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Catalytic Dehydrocondensation of Methane with CO and CO_2 toward Benzene and Naphthalene on Mo/HZSM-5 and Fe/Co-Modified Mo/HZSM-5

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The catalytic dehydroaromatization of methane was performed by the addition of CO and CO_2 at 1 atm and 973 K on Mo/HZSM-5 and Fe/Co-modified Mo/HZSM-5. With pure methane as feed gas, ca. 10% of methane is initially converted to mainly benzene at a formation rate of 600 nmol/g cat/s (on carbon base) on Mo-supported catalysts, which are drastically deactivated owing to significant coke formation (35–40%). In contrast, addition of a few percent of CO and CO_2 to methane feed promotes benzene production and significantly improves the stability of the Mo/HZSM-5 catalyst at prolonged times-on-stream. For Fe- and Co-modified Mo/HZSM-5 catalysts the methane reaction with CO yields higher activities (950–1000 nmol/g cat/s in carbon base) of benzene production with good catalytic stability for more than 100 h owing to minimization of the coke formation to less than 20%. It is demonstrated that added CO_2 is converted to 2 mol of CO by the reforming process ($CO_2 + CH_4 = 2CO + 2H_2$) or by the reverse Boudart reaction ($CO_2 + C = 2CO$), which similarly promotes the catalytic stability. TPO experiments revealed that the amount of coke formed on the catalyst surface was greatly reduced by adding a few percent of CO or CO_2 to the methane feed gas. TPO experiments also showed that, in contrast to CO, addition of more than 4% CO_2 to the methane feed reduces not only the inert coke but also the reactive coke, which can be converted to aromatics such as benzene and naphthalene. ^{13}CO isotopic labeling tracer studies showed that ^{13}C from ^{13}CO is easily incorporated into methane and products such as benzene and ethene. From the studies mentioned above, it may be suggested that the unique role of CO addition to methane feed is based on the formation of minute amounts of CO_2 and C by the Boudart reaction, where C is hydrogenated to a common active carbon species [CH_x] involving methane conversion toward aromatic products such as benzene and naphthalene, while CO_2 reacts with the surface inert carbon species (coke) to regenerate CO, resulting in improved catalyst stability due to efficient suppression of coke formation on the catalyst. © 1999 Academic Press

Key Words: **promotion; CO/CO_2 addition; methane dehydroaromatization; Mo/ZSM-5 catalyst.**

1. INTRODUCTION

The catalytic conversion of methane to ethene and benzene as the petrochemical feed stocks and liquid fuel has been a great challenge in heterogeneous catalysis and an intriguing problem with respect to effective utilization of carbon resources such as natural gas. So far, there are some potential routes for methane conversion such as the oxidative coupling of methane to ethene over Li/MgO and Sm_2O_3 catalysts (1) and the two-step homologation of methane for lower hydrocarbons on Co and Ru catalysts (2), although these routes are not yet feasible because of lower yields and selectivities. Since the first report in 1993 by Wang *et al.* (3), the direct dehydrocondensation of methane to benzene has been widely studied on Mo-impregnated HZSM-5 catalyst in terms of the kinetics, reaction mechanism, and catalyst characterization by Xu (3, 4, 7–10), Solymosi (5, 6), and Lunsford (11, 12) and their co-workers. Recently, we demonstrated (13) that methane is effectively condensed with substantial evolution of hydrogen into various aromatics such as benzene, naphthalene, and their methyl substitutes not only on Mo/HZSM-5 but also on Co/Fe-modified Mo/HZSM-5 at 873–1073 K. Nevertheless, using pure methane feed, it was found that methane conversion and rates of benzene formation drastically decreased for a few hours owing to significant coke formation. In addition, the reaction mechanism and active sites for methane conversion to benzene and naphthalene on Mo/HZSM-5 catalysts remain a matter of controversy. To reduce coke formation, some preliminary efforts have been made to add selected oxidative reagents such as oxygen and carbon dioxide (10% or higher) to the methane gas feed, but the aromatic product formation was completely inhibited on Mo/HZSM-5 catalyst as reported previously (3, 12). We studied the additive effects of CO and CO_2 by controlling their concentration for the dehydrocondensation of methane on

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Mo/HZSM-5 and Fe/Co-modified Mo/HZSM-5 in terms of catalytic performance towards benzene and naphthalene and catalytic stability associated with coke formation. Furthermore, the unique promotional role of CO/CO_2 addition in the direct conversion of methane to aromatic products and the chemical origin to improve their catalyst stability were studied by ^{13}CO isotopic labeling and temperature-programmed oxidation (TPO) experiments in conjunction with coke formation and the bifunctional mechanism of methane dehydrocondensation on Mo-supported catalysts.

2. EXPERIMENTAL

2.1. *Materials and Catalyst Preparation*

Mo/HZSM-5 catalysts containing 3–6 wt% Mo were prepared by impregnation (incipient wetness) of NH_4ZSM-5 ($SiO_2/Al_2O_3 = 47$–52; surface area = 780–925 m^2/g; Toso Co. and CRI Zeolyst, Inc.) with $(NH_4)_6Mo_7O_{24}4H_2O$ (99.9%, Kanto Chem. Co., used as is) aqueous solution. The resulting materials were dried at 393 K and calcined at 773 K for 6 h, as reported previously (13–15). Fe- and Co-modified Mo/HZSM-5 catalysts were prepared by the sequential impregnation of 3 wt% Mo/HZSM-5 with $Co(NO_3)_2$ and $Fe(NO_3)_3$ aqueous solutions, followed by calcination in air at 773 K for 2 h.

2.2. *Product Analysis and Kinetic Measurements*

After the impregnated samples of Mo/HZSM-5 were calcined at 773 K in air, catalytic tests were carried out under the atmospheric pressure of methane with or without CO or CO_2 in a continuous microreactor system equipped with an 8-mm-i.d. quartz reactor charged with 0.30 g of catalyst pelleted and sized to 20-42 mesh, as reported previously (13–15). The reaction temperature was monitored by a thermocouple (K-type alumel/chromel) sheathed in a quartz tubing, which was attached to a catalyst fixed bed (5–10 mm in height). After flushing with He at 973 K, a feed gas of pure CH_4 or a mixture of methane with 1.8–12% (v/v) CO or CO_2 was introduced into the fixed-bed reactor at a total flow rate of 7.5 ml/min (space velocity = 1500 ml/h/g cat) through mass flow controllers (STEC Co., SEC-400). The outlet pipe line from the end of a quartz reactor and on-line sampling valves were kept higher than 500 K to prevent the condensation and strong adsorption of the higher hydrocarbon products. Two percent argon (Daido Hoxan Gas Co.; 99.9% purity) as internal standard for gas analysis was used in mixing with methane. A Shimadzu GC-14A gas chromatograph with a flame ionization detector (FID) was equipped with a six-way sampling valve (Valco Instruments Co. Inc.; AAVO816) for heating at 533 K for separation of hydrocarbon products including aromatic compounds such as benzene, naphthalene and their methyl-substituted derivatives on a 4 mm × 1 m Porapak-P column. Another Shimadzu GC-8A gas chromatograph was employed for on-line product analysis of H_2, Ar, CO, CH_4, and CO_2 on a 4 mm × 2 m activated carbon column with a thermal conductivity detector (TCD). Hydrocarbons produced in this reaction were C_2–C_4 alkanes (and/or alkenes) and C_6–C_{12} aromatic hydrocarbons such as benzene, toluene, xylene, naphthalene, and methyl-naphthalene which were identified by using on-line GC and GC–MS (Perkin–Elmer, Auto System GC with 910-Q mass spectrometer).

