The reaction performance and surface character of Ni modified Mo/HZSM-5 catalyst for methane aromatization

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The effect of Ni content, reaction temperature and pretreatment conditions on methane aromatization over Mo-Ni/HZSM-5 catalyst under oxygen-free condition have been studied. It is shown that adding a certain quantity of Ni is beneficial to methane conversion. When Ni/Mo molar ratio is 0.05, the methane conversion and aromatic selectivity reach 11.3% and 97.1% respectively at 973 K reaction temperature. Increase in temperature improves the catalytic behavior of Mo-Ni/HZSM-5 catalyst and 15.7% of the methane conversion is obtained at 1023 K. The reaction with pretreatment by N2 is better than those pretreated with H2, CH4 or air. The results of isopropanol decomposition show that the surface acidity on Mo-Ni/HZSM-5 is increased at high temperature. The NH3-TPD findings suggest that the Mo-Ni/HZSM-5 catalyst has much stronger acidity and more amount of acid sites than Mo/HZSM-5. This might be one of the reasons for the enhancement in the activity for methane aromatization over Mo-Ni/HZSM-5 catalyst.

Increasing attention has been paid to the more efficient use of natural gas, for developing a novel catalyst which would make it possible to directly aromatize methane under O2-free conditions. Few reports have appeared on the preparation of novel catalysts with reasonable reaction activity since ΔH value for the aromatization reaction is very high:

\[6\text{CH}_4=\text{C}_6\text{H}_6+9\text{H}_2(\Delta H=523.018 \text{ kJ mol}^{-1})\]

and the process is thermodynamically admissible only when the reaction is carried out at high temperature (see Fig. 1). For example, at 873 K, the methane thermodynamic equilibrium conversion is only about 5%, and at 973 K it is about 11.4%. Even at 1023 K, the conversion is ca.16.2%. So far, little attention has been paid to the direct aromatization of methane.

Among the first studies of benzene formation by catalytic aromatization of methane was that of Bragin et al.1, who employed a Pt-CrO2/HZSM-5 catalyst in the temperature range 873 – 1023 K and 0.1 MPa total pressure in a pulse reaction apparatus. Based on observed analytical results of reaction effluent, they concluded that methane could be selectively converted into benzene, but the conversion was very low. Recently, Wang and coworkers2 studied the aromatization reaction of methane over Mo/ZSM-5 catalysts, and reported that CH4 could be converted into C6H6 in higher conversion (7%) of methane at reaction temperature higher than 1023 K. We report herein the promotional effect of nickel additive in Mo/HZSM-5 catalyst for direct aromatization reaction of methane under O2-free conditions.

Experimental

Catalysts preparation

Mo/HZSM-5 catalyst was prepared by impregnating HZSM-5 support with SiO2/Al2O3 ratio of 60.65 with ammonium molybdate aqueous solution. The impregnated sample was dried at room temperature and at 393 K for 4 h, and then calcined in air of a furnace at 723 K for 4 h.

Similar method was also used for the preparation of Mo-Ni/HZSM-5 catalyst. On the base of 3.5wt%
Mo/HZSM-5. Mo-Ni/HZSM-5 catalysts were prepared by co-impregnating HZSM-5 support with ammonium molybdate and nickels acetate mixed aqueous solutions in desired proportion, followed by drying at room temperature and at 393 K for 4 h, and then calcined at 723 K for 4 h.

Activity measurement

Direct aromatization reaction of methane was carried out in a fixed bed flow apparatus with a tubular quartz reactor, by passing a feed of methane which was further purified by MnO deoxidizer, over about 0.5 g catalyst. Analyses of reactant/product mixtures were made by periodically directing the reactor effluent through the sampling loop of a thermal gas sampling valve which was maintained at 373 K in a Shimadzu GC-8A model gas chromatograph with FID detector, which contained two columns in series. Separation of the mixtures of CH₄ + C₂H₄ + C₂H₆, C₃H₆ and C₆H₆ was accomplished on a stainless steel column containing methylsilastic (i.e. OV-01) at 353 K, while separation of CH₄, C₂H₄ and C₂H₆ from main components occurred on a stainless steel column containing Porapak Q at the same temperature. The reaction temperature was raised from room temperature in nitrogen flow before methane feed being drawn into the quartz reactor.

Methane conversion and product selectivity were both calculated on the carbon number basis.

Catalyst characterization

Isopropanol decomposition was carried out using 0.5 g of the catalyst, and the products were analyzed by an on-line gas chromatograph.

NH₃-TPD experiment was performed in a locally constructed apparatus. The catalyst (0.04 g) was pretreated in flowing helium at 773 K for 1 h and cooled to 293 K. The ammonia pulse adsorption was carried out to complete saturation. After physisorbed ammonia was removed by flowing helium for 20 min, the TPD run was performed with a heating ramp of 10 K/min up to 873 K.

Results and discussion

Influence of Ni addition for aromatization activity over Mo/HZSM-5 catalyst

The results in Table 1 reveal that the activity and selectivity of Mo/HZSM-5 catalyst is increased after incorporating Ni additive for methane aromatization at 973 K and low space velocity (600 h⁻¹). It indicates that maximum activity is observed when mol ratio of Ni/Mo=0.05. It is of interest to note that the aromatics yield is 11.0%, which is near to the thermodynamically equilibrium conversion (ca. 11.4%) at the temperature of 973 K.

