

Synergistic Effect of Nickel Species and γ -Alumina Added to HZSM-5 on the Methanol to Aromatics

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Abstract Ni/HZSM-5 catalysts with γ -alumina were prepared by the sol–gel method. At first, reaction performances were investigated over the HZSM-5 catalysts with and without γ -alumina. Then, reaction evaluations were conducted over the Ni/HZSM (different loading amounts of nickel species were investigated) catalysts with and without γ -alumina. The addition of nickel species and γ -alumina increased the total acidity of the catalysts. Furthermore, the introduction of γ -alumina increased the amount of mesopores in the catalysts. Nickel species were much more stable with the presence of γ -alumina. Both nickel species and γ -alumina contributed the aromatization of methanol.

Keywords Ni/HZSM-5 · γ -Alumina · Mesopores · Aromatization

1 Introduction

Since the emergence of methanol to aromatics (MTA) [1–4], much attention has been paid on this field. Conventional aromatics mainly originate from crude oil routes [5], and furthermore the demand for aromatics has been increasing for the past decades. However, the proven crude oil reservoirs have been reducing at a considerably consuming rate. Syngas, a mixture of hydrogen and carbon monoxide, can be obtained via coal route, which is able to further

synthesize methanol [6–10]. Therefore, MTA, as an alternative process, can alleviate the tense situation in the demand for aromatics.

HZSM-5 zeolite is the most frequently used active component for MTA because of its peculiar three-dimensional network that is especially selective for aromatics [11–13]. Despite the high selectivity for aromatics of HZSM-5 itself, the maximum selectivity is limited. In order to further elevate the aromatic selectivity, much work about modifications for HZSM-5 catalyst has been done. Ag/HZSM-5 catalysts [14, 15] and Ga/HZSM-5 catalysts [16–18] have been widely investigated, both of which can significantly promote the formations of aromatics. However, due to their high price, they are not appropriate for commercial application. Therefore, it is necessary to look for a cheaper modified metallic or nonmetallic element. Nickel species with a high capability of dehydrogenation might enhance the formations of intermediates such as olefins and promote the subsequent aromatization. Conte et al. [19] have ever reported that 1 wt% nickel species loaded on the HZSM-5 zeolite can enhance the selectivity to C₆–C₁₁ aromatics by a factor of two.

In addition, several papers have reported on the function of γ -alumina in the methanol reaction. However, their emphasis is simply focused on the critical role of γ -alumina alone in the reaction of methanol dehydration to dimethyl ether [20–24]. As is known that γ -alumina mainly includes Lewis acid when the calcine temperature is around 700 °C. Furthermore, Cheng et al. [25] have shown that Lewis acid has a capability of dehydrogenation. Accordingly, γ -alumina added to HZSM-5 catalyst might also enhance MTA.

With the aim of elevating the selectivity for aromatics, HZSM-5 catalysts modified with nickel species and γ -alumina were investigated. In this study, HZSM-5 catalysts with and without only γ -alumina, catalysts with only nickel

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species, and catalysts with both nickel species and γ -alumina were prepared, characterized, and evaluated, respectively.

2 Experimental

2.1 HZSM-5 Catalyst Preparation

The HZSM-5 catalyst without γ -alumina was prepared by blending 30 wt% HZSM-5 zeolite (Si/Al ratio is 18, Nankai University Catalyst Factory) with 5 wt% of silica (silica is in the form of silica sol) as binder and 65 wt% of kaolin as inert matrix. The Ni/HZSM-5 catalysts without γ -alumina were also based on the above formula, but the HZSM-5 zeolite was first modified with nickel species before the catalyst preparation. The HZSM-5 catalyst with γ -alumina was acquired by the sol-gel method by which γ -alumina replacing 30 wt% of kaolin was introduced into the catalyst. And the Ni/HZSM-5 catalyst with γ -alumina also underwent modification with nickel species first. In addition, different loading amounts of nickel species (0.5, 1.0, 1.5, 3.0, 4.5, and 6.0 wt%) were investigated. The loading amount of nickel species (nickel oxide) was calculated based on the amount of HZSM-5 zeolite and the source of nickel species came from nickel nitrate. Hereafter, the HZSM-5 refers to no nickel species loaded on the zeolite while Ni/HZSM-5 implies the existence of nickel species. After mixing evenly, all catalyst samples were dried at 140 °C overnight and calcined at 700 °C in static air for 2 h, then all samples were crushed and sieved to 80–180 mesh particles for later use.

