Unique promotion effect of CO and CO_2 on the catalytic stability for benzene and naphthalene production from methane on Mo/HZSM-5 catalysts

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The addition of CO and CO_2 to the methane feed results in a remarkable promotion of catalyst stability for direct benzene and naphthalene production from methane on Mo/HZSM-5 and Co modified Mo/HZSM-5 catalysts at 973 K owing to the efficient suppression of coke formation.

The catalytic conversion of methane to petrochemical feedstocks such as ethylene and benzene is of current importance and industrial interest in the effective utilization of carbon resources of natural gas. During the past five years, the non-oxidative conversion of methane to benzene has been studied on zeolite-supported Mo catalysts in terms of the reaction mechanism and catalyst characterization.[1–6] Our recent works demonstrate the methane is effectively dehydrocondensed into various aromatics such as benzene and naphthalene on Mo/HZSM-5 and modified Mo/HZSM-5 at high temperatures of 873–1073 K.[7] Nevertheless, methane conversion decreased drastically after a few hours owing to serious coke deposition on the catalysts. To reduce coke formation, some preliminary efforts have been reported using selected oxidative reagents such as oxygen[2] and carbon dioxide (10% or higher in the methane gas feed),[6] but aromatic product formation was completely inhibited on Mo/HZSM-5 catalysts. Here we describe that the inclusion of CO and/or CO_2 in the methane flow results in the promotion of aromatic product formation and a remarkable improvement of the catalyst stability in the prolonged dehydrocondensation reaction of methane at 973 K on Mo/HZSM-5 and CoMo/HZSM-5 catalysts owing to the substantial suppression of coke formation on the catalysts. Furthermore, ^{13}CO isotopic labeling and temperature programmed oxidation (TPO) experiments demonstrate that the CO added to the methane feed, as a carbon and oxygen donor when it is dissociated on the catalysts, not only is efficiently incorporated into aromatics such as benzene, but also results in removal of the surface coke.

Mo/HZSM-5 and Co modified Mo/HZSM-5 catalysts with 3 wt.% Mo loading were prepared by impregnation (incipient wetness) of NH_4ZSM-5 (SiO_2/Al_2O_3 = 20–1900; surface area, 780–925 $m^2\ g^{-1}$, Toso Co. and CRI Zeolyst, Inc.) with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Co(NO_3)_2$ aqueous solutions. After the impregnated samples were dried at 393 K and calcined at 773 K in air, catalytic tests were carried out under methane (1 atm), both with and without CO or CO_2, in a continuous microreactor system equipped with a quartz tube (8 mm id) packed with 0.3 g of catalyst pellets of 20–24 mesh, as reported previoulsy.[7] After flushing with He at 973 K, a feed gas mixture of 98% CH_4 with 2% Ar as internal standard for analysis both with and without CO or CO_2 was introduced into the fixed bed reactor at a flow rate of 7.5 ml min^{-1} [space velocity = 1500 ml h^{-1} (g cat)$^{-1}$] through a mass flow controller (Brooks 5850E). Using an internal standard analyzing method, conversion of methane, CO and CO_2, selectivities of hydrocarbon products and coke formed on the catalyst were evaluated to the mass balance for carbon and hydrogen.[7] The reaction between CO and CH_4 on Mo/HZSM-5 was studied by using the isotopic labeling (^{13}CO, 99% enriched) technique in a closed circulating reaction system, and both the gas phase mixture (containing mainly methane, carbon monoxide, ethane and ethylene) and the condensed products (mainly benzene collected using an ethanol–dry ice trap) were analyzed by GC-MS (Perkin-Elmer, Auto System GC, 910 Q-Mass). The coke deposited on the catalyst surface after reaction was evaluated by a TPO technique using 20% O_2 + 80% N_2 as the oxidant, and the tail gas was intermittently analyzed by on-line GC.

The addition of CO to the methane feed gas exerts a significant effect on the catalytic performances of Mo/HZSM-5 and CoMo/HZSM-5 for methane dehydrocondensation to promote the formation of benzene and naphthalene, and on the catalyst stability, as shown in Figs. 1 and 2. Using pure methane as the feed gas the methane conversion and benzene formation rates decreased greatly (less than 1/4–1/5 of the initial activities during 24 h reaction time on stream). By contrast, for methane with 1.8–12% CO in the feed gas, the decrease in methane conversion was much lower, regardless of the partial pressure of CO, as shown in Fig. 1. After attaining a moderate increase of benzene and naphthalene formation rates, compared with those achieved using pure methane in the early stage of the reaction, their formation rates were almost constant during prolonged reaction of more than 50 h. In the steady reaction stage, the amount of CO is almost constant before and after reaction

