stationary stage of the reaction may suggest that both products are derived from a common intermediate CH_x formed on the Mo/HZSM-5 catalysts. In the initial stage of the reaction, the composition of gas-phase hydrocarbons comprised 31 and 62% of naphthalene and benzene on carbon basis, respectively, and after 20 h of reaction time changed to 6 and 67% while the C_2 products increased to 20%. This may suggest that benzene, naphthalene and their derivatives may
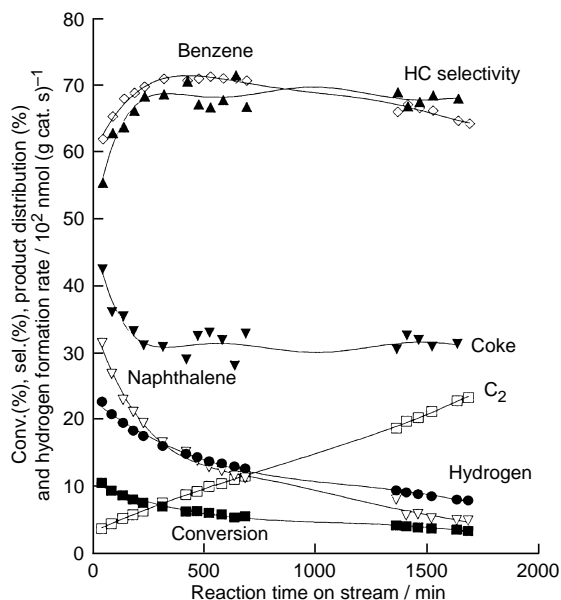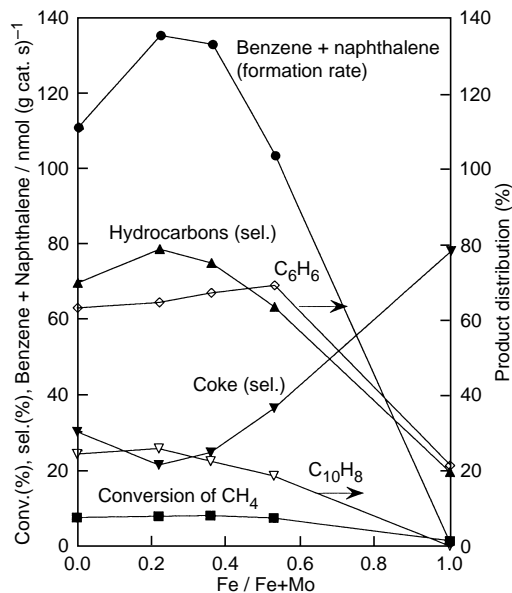
Fig. 1 Catalytic performances of 3% Mo/HZSM-5 zeolite catalyst for methane non-oxidative dehydrocondensation reaction at 973 K. (■) Methane conversion, (▲) selectivity of hydrocarbon products, (▼) selectivity of coke, (●) formation rate of hydrogen, (◇) percentage of benzene in hydrocarbon products, (▽) percentage of naphthalene in hydrocarbon products, (□) percentage of ethane + ethene in hydrocarbon products.

Fig. 2 Catalytic performances of Fe-Mo/HZSM-5 zeolite catalysts for methane non-oxidative dehydrocondensation reaction at 973 K (data are taken at 160 min of the reaction time on stream). (■) Methane conversion, (▲) selectivity of hydrocarbon products, (▼) selectivity of coke, (●) formation rate of benzene and naphthalene, (◇) percentage of benzene in hydrocarbon products, (▽) percentage of naphthalene in hydrocarbon products.

consequently be produced *via* $[CH_x]$ and/or C_2H_y intermediates as proposed previously[7,8] and the reaction may occur *via* Scheme 1.

Scheme 1

From Fig. 2 it is clear that addition of Fe, as for Co, to Mo/HZSM-5 catalysts yields a considerable enhancement of aromatic products such as naphthalene and benzene in the reaction at 973 K. It is of interest to observe that a maximum yield of benzene and naphthalene was attained in low concentrations of Fe or Co in Mo/HZSM-5 [atomic ratio *ca.* 0.2–0.4 for M/(M + Mo) (M = Fe, Co)]. 1% Co loading into 3% Mo/HZSM-5 resulted in an increase of benzene yield from 3.2 to 4.7% owing to higher conversion of methane and higher benzene selectivity in gas-phase hydrocarbon products as compared with 3% Mo/HZSM-5. On the other hand, the promotion of benzene yield upon addition of Fe to Mo/ZSM-5 is due to the suppression of coke formation from 31 to 21%, although the Fe/HZSM-5 catalyst showed preferential formation of coke (75% selectivity) in the reaction. Further addition of Fe or Co to Mo/HZSM-5 resulted in a decrease of the aromatic products owing to substantial increase of coke formation in methane conversion. The results suggest that the binary FeMo and CoMo oxide/carbides formed on the ZSM-5 support are active for the dehydrogenation of methane towards aromatics

such as naphthalene and benzene. In this regard, it was of interest to find that a $Fe_2(MoO_4)_3$ powdered sample prepared by coprecipitation[9] gave a remarkable evolution of hydrogen to form coke, whereas a negligible amount of hydrocarbon was produced upon admission of methane at 973 K. This implies that the FeMo binary site may highly active for the dehydrogenation of methane to promote the formation of CH_x as the common species to be converted to aromatic compounds on the FeMo/HZSM-5 supported catalysts.

Footnote

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