By using an internal standard analyzing method, important variables such as conversion, and selectivity were evaluated under the mass balance with respective to carbon and hydrogen. The total gas flow rate at the outlet of the reactor (F^{outlet}) can be calibrated with the equation

$$F^{\text{inlet}} \times X_{\text{Ar}}^{\text{inlet}} = F^{\text{outlet}} \times X_{\text{Ar}}^{\text{outlet}} \qquad [1]$$

since the mass flow rate of nonreactive Ar as internal standard should be constant throughout the reaction. Assuming that a mole fraction of methane in a TCD sampling loop takes the same value as that in an FID sampling loop, the mole fraction of each product (X) in the gas phase was calculated with the equation

$$X_{\text{product}} = \frac{\dfrac{f_{\text{product}}^{\text{TCD}} \times A_{\text{product}}^{\text{TCD}}}{f_{\text{methane}}^{\text{TCD}} \times A_{\text{methane}}^{\text{TCD}}} \ \text{or}\ \dfrac{f_{\text{product}}^{\text{FID}} \times A_{\text{product}}^{\text{FID}}}{f_{\text{methane}}^{\text{FID}} \times A_{\text{methane}}^{\text{FID}}}}{\dfrac{\sum_{\text{TCD}} f_{\text{product}}^{\text{TCD}} \times A_{\text{product}}^{\text{TCD}}}{f_{\text{methane}}^{\text{TCD}} \times A_{\text{methane}}^{\text{TCD}}} + \dfrac{\sum_{\text{FID}} f_{\text{product}}^{\text{FID}} \times A_{\text{product}}^{\text{FID}}}{f_{\text{methane}}^{\text{FID}} \times A_{\text{methane}}^{\text{FID}}} - 1} \qquad [2]$$

where f and A represent a sensitivity factor and the area of a peak corresponding to the compound on the GC chromatogram, respectively. Such an assumption is considered to be proper because calculated mole fractions of condensable products in a TCD loop at room temperature are 0.5 mol% at most. Using Eq. [2], conversion of methane (Conv), selectivity ($S_{\text{product}}^{\text{carbon}}$), and formation rate ($R_{\text{product}}^{\text{carbon}}$) of hydrocarbon products, such as C_2 hydrocarbons, benzene, and naphthalene, CO, and CO_2, on a carbon base, are respectively calculated from the equations

$$\begin{aligned}\text{Conv.} &= \frac{F^{\text{inlet}} \times X_{\text{methane}}^{\text{inlet}} - F^{\text{outlet}} \times X_{\text{methane}}^{\text{outlet}}}{F^{\text{inlet}} \times X_{\text{methane}}^{\text{inlet}}} \\ &= 1 - \frac{X_{\text{methane}}^{\text{outlet}} \times X_{\text{Ar}}^{\text{inlet}}}{X_{\text{methane}}^{\text{inlet}} \times X_{\text{Ar}}^{\text{outlet}}}, \qquad [3]\end{aligned}$$

$$\begin{aligned}S_{\text{product}}^{\text{carbon}} &= \frac{F^{\text{outlet}} \times X_{\text{product}}^{\text{outlet}} \times N_{\text{product}}^{\text{carbon}}}{F^{\text{inlet}} \times X_{\text{methane}}^{\text{inlet}} - F^{\text{outlet}} \times X_{\text{methane}}^{\text{outlet}}} \\ &= \frac{X_{\text{Ar}}^{\text{inlet}} \times X_{\text{product}}^{\text{outlet}} \times N_{\text{product}}^{\text{carbon}}}{X_{\text{Ar}}^{\text{outlet}} \times X_{\text{methane}}^{\text{inlet}} - X_{\text{Ar}}^{\text{inlet}} \times X_{\text{methane}}^{\text{outlet}}}, \qquad [4]\end{aligned}$$

$$R_{\text{product}}^{\text{carbon}} = F^{\text{outlet}} \times X_{\text{product}}^{\text{outlet}} \times N_{\text{product}}^{\text{carbon}}/\text{Wt.} \qquad [5]$$

Thus, the selectivity for coke formation on a carbon base is derived from 1 − the sum of product selectivity and includes undetected heavy aromatics, amorphous carbon, and graphitic carbon on the catalysts. In Eqs. [4] and [5], Wt and N^{carbon} represent weight of catalyst and carbon number in a molecule, respectively. Similarly, selectivity for the formation of a hydrogen-containing product on a hydrogen base can be calculated and, thus, the ratio of hydrogen to carbon in the coke formed can be estimated.

2.3. *TPO Measurements*

The amount of coke deposited on the catalysts was measured by the temperature-programmed oxidation (TPO) method. For the series of Mo/HZSM-5 catalysts (300–500 mg) after methane aromatization for 6 h at 973 K using pure methane and addition of various amounts of CO and CO_2 to the methane feed, the TPO measurement were made. Each catalyst sample was charged to a U-type quartz microreactor. After purging in a helium flow (30 ml/min) at 423 K for 1 h, the temperature of the sample was lowered to 313 K and the helium flow switched to air at a flow rate of 20 ml/min. CO_2 formation was monitored intermittently by a gas chromatograph at the ramping temperature rate (2 K/min).

2.4. *Isotopic Labeling Tracer Study*

The isotopic labeling experiment was conducted at 973 K using a gas mixture (220 Torr) of 92% methane and 8% ^{13}CO (99% purity, Prochem B.O.C. Limited) on 3 wt% Mo/HZSM-5 catalyst which was charged in a Pyrex-glass reactor equipped with a closed circulating reaction system. The benzene formed was collected at the ethanol–dry ice trap, which was subject to the on-line GC–MS analysis using a Perkin–Elmer gas chromatograph–mass spectrometer (Auto System GC with 910 Q-Mass). The Mo/HZSM-5 catalyst was pretreated with the gas mixture at 773–873 K for 1 h for the precarburization and was evacuated at 973 K for 1 h prior to starting the reaction at 973 K.

3. RESULTS AND DISCUSSION

3.1. *Reaction Analysis in Methane Dehydrocondensation on Mo/HZSM-5 Catalyst*

Using 2% Ar as internal standard for the reaction analysis, the present work was conducted to carefully evaluate the rates of formation and selectivities of hydrocarbon products and coke formation in the methane condensation reaction on HZSM-5 zeolite-supported Mo catalysts such as Mo/HZSM-5 and Co/Fe-modified Mo/HZSM-5. As was stated, coke evaluated from GC analysis consists of all the undetected carbon products such as amorphous and graphitic inert carbons and higher-boiling compounds that are difficult to detect and analyze with on-line FID and TCD gas chromatographs. To look at undetected carbon species, we analyzed all the condensable products except lower C_2–C_3 hydrocarbons in the effluent gas separated for 4 h by using the ethanol–dry ice trap in the methane reaction on 3 wt% Mo/HZSM-5 catalyst at 978 K. The collected reaction products were analyzed by the GS/MS with a capillary column (OV-1, 25 m) up to 553 K and TOFRM (time-of-flight reflect-mass) spectrometer (VOYGER MALDI-TOF; $m/e = 10$–2500; PerSeptive Biosystems Co.). Figure 1 shows the average product distribution (in percent selectivity on carbon base) of the aromatic compounds, which consist of benzene (69%), naphthalene (27%), and toluene (3.5%) as the major aromatic products and other polycondensed hydrocarbons such as anthracene, pyrene, tetracene, and their methyl-substituted derivatives in trace amounts. The latter polycondensed aromatic compounds are difficult to analyze with an on-line FID GC system using a Porapak-P column owing to their high boiling points and strong adsorption on separation columns. Thus, they are considered part of of coke materials in routine analyses of the reaction. Nevertheless, the total amount of such polycondensed products having more than 13 carbons was estimated to be not more than 2% on a carbon base with respect to the hydrocarbon products detected.