2.2 HZSM-5 Catalyst Characterization

X-ray powder diffraction (XRD) patterns were recorded on an X'Pert PRO MPD diffractometer system using Cu K α radiation at 40 kV and 40 mA, running from 5° to 75° with a speed of 10° min⁻¹.

Textural properties were determined by adsorption-desorption measurements of nitrogen at liquid nitrogen temperature using a Quadrasorb SI instrument. Prior to the measurement, all samples were evacuated at 300 °C for 4 h at the pressure of 1.0×10^{-3} kPa.

Total amount of acid (Lewis acid and Brönsted acid) was obtained by Temperature-programmed Desorption of NH₃ (NH₃-TPD). During the test, 0.1 g of sample was loaded into the apparatus, preheated in a flow of helium to 650 °C at which the treatment remained for 30 min, and then cooled down to 100 °C. Later, the catalyst was treated in a flow of NH₃ for 30 min until the catalyst reached the top adsorption point. After the baseline went smoothly, the

chemical desorption was carried out by heating the catalyst to 650 °C with a speed of 10 °C/min.

Surface acidity of the catalysts was confirmed by IR spectra of pyridine adsorption with a Mercury Cadmm Telluride (MCT) detector using a NexusTM FT-IR spectrometer. The spectra were recorded with 4 cm⁻¹ and 64 scans.

Reduction properties of the catalysts were determined by Temperature-programmed reduction of H₂ (H₂-TPR). During the test, 0.1 g of sample was loaded into the apparatus, preheated in a flow of helium to 200 °C at which the treatment remained for 30 min, and then cooled down to 80 °C. Later, the catalyst was in contact with a mixture of 10 vol% H₂/N₂ for 30 min and then heated to 800 °C at a fixed rate of 10 °C/min. The effluent gas was analyzed by a GAS-100Q mass spectrometer.

2.3 Reaction Performance Evaluation

The experiments were performed on a continuous fixed bed microreactor at 400 °C under atmospheric pressure with a fixed value of 3 g of catalyst in the reactor. Before reaction, the reactor was purged with a flow of nitrogen to remove the adsorbed moisture on the surface of the samples. Then pure methanol was fed to the reactor at a fixed rate of 0.4 mL/min for 30 min, after which the nitrogen was fed to the reactor to drive the residual products out of the reactor. A portion of effluents were condensed in an ice trap, and the remaining effluents were gathered in a gas bottle.

In this study, the experiments over the HZSM-5 catalyst with and without γ -alumina were first carried out followed by the ones over the Ni/HZSM-5 catalysts with and without γ -alumina. The gaseous products were confirmed by a Bruker 450 Gas Chromatograph equipped with a FID detector to determine the hydrocarbons and two TCD detectors to analyze the hydrogen, carbon monoxide, and carbon dioxide. The remaining methanol collected in an ice trap after reaction was determined by introducing a fixed value of ethanol as the internal standard into the collected liquid products using an Agilent 6820 Gas Chromatograph. The aromatics were determined by combination of a PerkinElmer PONA Gas Chromatograph to analyze the gasoline compositions and a Bruker 450 Simulated Distillation Gas Chromatograph according to the ASTM-2887 method to determine the gasoline and diesel contents. The coke deposited on the catalyst after reaction was determined by analyzing the amount of the carbon oxide obtained from the burning of the coke using a TengHai 2000 GC Chromatograph with CaCO₃ as the contrast sample.