Figure 2 shows the aromatization rate of methane as a function of time on stream for Mo/HZSM-5 and Mo-Ni/HZSM-5 catalysts. One can see that even after reacting 4 h, methane conversion was also maintained at the value of 9.2% over Mo-Ni/HZSM-5 catalyst.

Influence of reaction temperature on methane aromatization over Mo/HZSM-5 catalyst before and after Ni addition

Effect of temperature on the reaction behavior is shown in Fig. 3. The data were recorded after reacting for 1 h. It can be seen that the conversion of methane was significantly enhanced with the increase in reaction temperature. Under the lower-temperature reaction condition, the influence of Ni addition was clearly apparent, the conversion of methane over Mo-Ni/HZSM-5 was much higher than that over

<table>
<thead>
<tr>
<th>Ni/Mo (mol ratio)</th>
<th>CH₄ conversion (%)</th>
<th>Selectivity (%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C₆H₆</td>
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<td>9.6</td>
<td>91.9</td>
</tr>
<tr>
<td>0.11</td>
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<td>92.5</td>
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</table>

The data were recorded after reacting for 1 h.

Table 1—The influence of Ni loading on the behavior of direct aromatization over Mo/HZSM-5 catalyst

NOTES
Fig. 2—Plot of methane conversion versus reaction time for methane aromatization over Mo/HZSM-5 and Mo-Ni/HZSM-5 catalyst.

Mo/HZSM-5. At the reaction temperature of 953 K, the methane conversion over Mo-Ni/HZSM-5 was 7.6% while that was 4.2% over Mo/HZSM-5 catalyst. With the increase in reaction temperature, the difference of methane aromatization activity between the two catalysts decreased, the values of methane conversion over Mo-Ni/HZSM-5 and Mo/HZSM-5 were in close proximity. At 1023 K, those were 15.7% and 15.2%, respectively.

Influence of pretreatment condition on methane aromatization over Mo-Ni/HZSM-5 catalyst

The catalytic performances of Mo-Ni/HZSM-5 catalyst, which was pretreated in various gaseous flows, were given in Table 2. The data were recorded after reacting for 1 h. The reaction temperature was raised from room temperature to 973 K in various gaseous flows, and to H2 pretreatment condition, the temperature was maintained at 873 K for 2 h during rising.

It was found that methane conversion and selectivity for benzene were very low when the reaction temperature increased from room temperature to 973 K in air before CH4 feed being drawn into the quartz reactor. Instead of in air, the same procedure was carried
In a flow of N₂, the activity and benzene selectivity were dramatically enhanced from 5.3% to 11.3% and 48.1% to 91.5% respectively, although the catalyst was unreacted before reaction. However, the reduced catalyst showed the medium activity (8.6%) and relatively high selectivity (90.4%). When the reaction temperature was raised in CH₄ atmosphere, the methane conversion was 9.5% and benzene selectivity was 81.1%. Further work is necessary for understanding the active sites responsible for benzene formation.

Isopropanol decomposition

In order to study why the addition of Ni stimulated the activity of Mo/HZSM-5 catalyst, the catalysts were characterized with isopropanol decomposition. The decomposition of isopropanol was used to study the surface character of catalyst. The catalytic decomposition reaction of isopropanol was as follows:

\[
\begin{align*}
\text{CH₃CH(OH)CH₃} & \rightarrow \text{CH₃CH=CH₂+H₂O} \\
\text{CH₃CH(OH)CH₃} & \rightarrow \text{CH₃COCH₃+H₂}
\end{align*}
\]

The dehydration of isopropanol is catalyzed by acid site and forms propene, whereas the dehydrogenation is catalyzed by basic site or free radical and forms acetone. So the yield of dehydration product propene is regarded as the symbol of acidity intensity of catalyst, and the intensity of dehydrogenating site is measured by the yield of acetone.

The results of isopropanol decomposition were shown in Fig. 4. In the range of 373 - 453 K, isopropanol completely decomposed to propene and acetone both over Mo/HZSM-5 and Mo-Ni/HZSM-5. The lower temperature (373 K) is beneficial to the dehydrogenation of isopropanol. With the increase in reaction temperature (453 K), the dehydration activity was found to be enhanced due to the improvement of the degree of the exposure of the surface of the catalyst. It is worth to note that after Ni addition, the propene yield increased while the acetone yield decreased over Mo/HZSM-5 catalyst. This fact indicates that the addition of Ni stimulated the dehydration activity of Mo/HZSM-5 catalyst and inhibited the dehy-
The results show that the addition of Ni to Mo/HZSM-5 can modify the surface acid properties. The reason for higher aromatization activity of Mo-Ni/HZSM-5 might be the cooperation effect of Mo, Ni which function as bifunctional catalyst. Yide Xu proposed a reaction model for hydrocarbon formation over Mo/HZSM-5 catalyst which involved acid-assisted heterolytic splitting of methane, the promotional effect of Ni addition is probably in line with the model.

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References