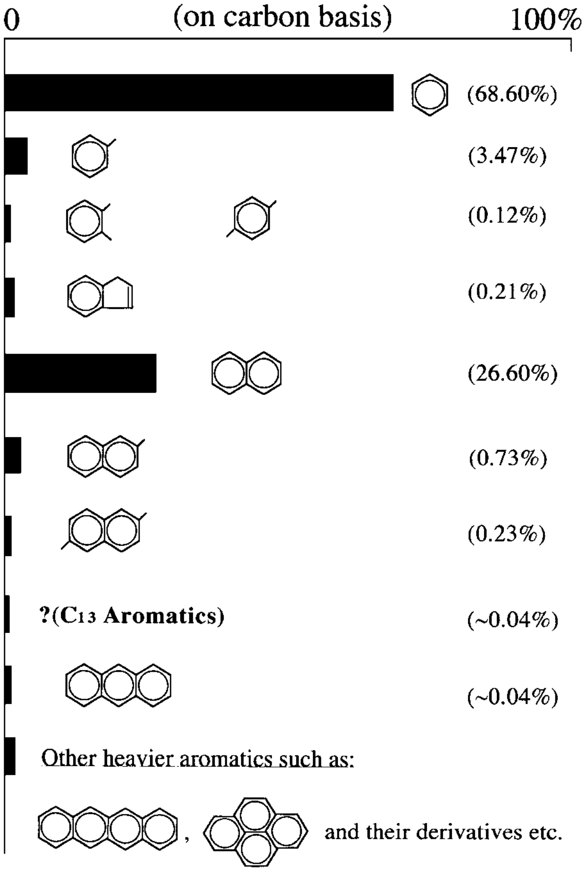


FIG. 1. Average distribution of aromatic compounds on carbon base formed in the methane dehydrocondensation on 3 wt% Mo/HZSM-5 at 973 K for 4 h.

3.2. Methane Conversion at 973 K on Mo/HZSM-5 Catalysts Using Pure Methane

The dehydrocondensation of methane was conducted by flowing pure methane (98% CH_4 + 2% Ar, 1 atm, SV = 1500 ml/g cat/h) on the catalysts in the fixed bed at 973 K. C_2 hydrocarbons and aromatic products such as benzene and naphthalene were continuously obtained together with a considerable evolution of hydrogen (H_2/benzene = 9–18 mol/mol) on 3 wt% Mo/HZSM-5 catalyst as shown in Fig. 2. Along with the mechanism proposed in previous reports (7–13, 15), it is conceivable that the catalytic dehydrocondensation of methane proceeds primarily by methane dissociation on Mo/HZSM-5 catalysts to form surface carbon species such as CH_x and C_2H_y ($x, y > 0$) on the Mo site of Mo carbide, which are oligomerized on HZSM-5 support having the proper acidity toward aromatic compounds such as benzene and naphthalene by bifunctional catalysis (15) as represented in Scheme 1.

As shown in Fig. 2, a part of the consumed methane is converted to CO and hydrogen besides benzene, naphthalene, and C_2 hydrocarbons, in the reaction of methane on Mo/HZSM-5. At the initial stage of the reaction, it has been suggested by XRD, XPS, and XAFS studies that the impregnated Mo oxides are converted to Mo carbide which was highly dispersed on the HZSM-5 support, as previously reported (8, 14, 15). As indicated in Figs. 2a and 2b, the conversion of methane (10–12%) and rates of total hydrocarbon formation (800–1000 nmol/g cat/s) on a carbon base obtained at an early stage of the reaction on 3 wt% Mo/HZSM-5 at 973 K usually decrease rapidly at the initial stage of a few hours and moderately at the later stage of the reaction down to less than 4% and 500 nmol/g cat/s in 30 h (1800 min), respectively, possibly due to the significant coke formation. Both the hydrocarbons and coke produced show stable carbon-based selectivities of 60–68 and 38–32%, respectively, with a negligible CO selectivity of less than 1%. As shown in Fig. 2c benzene and naphthalene were equally obtained on carbon base at the initial stage of the methane reaction on Mo/HZSM-5. It is interesting to find that the carbon-base composition of benzene in hydrocarbon products increased and maintained higher levels of 63–68% at the prolonged time-on-stream of 30 h. By contrast, C_2 hydrocarbons such as ethene and ethane increased linearly from 4 to 20% at the expense of naphthalene (42–12%). The other aliphatic compounds such as propene and butene and other aromatics such as toluene were produced in small amounts (totally less than several percent selectivity) as shown in Fig. 1. Further bulky substituted aromatic compounds such as xylene, mesitylene, methyl-naphthalene, dimethylnaphthalene, phenanthrene, anthracene, dimethylanthracene, and tetracene were obtained in trace amounts on these catalysts at 973 K, possibly because of the higher reactivity of hydrogenolysis and molecular shape selectivity of the HZSM-5 support due

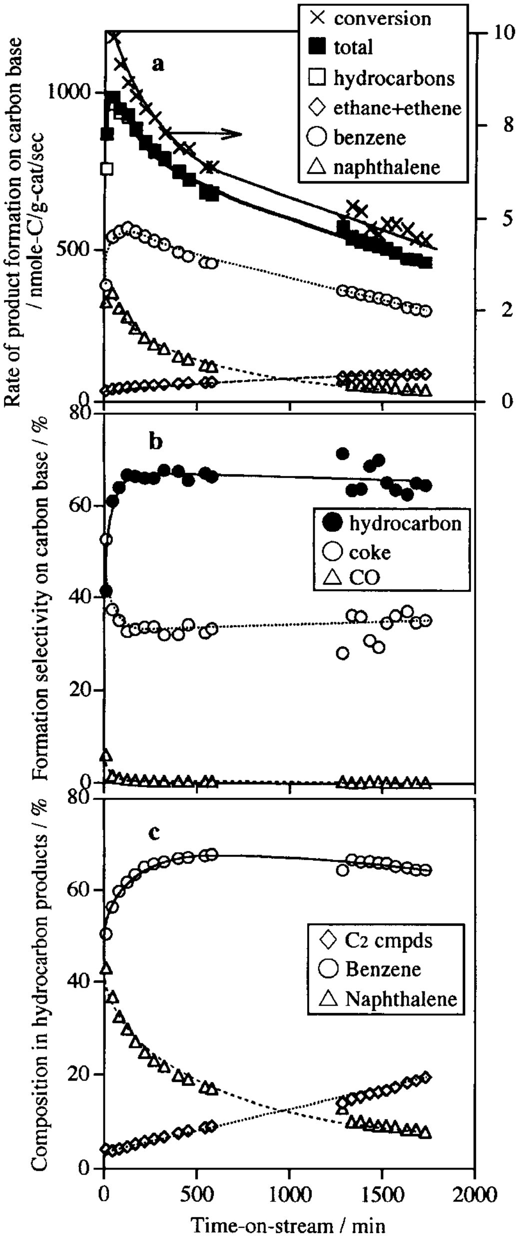
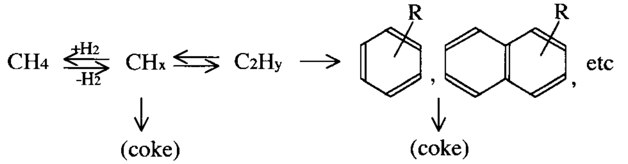


FIG. 2. Catalytic performance in the methane conversion at 973 K on 3 wt% Mo/HZSM-5: (a) methane conversion (%) and rates of product formation for benzene, naphthalene, and C_2 hydrocarbons on carbon base (nmol/s/g cat), (b) selectivities of hydrocarbons, coke, and CO formation (%), and (c) product composition (%) on carbon base for hydrocarbon products versus time on stream (min).