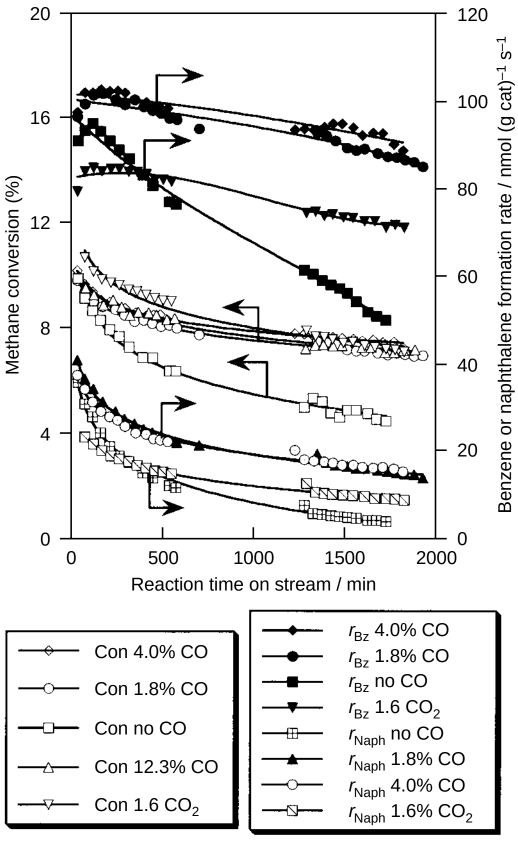


Fig. 1 Catalytic performances of 3% Mo/HZSM-5 for methane aromatization with the addition of CO and CO_2 to the methane feed gas at 973 K [Open symbols represent methane conversion and solid symbols the formation rates of benzene (r_{Bz}) and naphthalene (r_{Naph}), respectively]

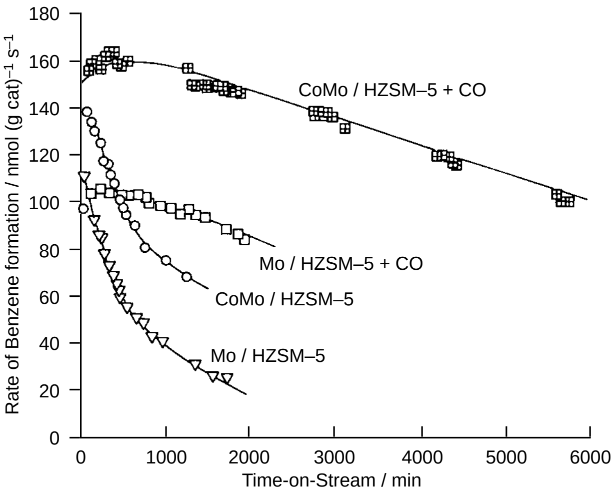
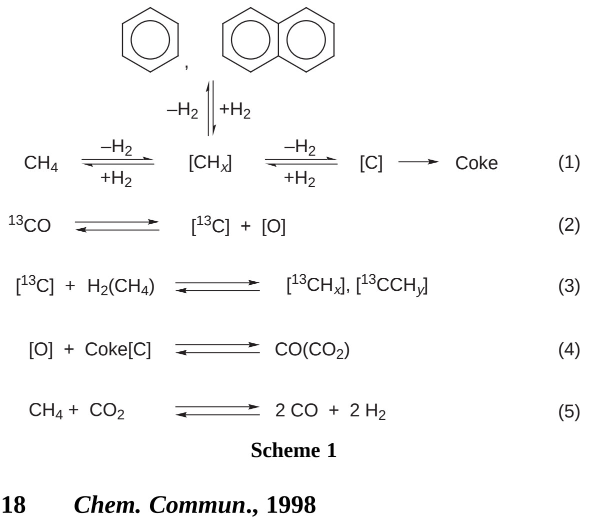


Fig. 2 Rates of benzene formation in methane aromatization reaction on 3% Mo/HZSM-5 (▽) and 1% Co, 3% Mo/HZSM-5 (○) catalysts using pure methane and (□) on 3% Mo/HZSM-5 and (⊞) on 1% Co, 3% Mo/HZSM-5 using methane + 4% CO at 973 K and 1 atm

through the catalyst beds in all cases of CO addition. The results imply that CO is regenerated, possibly due to the reaction of the surface carbon with the active oxygen species derived from CO dissociation as shown in Scheme 1.

