

DOCTORAL THESIS

Methane dehydrogenation and aromatization over Mo(Re, Mn)/HZSM-5 in the absence/presence of an oxidant

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Methane Dehydrogenation and Aromatization over
Mo(Re, Mn)/HZSM-5 in the Absence/Presence of an Oxidant

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Abstract

We first investigated the effects of calcination temperature (500-900°C) and Mo loading (2-50 wt%) on the performance of Mo/HZSM-5 in methane aromatization (700°C, GHSV = 1600 ml g⁻¹ h⁻¹). At a calcination temperature (T_c) of 500°C, an increase in Mo loading (≥ 2 wt%) enhances methane conversion as well as the yield of aromatic compounds; maximum yield (about 6.6%) was observed at a loading of 23 wt%. The Mo species are not uniformly distributed; they exist as microcrystalline MoO₃, polymolybdate, and well-dispersed entities. Since the synergetic effect between the Mo species and the Brønsted acid sites features the bifunctionality of the catalysts, we deduce that the well-dispersed Mo species are sites for methane activation, and the amount of active sites increases with suitable increase in Mo loading. At $T_c = 700^\circ\text{C}$, the performance of 2 wt% Mo/HZSM-5 was compatible with that of the 500°C-calcined one. According to the results of IR, XPS, NH₃-TPD, and BET studies, HZSM-5 dealumination and Mo species dispersion both on the external surface and into the channels of the zeolite occurred. With the rise in Mo loading, dealumination became serious and the activity of Mo/HZSM-5 drastically decreased. At a Mo loading of 15 wt% or higher, the 700°C-calcined catalysts failed to function for aromatization. At $T_c \geq 750^\circ\text{C}$, reduction in catalytic activity over 2 wt% Mo/HZSM-5 was accompanied with a considerable extent of zeolite dealumination and loss in zeolite crystallinity. On the other hand, the results of AAS analysis confirmed that Mo loss during calcination (500-900°C) was not significant at a Mo loading of 2 wt%. At high calcination temperature and high Mo loading, we considered the decreases in the amount of acidic sites and the density of Si-OH-Al groups on zeolite are the main reasons for loss in catalytic activity as well as poor stability of Mo/HZSM-5.

With a rise in reaction temperature (T_r) from 700 to 770°C, 2 wt% Mo/HZSM-5 would have been completely deactivated within 4 hours for aromatic formation. XRD and AAS results showed that the coked catalyst still maintain a high crystallinity of the zeolite and there was no loss in Mo content after reaction for 6 hours at $T_r \leq 770^\circ\text{C}$. Accordingly, we consider the deposition of coke to be the main cause of the gradual deactivation of Mo/HZSM-5 in the nonoxidative aromatization of methane. The addition of O₂, NO or CO₂ up to 5.3 vol%, 9.1 vol%, and 12.8 vol%, respectively, reduces deactivation of the catalyst so that, at a reaction temperature of 770°C, an aromatics yield of *ca.* 4% can be maintained for 6 hours. XPS analysis revealed that, in the presence of O₂ or CO₂, the molybdenum oxide on the HZSM-5 located at the reactor inlet was not converted to molybdenum carbide, whereas in the zone away from the reactor inlet, Mo₂C was found. Investigation by temperature-programmed surface reaction showed that the production of aromatic compounds was always preceded by the reaction of molybdenum oxide with methane to form Mo₂C and CO. The beneficial effect of adding CO₂ and O₂ in low concentrations was attributed to the formation of CO and H₂ via the reforming of methane in the zone close to the reactor inlet. TPO results showed that the H₂ and CO formed could suppress the excessive dehydrogenation of the reaction intermediates into inactive entities as reflected in the decrease in the amount of cokes as well as in the lowering of the

carbon-burning temperatures. Further rise in O_2 (≥ 8.4 vol%), NO (≥ 14.2 vol%) or CO_2 (≥ 18.6 vol%) concentration would result in the entire catalyst bed being oxidized: CO and CO_2 became the predominant carbon-containing products; C_2H_4 and C_2H_6 were generated in small amounts and no aromatics were detected.