SCHEME 1. Proposed bifunctional mechanism of the dehydrocondensation of methane toward aromatic products such as benzene and naphthalene via the surface hydrocarbon species on Mo/HZSM-5 catalysts.

to its limited channel size of 5–6 Å accessible to smaller-sized products such as benzene and toluene. During catalyst deactivation on the 3 wt% Mo/HZSM-5 at 973 K, it was suggested that the formation of aromatics decreased more seriously in the order of the more polycondensed hydrocarbons as follows: benzene $\ll$ naphthalene, anthracene, pyrene and tetracene. Those of C_2 hydrocarbons increased effectively possibly owing to the coke formation. This evidence is implicated in the effective poisoning by coke to retard the successive formation of polycondensed aromatic compounds from precursor carbon species such as CH_x and C_2H_y derived from methane on Mo sites impregnated on HZSM-5 supports. It is conceivable from the mechanism proposed in Scheme 1 that the formation of benzene and naphthalene is a structure-sensitive reaction that requires larger ensembles (concentration) of the precursor carbon species. The deactivated Mo/HZSM-5, after the prolonged reaction of methane for 30 h at 973 K, was almost completely regenerated by its calcination with flowing air (or pure O_2) at 873 K for 2 h, showing methane conversions and product selectivities similar to those of fresh Mo/HZSM-5. The observed catalytic performance of Mo/ZSM-5 in methane conversion differs largely from those overestimated values reported by Wang *et al.* (3, 4, 7, 8) and others (9–11) in previous papers. Such a large discrepancy with the previous data may be due mainly to the analytic accuracy of the consumed methane concentration without properly using an internal standard such as Ar and N_2 and neglecting, in previous reports, the appreciable contribution of higher polycondensed hydrocarbons such as naphthalene, methyl-naphthalene, and anthracene except benzene and toluene as aromatic products in the reaction.

3.3. Remarkable Promotion of CO Addition to the Methane Feed in the Catalytic Production of Benzene and Naphthalene on Mo/HZSM-5

Figures 3 and 4 show that the addition of 1.8–12% (v/v) CO to methane feed gas induces a significant effect on the catalytic performance of 3 wt% Mo/HZSM-5 and improves catalyst stability. Using pure CH_4 (balanced with 2% Ar) as the feed gas, methane conversion and benzene formation rate on those catalysts decreased greatly during 30 h of reaction time-on-stream, as shown in Fig. 2. While with the addition of 1.8% (v/v) CO in the feed gas, the early drop in methane conversion was substantially moderated and the higher levels of methane conversion (8–9%) retained at the prolonged time-on-stream of 30 h, as indicated in Fig. 3a. Moreover, Fig. 3b shows that the conversion of methane with 1.8% CO provided stable performance for carbon-base selectivities (ca. 70%) of hydrocarbons and lower coke formation (ca. 30% selectivity), compared with those using pure methane. On the other hand, it is shown in Fig. 3a that after attaining a maximum value in the early stage, the rate of benzene formation remained almost constant at 520 nmol/g cat/s on carbon base during the prolonged reaction of methane with 1.8% CO. In addition, as shown in Fig. 3c, the catalytic conversion of methane with 1.8% CO yielded higher selectivities of naphthalene

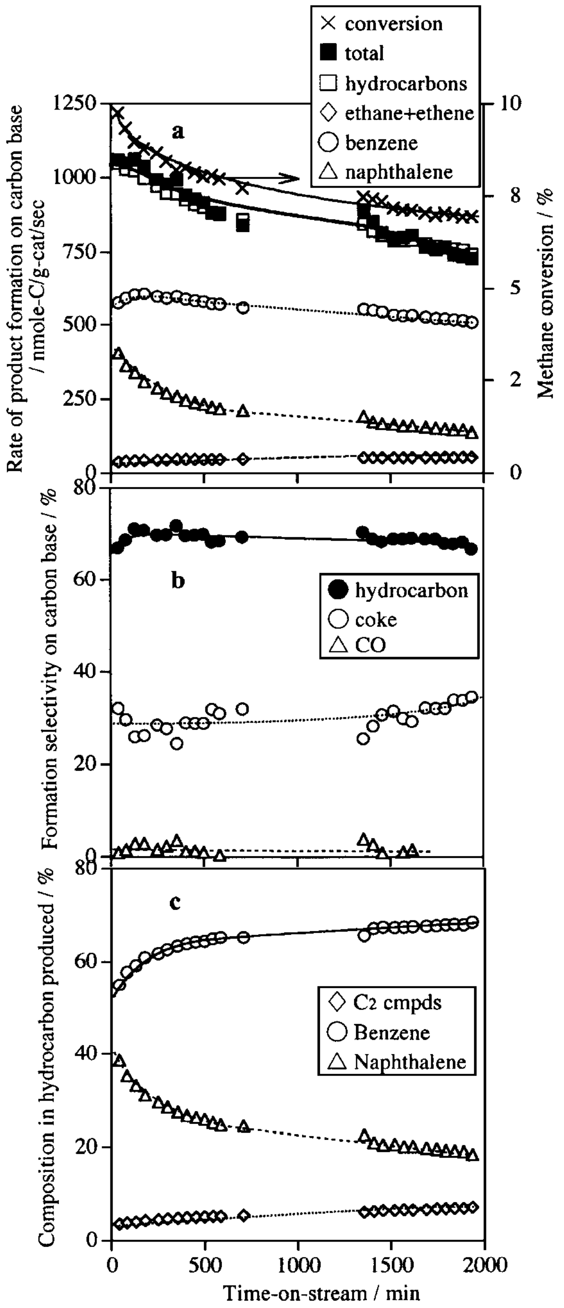


FIG. 3. Effect of 1.8% CO addition to methane feed on (a) methane conversion (%) and rates of product formation for benzene, naphthalene, and C_2 hydrocarbons on carbon base (nmol/s/g cat), (b) selectivities of hydrocarbons, coke, and CO formation (%), and (c) product composition (%) on carbon base for hydrocarbon products versus time on stream (min).

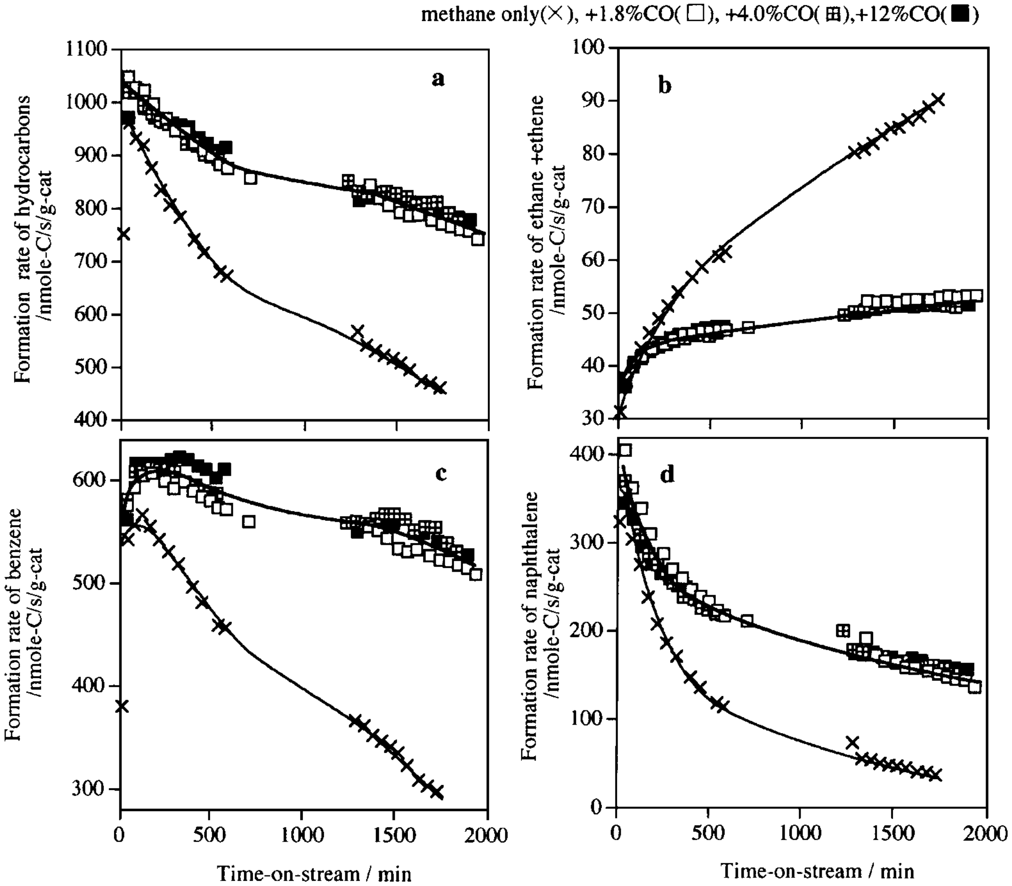


FIG. 4. Effect of CO addition to methane feed by varying CO concentration (1.8, 4.0, and 12%) for formation rate (nmol/s/g cat) on carbon base of (a) hydrocarbons, (b) ethene + ethane, (c) benzene, and (d) naphthalene versus time on stream (min).