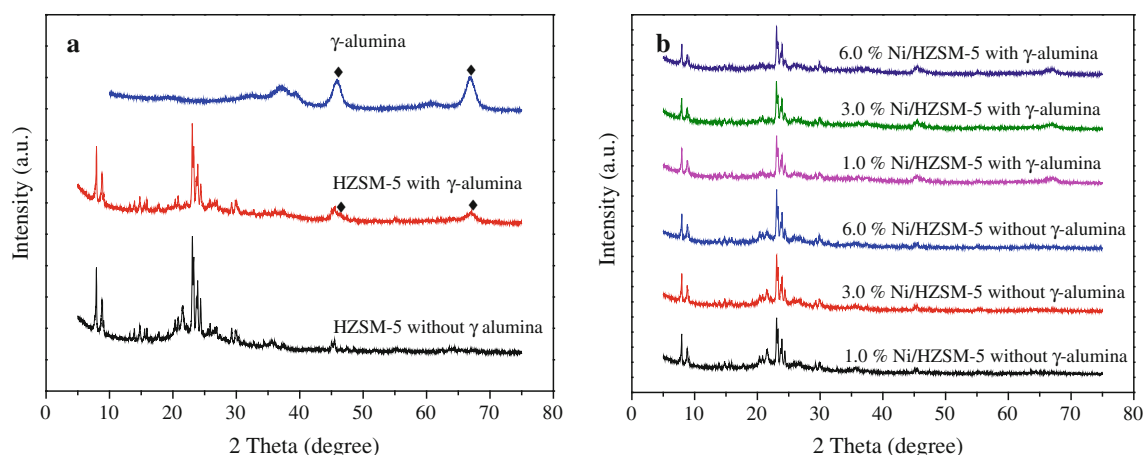


Fig. 1 XRD patterns of samples investigated. **a** XRD patterns of γ -alumina, HZSM-5 catalysts with and without γ -alumina. **b** XRD patterns of Ni/HZSM-5 catalysts with and without γ -alumina

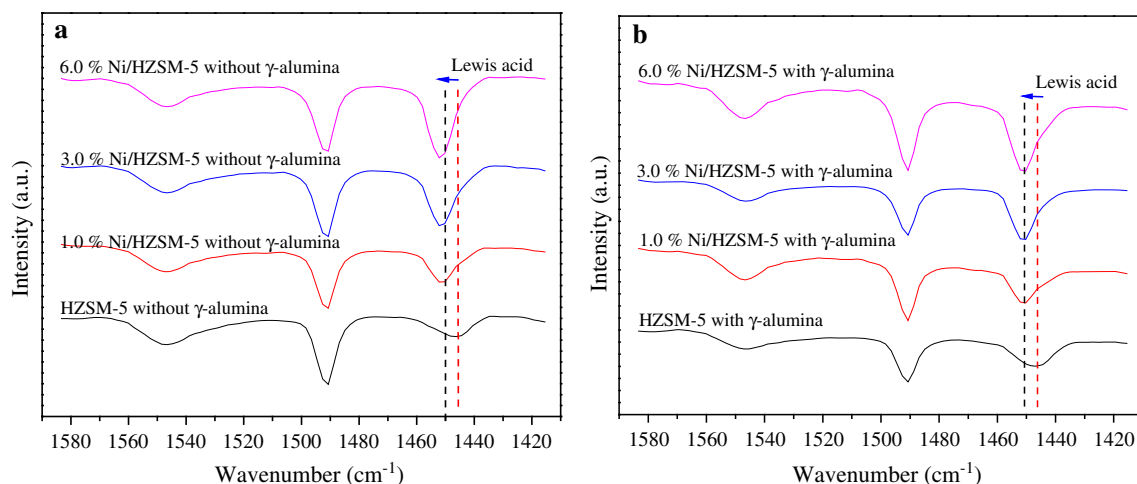


Fig. 2 Surface acidity of Ni/HZSM-5 catalysts with and without γ -alumina measured by IR spectra of pyridine adsorption. **a** Ni/HZSM-5 catalysts without γ -alumina. **b** Ni/HZSM-5 catalysts with γ -alumina

3 Results and Discussion

3.1 Characterization

The XRD patterns of γ -alumina, HZSM-5 catalysts with and without γ -alumina, and Ni/HZSM-5 catalysts with and without γ -alumina are shown in Fig. 1. The HZSM-5 catalyst with γ -alumina had the characteristic diffraction peaks in common with γ -alumina while the one without γ -alumina did not. It demonstrated that γ -alumina was successfully incorporated into the HZSM-5 catalyst with γ -alumina. In addition, there were no obvious characteristic diffraction peaks of nickel species for Ni/HZSM-5 catalysts with and without γ -alumina, which indicated that nickel species were in the form of amorphism or highly dispersed on the surface of the catalyst in the form of microlites that could not be detected within measuring range. Meanwhile, the relative

crystallinities of HZSM-5 zeolite for 3 wt%Ni/HZSM-5 catalysts with and without γ -alumina were also calculated based on the raw HZSM-5 zeolite. The calculation showed that both crystallinities decreased to around 92 %, which indicated that the introduction of nickel species damaged the structure of HZSM-5 zeolite in the catalysts.

The surface acidity of Ni/HZSM-5 catalysts with and without γ -alumina determined by IR spectra of pyridine adsorption is exhibited in Fig. 2. The bands at 1,445 and 1,545 cm^{-1} are assigned to Lewis acid and Brønsted acid, respectively. And the band at 1,490 cm^{-1} is assigned to both Lewis and Brønsted acid. It can be clearly seen that the amount of Lewis acid increased gradually with the increasing addition of nickel species regardless of γ -alumina. In addition, nickel species gave rise to a new Lewis acid site (1,450 cm^{-1}), which might be in correlation with the empty orbitals of Ni^{2+} [26].