The pH value of ammonium heptamolybdate solution during impregnation was found to affect the catalytic performance of $Mo/HZSM-5$ significantly in methane dehydro-aromatization due to zeolite dealumination and/or changes in acid properties and concentration of mono-molybdate ions. At a calcination temperature of $500^\circ C$, a H_2SO_4 -acidified 2 wt% $Mo/HZSM-5$ gives an initial aromatics yield of 7.3% at $700^\circ C$ but declines drastically in catalytic activity. An enhancement in the amount of acid sites due to the remaining H_2SO_4 on the catalyst surface accounts for the promotion of the initial catalytic activity. However, owing to the dealumination of zeolite and the diminution of H_2SO_4 (via decomposition) after 6 hours on-stream at $700^\circ C$, there is a decline in catalytic activity. On the other hand, a NH_3 -basified 2 wt% $Mo/HZSM-5$ shows both high activity (7.1% aromatics yield) and good stability for methane aromatization. Since no significant dealumination was observed, the improvement in dispersion of Mo species at the expense of zeolite acidity is responsible for the enhancement in performance of the NH_3 -basified catalyst.

There are four kinds of carbonaceous entities observed on a deactivated $Mo/HZSM-5$ catalyst: carbide, hydrogenated coke with low carbon-burning temperature, and two kinds of poly-aromatic cokes with high carbon-burning temperatures. TPO and catalytic activity results showed that the polyaromatic cokes deposited at acidic sites of $HZSM-5$ suppressed the oligomerization and cyclization of intermediate to aromatic compounds, whereas, the coke with low carbon-burning temperature deposited at Mo sites deactivated the catalyst entirely. With a rise in reaction temperature or space velocity of reactant, there is an increase in both amounts of cokes and carbon-burning temperatures. The TPO results showed that decreases in the amount and density of Brønsted acid sites due to Mo dispersion or dealumination of zeolite, and the addition of a small amount of CO_2 or O_2 in methane feed could inhibit the further dehydrogenation and condensation of reaction intermediates.

DTA-TG and XPS results showed that Mn_3O_4 was formed on $500^\circ C$ -calcined $Mn/HZSM-5$ after impregnation of $HZSM-5$ with manganese acetate aqueous solution. An intensity of $O 1s$ at 529.7 eV indicated that there were Mn_3O_4 crystallites on the surface of the zeolite, a reason for no catalytic activity for methane aromatization at high Mn loading. There was a long induction period over the 4 wt% $Mn/HZSM-5$ catalyst; this period shortened with a rise in reaction temperature from 700 to $800^\circ C$. XPS and TPO results showed that carburized Mn species were formed and are probably responsible for methane activation. For a $Re/HZSM-5$ catalyst, XPS and XRD results showed that the Re species were well dispersed on zeolite surface. The induction period was short during aromatization, and initial activity was comparable with that of $Mo/HZSM-5$. However, a drastic decline in catalytic activity accompanied with an increase in C_2 -hydrocarbon yield was observed over $Re/HZSM-5$. The TPO results showed that there was no carbide formation on the used $Re/HZSM-5$; XPS results showed that the metallic rhenium formed

in the induction period was the active phase for methane activation. NH_3 -TPD results indicated that rhenium modification of 4 wt% could give an enhancement in the amount of Brønsted acid sites on HZSM-5.

As a concluding remark, there are three kinds of Mo species distributed on 2 wt% Mo/HZSM-5; the well-dispersed Mo species are responsible for sites for methane activation. Suitable increasing in Mo loading or NH_3 -basification could increase the active sites on Mo/HZSM-5, resulting in increasing methane conversion and aromatics yield. Dealumination of the zeolite would affect the selectivities of hydrocarbons as well as the stability of the catalyst. Suitable amount of O_2 , NO or CO_2 added in methane feed would significantly improve the stability of the catalyst via complete conversion of the additive to CO and H_2 at the zone of the catalyst close to gas inlet, which could inhibit the further dehydrogenation of aromatic products to inactive cokes on acidic sites. Besides Mo species, carburized manganese species or metallic rhenium were found to be able to activate methane with the assistance of the Brønsted acid sites.

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