(20–30%) and lower selectivities of C_2 hydrocarbons (5–7%) in the hydrocarbon products than the conversion of pure methane (Fig. 2c) in due course of the reaction over 20 h.

By varying the concentration (1.8–12%) of CO in the methane feed it was demonstrated that the similar promotion, regardless of CO concentration, was attained at 973 K on 3 wt% Mo/HZSM-5 catalyst to greatly stabilize the formation rates of hydrocarbons (Fig. 4a), C_2 hydrocarbons (Fig. 4b), benzene (Fig. 4c), and naphthalene (Fig. 4d) at prolonged times-on-stream over 30 h, compared with those using pure methane. It is obvious as shown in Figs. 4d and 4b that the addition of CO to the methane resulted in enhancement of naphthalene formation, while suppressing C_2 hydrocarbons, possibly due to the reduction of coke poisoning on the catalyst. Although the product selectivities and promotion of catalyst stability were greatly affected by adding CO to the methane feed, it is interesting to find that the concentrations of CO in the gas phase of the reaction remained unchanged similar to those in the feed gas, as indicated in Fig. 7, which is discussed in next section.

3.4. Effect of CO_2 Addition in Methane Conversion on Mo/HZSM-5

Similarly, catalyst stability for the methane dehydrocondensation at 973 K on 3 wt% Mo/HZSM-5 was also improved by adding 1.6% CO_2 to the methane feed gas, as shown in Fig. 5a. The addition of 1.6% CO_2 yielded a higher methane conversion and higher formation rate than the addition of CO for 600 min, possibly owing to the reforming reaction ($CO_2 + CH_4 = 2CO + 2H_2$). It was also demonstrated as shown in Figs. 5a and 5b that methane conversion (%) and composition (%) of benzene among the hydrocarbon products are stable, maintaining higher values of more than 8 and 62–68%, respectively, by adding CO_2 to methane feed at the prolonged time on stream, as is the case for CO added to methane feed.

Although the rates of hydrocarbon (Fig. 6a) and benzene (Fig. 6c) formation were relatively suppressed by increasing the CO_2 concentration from 1.6 to 4.1% and were lower than those using CO (Figs. 4a and 4c), the rates do not change for long time-on-stream as in the case of CO addition to the feed gas. Similarly, the rates of formation of C_2

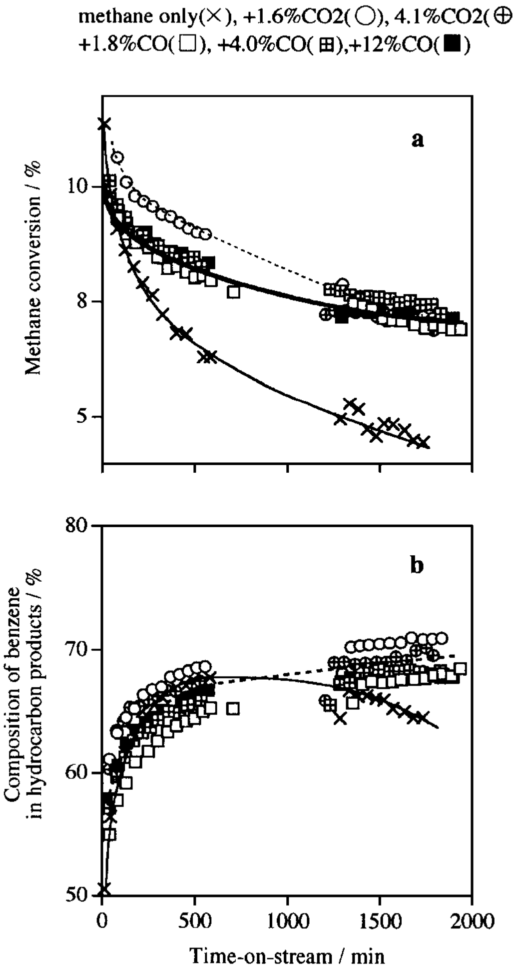


FIG. 5. Effect of CO and CO_2 addition to the methane feed at 973 K on 3 wt% Mo/HZSM-5 for (a) methane conversion (%) and (b) composition (%) of benzene on carbon base in the hydrocarbon products versus time on steam (min).

hydrocarbons and naphthalene change a little, as shown in Figs. 6b and 6d, in a manner similar to that of CO, whereas those effects were dependent on the amount of CO_2. In contrast with CO, it was found that excessive addition of CO_2 (>4%) in the methane feed gas largely inhibits the formation of aromatic products such as benzene and naphthalene with significant evolution of CO and hydrogen at 973 K. Figure 6a shows that the addition of 12% CO_2 to the methane feed results in complete inhibition of the formation of aromatic products such as benzene and naphthalene. Only a small amount of C_2 hydrocarbons was produced in the conversion of methane with 12% CO_2 at 973 K on Mo/HZSM-5 (Fig. 6b). This evidence is in agreement with the marked suppression of benzene formation by the pulse addition of 10% CO_2 in the methane reaction on Mo/ZSM-5, which has been reported previously by Lunsford and coworkers (12). The similar results in the reaction with 12% CO_2 were obtained by the addition of a few percent of O_2 to the methane feed at 973 K, which resulted in complete inhibition of benzene formation on 3 wt% Mo/HZSM-5.

As indicated in Fig. 7, it is interesting that when the partial pressure of CO_2 was low (<4%) in the feed gas, double the amount of CO with respect to CO_2 added to the methane feed gas was produced on a carbon base, while no CO_2 was observed in the outlet gas of the reaction. In contrast, the concentration of CO did not change from inlet to outlet of the reactor. It is suggested that CO_2 is completely converted with CH_4 or carbon to produce double the amount of CO by the reforming process ($CO_2 + CH_4 = 2CO + 2H_2$) or reverse Boudart reaction ($CO_2 + C = 2CO$) under the reaction conditions. To examine the fate of CO, equilibrium constants were calculated for the three possible reactions of $C + CO_2 = 2CO$, $CH_4 + CO_2 = 2CO + 2H_2$, and $CH_4 + H_2O = CO + 3H_2$ and determined to be 1.1, 8.7, and 13.4, respectively, at 973 K (16). It is clear in the second and third reactions that the equilibriums lie far to the right. Even in the first reaction the equilibrium should shift to the right because that some amount of coke derived from methane is present as shown in Figs. 2b and 3b. Accordingly, it is understood from thermodynamic considerations that the concentration of CO apparently remains unchanged in the reactor under the experimental conditions. The different effects of CO and CO_2 on methane aromatization may be associated with their different chemical stabilities in the reaction media: CO is stable and CO_2 reacts with methane and surface coke to form CO and H_2. Similar to the previous discussion on the poisoning effect of coke in Section 3.2, there is an analogous explanation that the catalytic formation of aromatics such as benzene requires a large ensemble (surface concentration) of active CH_x species on the Mo sites in the vicinity of the HZSM-5 support (13, 15). It may be plausible that excessive addition of CO_2 (more than 10%) and a few percent of O_2 as an oxygen donor with respect to methane results in vital suppression of surface-active carbon species, which may possibly be Mo_2C, and the conversion toward the aromatic products such as benzene and naphthalene. The results for CO_2 may be closely related to the promotional role of CO addition in stabilizing the catalyst performance in the methane aromatization reaction.