These remarkable effects (improved catalytic stability, increased promotion of benzene formation) caused by the inclusion of CO have also been observed for modified catalysts such as CoMo/HZSM-5, as is shown in Fig. 2. The benzene formation rates are above 100 nmol (g cat)$^{-1}$ s^{-1} even after 100 h on the CoMo/HZSM-5 in the reaction of CH_4 + 3.5% CO, while the activity decreased greatly [less than 10 nmol (g cat)$^{-1}$ s^{-1}] using pure methane under the same reaction conditions.

Similarly, the stability of the catalyst was also improved by adding a few per cent CO_2 into the feed gas, as shown in Fig. 1. The addition of 1.6% CO_2 yielded higher methane conversion and hydrogen formation rate. Benzene formation was suppressed in comparison with that achieved with CO addition, but it was stable during the prolonged reaction time. Nevertheless, it was found that the addition of larger amounts of CO_2 (> 10%) in the methane feed gas largely inhibited the formation of aromatic products such as benzene. When the partial pressure of CO_2 was low (< 4%) in the feed gas, twice the amount of CO was detected compared with when CO_2 was added to the feed gas on the basis of the carbon content, while no CO_2 was observed in the outlet gas of the reaction. It is suggested that CO_2 is converted with CH_4 to produce twice the amount of CO under these reaction conditions by a reforming process ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$). The formed CO may cause a similar promotion of product formation and improvement of catalytic stability.



Scheme 1

The different effects of CO and CO_2 on methane aromatization may be associated with their different chemical properties: CO is dissociated on the Mo/HZSM-5 catalyst to form the common active CH_x surface species, similar to methane, which is converted to aromatics, and the dissociated [O] may react with surface coke to regenerate CO. However, CO_2 is more active towards reaction with surface CH_x derived from methane dissociation, yielding 2 mol of CO and H_2. Such effective consumption of surface intermediates with CO_2 causes the marked suppression of methane aromatization towards benzene. It is conceivable that benzene formation is a structure sensitive reaction, which requires a large concentration of active CH_x species on the catalysts. No appreciable differences in product selectivities for benzene and naphthalene were found, whether pure methane, or methane plus CO or CO_2 on the Mo/HZSM-5 and Co modified Mo/HZSM-5 catalysts, were used.

It was demonstrated by the TPO experiments that the amount of coke formed on the catalyst surface was greatly reduced by adding various amounts of CO or CO_2 to the methane feed gas. Increasing the CO concentration from 1.7% to 12.0% resulted in suppression of coke formation on the catalyst surface, particularly the irreversible or inert coke which was oxidized to CO_2 at temperatures above 773 K. Increasing the CO_2 partial pressure in the methane feed gas decreased the coke formation to a much lower level; this may be related to its weak oxidizing property (mentioned above).

To understand the role of CO in the methane aromatization reaction, the $^{13}CO + CH_4$ reaction was conducted. The starting composition of the reactant mixture was 8% ^{13}CO + 92% CH_4 with a total pressure around 220 Torr. Even after 5 min at 973 K, the level of ^{13}C incorporation in methane ($^{13}CH_4$) reached 8%. The isotopic abundance of ^{13}C incorporated in the benzene molecules was detected by GC-MS analysis as a random distribution ($^{13}CC_5H_6$ 47.6%, $^{13}C_2C_4H_6$ 36.7%, $^{13}C_3C_3H_6$ 13.0%, $^{13}C_4C_2H_6$ 2.4%, $^{13}C_5CH_6$ 0.3%) regardless of the reaction time of methane on Mo/HZSM-5. These results suggest that the carbon derived from CO dissociation is efficiently incorporated into the benzene formation and the isotopic scrambling reaction between ^{13}CO and $^{12}CH_4$ proceeds rapidly under these reaction conditions at 973 K.

Based on the above results we suggest a unique role of CO in the methane aromatization reaction, resulting in stabilization of catalyst performance and promotion of benzene formation, as shown in Scheme 1. Firstly, CO and CH_4 may dissociate on the catalyst surface, mostly on the Mo sites, to form active species such as [C], [O] and [CH_x] through reactions (1) and (2); the active carbon species [C] from CO is hydrogenated to [CH_x] fragments as illustrated in reaction (3), followed by the oligomerization with [CH_x] derived from CH_4 to form higher hydrocarbons such as benzene and naphthalene in reaction (1) on the catalyst; the dissociated oxygen species [O] from CO may react with the surface inert carbon species (coke) to regenerate CO, resulting in the suppression of coke formation on the catalyst through reaction (4).

Notes and References

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