3.5. Stable Catalytic Conversion of Methane Together with CO toward Benzene on Fe- and Co-Modified Mo/HZSM-5 Catalysts

By the addition of 4% (v/v) CO to 1 atm methane flow at 973 K, Co- and Fe-modified Mo/HZSM-5 catalysts markedly improve their catalytic performance in the methane aromatization reaction, as shown in Figs. 8 and 9, respectively. These figures show that the rates of benzene formation in the conversion of methane together with 4% (v/v) CO on 1 wt% Fe- or 1 wt% Co-modified 3 wt% Mo/HZSM-5 catalyst are enhanced by 1.2–1.5 times

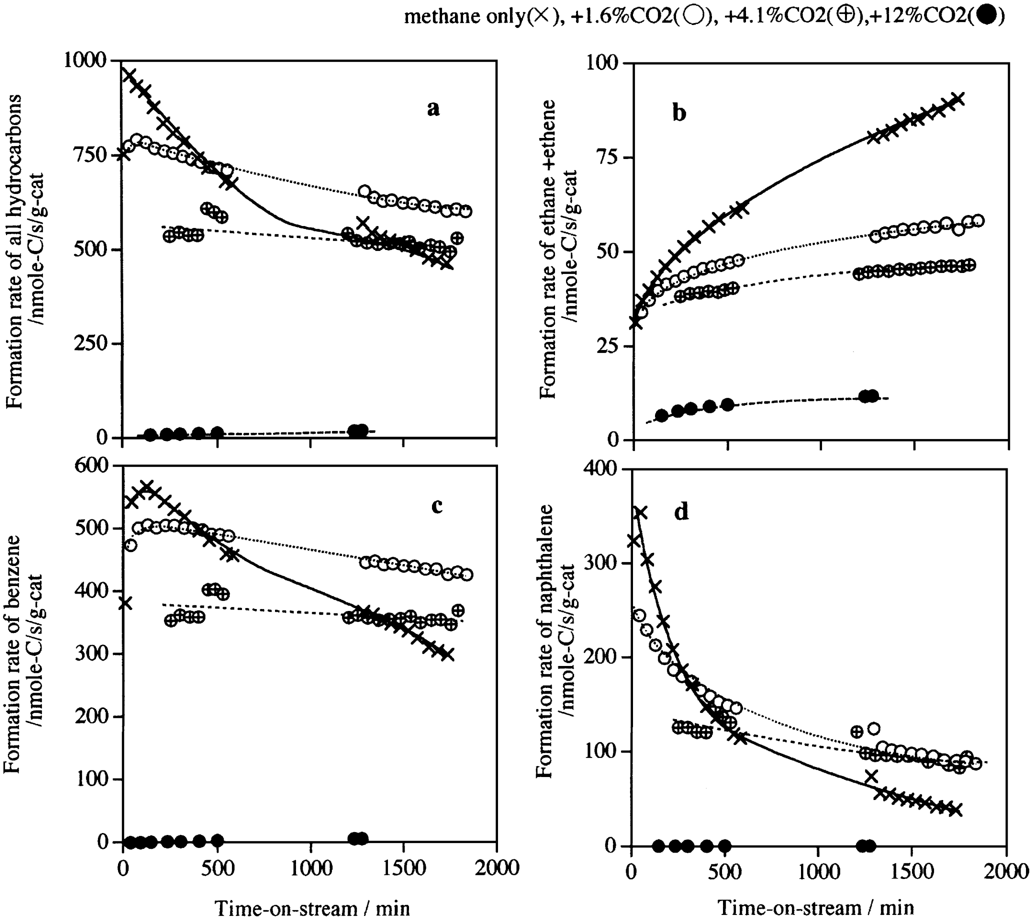


FIG. 6. Effect of CO_2 addition to methane feed by varying CO_2 concentration (1.6, 4.1, and 12%) for formation rate (nmol/s/g cat) on carbon base of (a) hydrocarbons, (b) ethene + ethane, (c) benzene, and (d) naphthalene versus time on stream (min).

compared with those using pure methane, and a marked improvement in catalyst stability is effected by maintaining rates of benzene formation high (700–1000 nmol/g cat/s) and selectivities greater than 80% at the prolonged time-on-stream of 30–100 h. Moreover, it was found that coke selectivity was greatly reduced to less than 20% using methane with CO, as shown in Figs. 8b and 9b. CO addition to methane feed is usually effective in improving catalyst stability on Fe/Co-modified Mo/HZSM-5, similar to Mo/HZSM-5, regardless of variations in Mo loading (3–20 wt% Mo) and reaction conditions, e.g., reaction temperatures of 773–1023 K.

3.6. TPO Studies on Effective Suppression of Coke Formation in the Conversion of Methane Together with CO and CO_2 on Mo/HZSM-5 Catalyst

The TPO experiments were conducted to evaluate coke formation on Mo/HZSM-5 catalysts after the reaction using pure methane and a mixture of methane and CO (or CO_2) at 973 K for 6 h. Figure 10 shows the TPO patterns as a function of CO_2 formation on each sample of 3% Mo/HZSM-5. The TPO studies demonstrated that the total amounts of coke deposited on Mo/HZSM-5 catalyst were greatly reduced by adding various amounts of CO or CO_2 to the methane feed gas. Using pure methane, irreversible or inert coke (referred to the TPO peak at temperatures above 773 K) is preferentially formed on Mo/HZSM-5, which was not easily oxidized to CO_2 in the TPO experiment. By the addition of higher concentrations of CO (4.0–12%) the reaction of methane with CO preferentially reduced such inert coke and left the more reactive coke as the TPO peak at temperatures lower than 673 K, which may be associated with Mo_2C. On the other hand, addition of CO_2 (1.4–4.0%) to methane feed gas more effectively reduced not only the inert coke but also the reactive coke, leaving a small contribution of the reactive coke, which is oxidized at temperatures lower than 690 K. These TPO data are consistent with the catalytic performance of methane aromatization by addition of CO_2 to methane feed, different from those of CO addition as is discussed in Section 3.4. This is because of the higher oxygen-donor ability of CO_2 to eliminate the surface

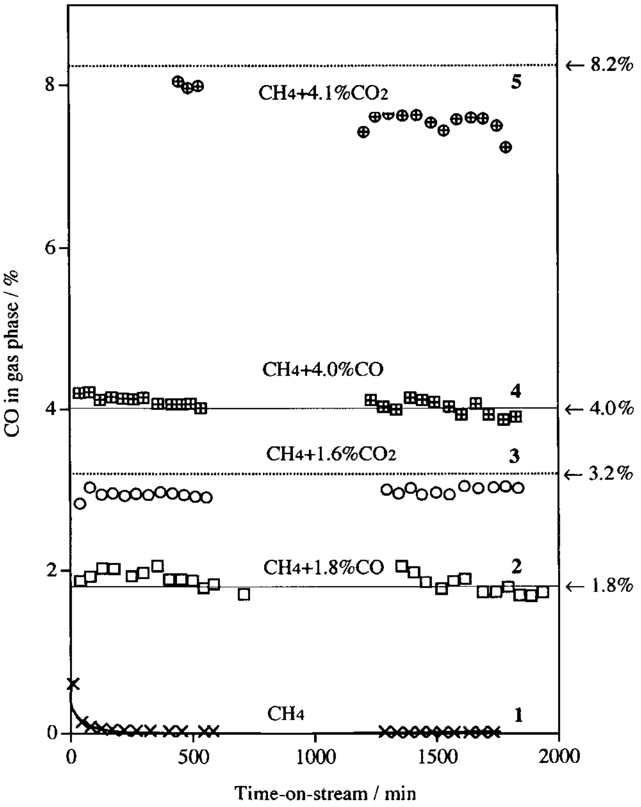


FIG. 7. Percentage CO in gas phase for a reacting gas of (1) methane, (2) methane + 1.8% CO, (3) methane + 1.6% CO_2, (4) methane + 4.0% CO, and (5) methane + 4.1% CO_2 versus time on stream (min).

carbon (coke) by forming CO ($CO_2 + C$ or $CH_x \rightarrow 2CO$) on Mo/HZSM-5 and Co/Fe-modified Mo/HZSM-5 catalysts at the higher temperature of 973 K. The excessive addition of CO_2 (more than 10%) to methane feed results in vital suppression of surface-active carbon species to form aromatic products such as benzene and naphthalene.

3.7. Isotopic Labeling Tracer Experiments in the Dehydrocondensation of Methane with ^{13}CO on Mo/HZSM-5 Catalyst

To understand the role of CO in the methane aromatization reaction, the $^{13}CO + CH_4$ reaction was conducted at 973 K in a closed circulating reaction system. The starting composition of the mixture reactant is 8% ^{13}CO + 92% CH_4 with a total pressure around 220 Torr. As shown in Fig. 11, even at the early stage of the reaction or after 5–10 min, ^{13}C atoms incorporated into methane ($^{13}CH_4$) and ethene reached an equilibrium value of 8% on one carbon, and the proportion of ^{13}CO in carbon monoxide decreased to 18% from 99%, while the abundance of ^{13}C on one carbon in a benzene molecule formed was higher (12–15%) than that at equilibrium (8%). GC-MS analysis of benzene revealed ^{13}C to be randomly distributed and multiply incorporated into a benzene molecule produced (up to $^{13}C_4C_2H_6$) on the admission of 8% ^{13}CO + 92% CH_4 on Mo/HZSM-5. These results suggest that the carbon derived from CO is efficiently incorporated into the benzene molecule in comparison with the isotopic scrambling reaction between ^{13}CO and $^{12}CH_4$ which proceeds under the reaction conditions at 973 K. Naito *et al.* conducted the reaction of methane + ^{13}CO (1 : 1 mixture) over silica-supported Rh catalyst at 623 K in a closed gas circulation

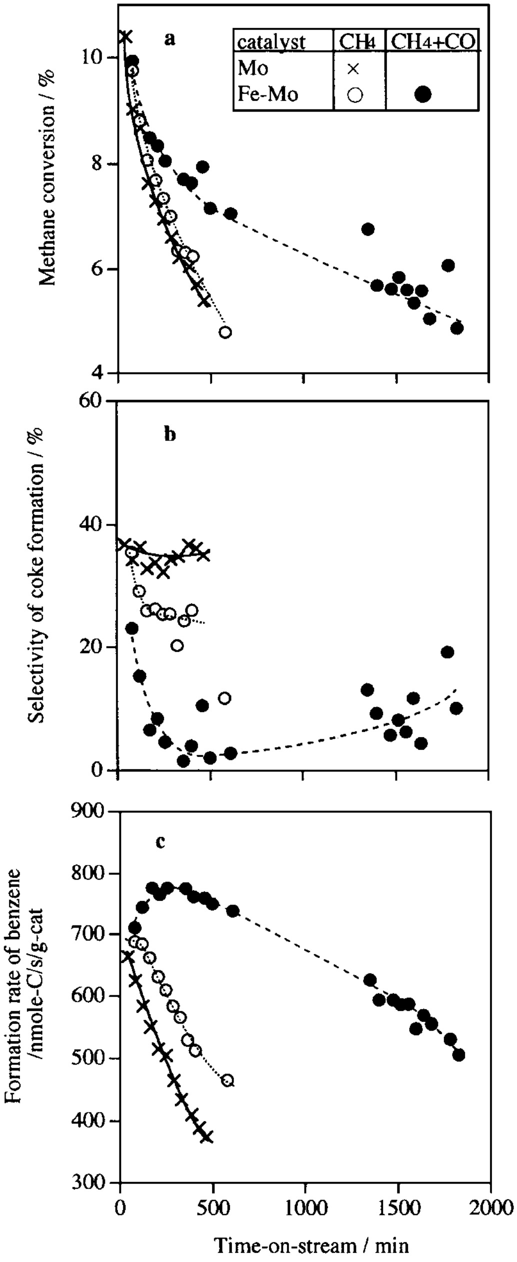


FIG. 8. Effect of 4% CO addition to methane feed on 1 wt% Fe 3 wt% Mo/HZSM-5 at 973 K for (a) methane conversion (%), (b) selectivity of coke formation (%), and (c) formation rate of benzene (nmol/s/g cat) on carbon base versus time on stream (min).

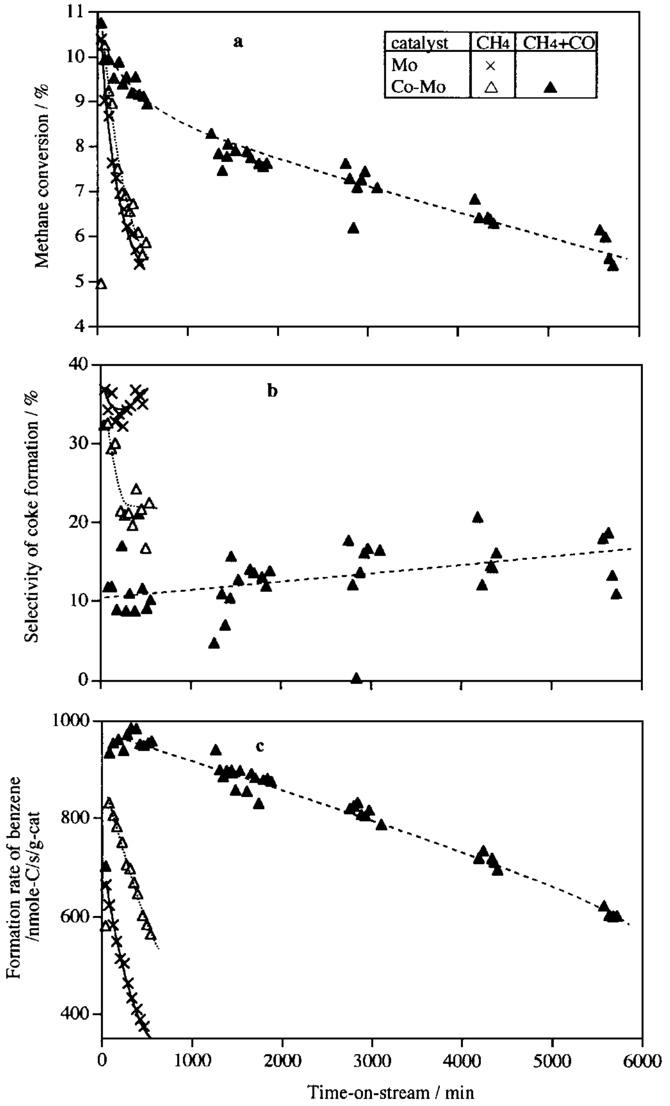


FIG. 9. Effect of 4% CO addition to methane feed on 1 wt% Co 3 wt% Mo/HZSM-5 at 973 K for (a) methane conversion (%), (b) selectivity of coke formation (%), and (c) formation rate of benzene (nmol/s/g cat) on carbon base versus time on stream (min).

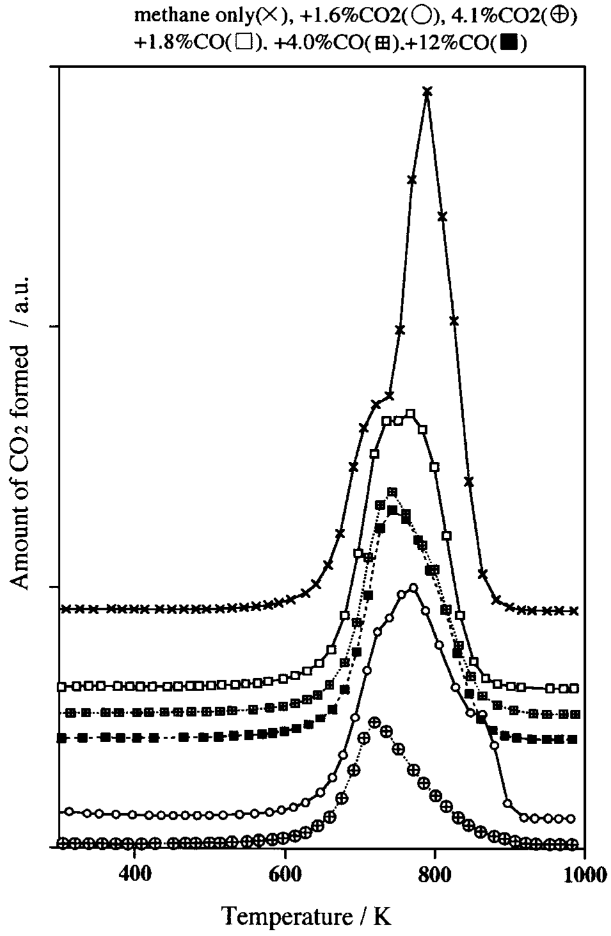
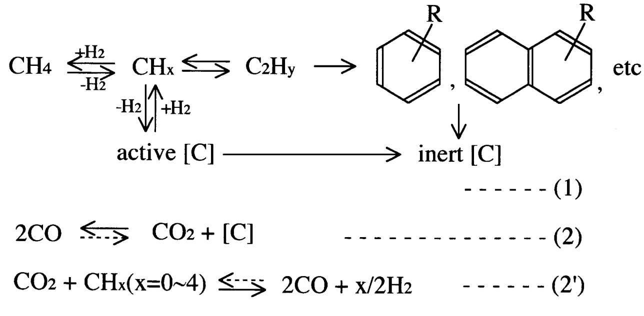


FIG. 10. TPO patterns of 3 wt% Mo/HZSM-5 catalyst after methane aromatization reaction running for 6 h at 973 K and 1 atm pressure with different amounts of CO or CO_2 added to methane feed gas. (TPO experiments were carried out using 300 mg of catalyst at an air flow rate of 20 ml/min and temperature raising rate of 2 K/min.)

system. In line with our results, they observed that more than 80% of the carbon in a benzene molecule comes from ^{13}CO, in forming of $^{13}C_6H_6 = 20\%$, $^{13}C_5{}^{12}CH_6 = 55\%$ and $^{13}C_4{}^{12}C_2H_6 = 25\%$ (17). It is conceivable that carbon [C] derived from CO is effectively hydrogenated to a common active carbon species CH_x similar to those from methane, which is converted to aromatics such as benzene and naphthalene.

Based on the TPO and ^{13}CO isotopic labeling experiments, we suggest a mechanism in which CO has the unique role in the methane aromatization reaction of stabilizing catalyst performances and promoting benzene formation as shown in Scheme 2. First, minute amounts of CO_2 and C are formed from CO via the Boudart reaction [reaction (2)] on Mo/HZSM-5. [C] is reacted with hydrogen and/or methane to form the active carbon intermediate species, CH_x and C_2H_y, which are dehydrocondensed to the higher hydrocarbons such as benzene and naphthalene on Mo/HZSM-5 catalyst with the help of acidic sites as shown in reactions



SCHEME 2. Proposed mechanism for promotion of CO/CO_2 addition to methane feed to improve catalyst stability and reduce coke formation on Mo/HZSM-5 catalysts.

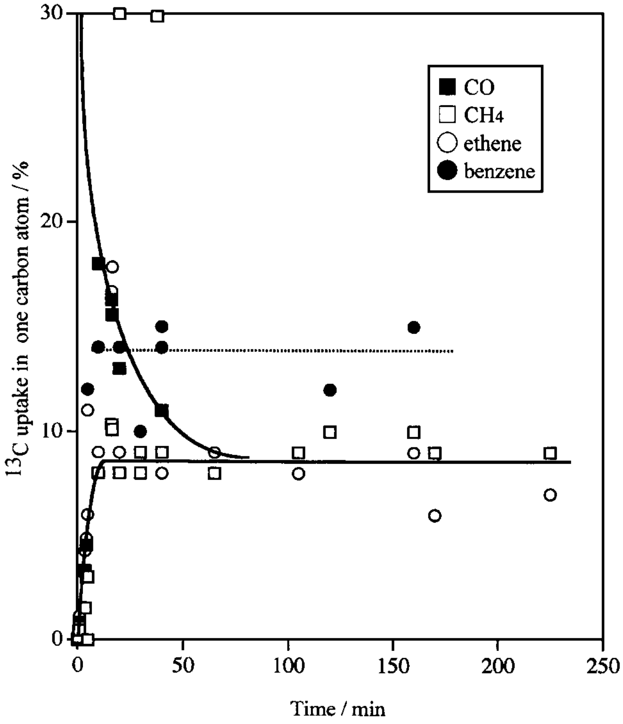


FIG. 11. Abundance (%) of ^{13}C atom in one carbon atom of methane, CO, ethene, and benzene formed versus exposure time (min) in the reaction with a gas mixture of methane (92%) and ^{13}CO (8%) (total pressure, 220 Torr) on 3 wt% Mo/HZSM-5 catalyst at 973 K in a closed circulating reactor.

(1), while CO_2 reacts with the surface carbon species to regenerate CO via reaction (2′). Similarly, CO_2 added to the methane feed partly reacts with methane, producing double moles of hydrogen and CO as reaction (2′) and $x = 4$, giving higher conversion of methane. Other CO_2 added effectively reacts with the surface coke (carbon species) and surface hydrocarbon species (CH_x and C_2H_y species) as reaction (2′). Such effective consumption of surface intermediates with an excess amount of CO_2 causes the marked suppression of methane aromatization toward benzene and naphthalene.

Independently, it was found that negligible amounts of aromatic products such as benzene and naphthalene were detected in the reaction of $CO + H_2$ 1 : 2 (v/v) as in the Fischer–Tropsch (FT) reaction on 3 wt% Mo/HZSM-5 under the similar reaction conditions of 1 atm and 873-973 K, although appreciable amounts of methane and CO_2 were detected in the gas phase. The results imply that CO is converted with methane, but not with hydrogen, toward aromatic products such as benzene and naphthalene on Mo/HZSM-5 catalyst. The FT reaction by CO and hydrogen produces a lot of water and CO_2, which poison the catalytic formation of aromatic compounds on Mo/HZSM-5 catalysts, although both the FT reaction and methane aromatization are proposed to proceed via the common intermediates (CH_x and C_2H_y species).

4. CONCLUSIONS

1. The addition of a few percent of CO and CO_2 to the methane feed gas significantly promotes catalytic stability in the dehydrocondensation of methane toward aromatic products such as benzene and naphthalene on Mo/HZSM-5 and Co/Fe-modified Mo/HZSM-5 catalysts at 973 K, compared with pure methane.
2. The reaction of methane with 1.6–12% CO on Co/Fe-modified Mo/HZSM-5 catalysts yields higher selectivities (70%) of benzene formation at 5–12% methane conversion and minimizes coke formation to less than 20% selectivity, resulting in the promotion of catalytic performance and improvement of catalyst stability.
3. Adding a few percent of CO_2 to the methane feed results in the promotion of catalyst stability in forming CO by the reforming reaction ($CO_2 + CH_4 = 2CO + 2H_2$) and/or the reverse Boudart reaction ($CO_2 + C = 2CO$) at 973 K on the catalysts. While excessive addition of CO_2 (>10%) to the methane feed gas largely inhibits the formation of aromatic products such as benzene, similarly to complete poisoning by addition of a few percent of O_2.
4. The TPO studies demonstrated that the formation of coke in the methane reaction with CO and/or CO_2 at 973 K on Mo/HZSM-5 was effectively reduced, compared with those using pure methane.
5. From the TPO and ^{13}CO isotopic labeling studies the unique promotion of CO addition in the dehydrocondensation of methane to improve catalytic stability is discussed in terms of the formation of CO_2 and C via the Boudart reaction. The [C] formed is preferentially incorporated into benzene and naphthalene over into methane, while CO_2 reacts with the coke to regenerate CO, resulting in effective reduction of coke formation on the catalysts.

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