Table 1 Total acidity of Ni/HZSM-5 catalysts with and without γ -alumina measured by NH_3 -TPD

| Loading amount of nickel species (wt%) | Total acidity (mmol/g) | |
|--|----------------------------------|-------------------------------------|
| | Ni/HZSM-5 with γ -alumina | Ni/HZSM-5 without γ -alumina |
| 0.0 | 0.217 | 0.135 |
| 1.0 | 0.251 | 0.198 |
| 3.0 | 0.291 | 0.214 |
| 6.0 | 0.312 | 0.253 |

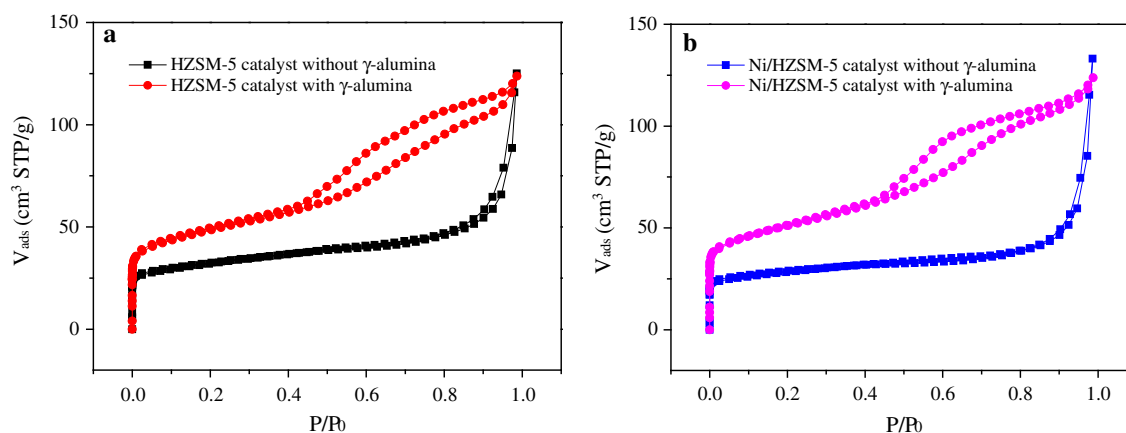
Meanwhile, the total acidity (Lewis acid and Brönsted acid) of Ni/HZSM-5 catalysts with and without γ -alumina measured by NH_3 -TPD were listed in Table 1. It can be observed that the introduction of nickel species increased the total acidity. Furthermore, the total acidity had a positive correlation with the adding quantity of nickel species, which might be ascribed to the new Lewis acid site. In addition, γ -alumina was also conducive to the increase in the total acidity of HZSM-5 catalysts.

Figure 3 gives the nitrogen adsorption and desorption isotherms for HZSM-5 catalysts with and without γ -alumina, and 3.0 wt% Ni/HZSM-5 catalysts with and without γ -alumina. Previous literature [3] has reported that hysteresis loops are usually accompanied by the filling and emptying of mesopores by capillary condensation. On the

basis of Fig. 3, the addition of γ -alumina gave rise to hysteresis loops, which might result from the preparation process. As has been mentioned above, HZSM-5 catalyst with γ -alumina was acquired by the sol-gel method. Elaloui et al. [27] and Jia et al. [28] have reported that mesopores are prone to generate through sol-gel synthesis.

Meanwhile textural data for 3 wt% Ni/HZSM-5 catalysts with and without γ -alumina were listed in Table 2. By comparison with the textural data between HZSM-5 catalyst without γ -alumina and 3 wt% Ni/HZSM-5 catalyst without γ -alumina, it can be found that the introduction of nickel species increased the average pore diameter and pore volume, which indicated that nickel species damaged the structure of the catalyst. The above-mentioned result was in agreement with that obtained by XRD characterization. In addition, it can be also found that the introduction of γ -alumina increased the total specific surface area of the catalyst. However, because of the presence of γ -alumina, the destruction led by nickel species could not be reflected in the textural data.

As metallic and nickel oxide species on the catalyst surface may have different catalytic behaviors, thus it is necessary to measure the reduction properties of catalysts. Figure 4 gives the H_2 -TPR profiles for 3 wt% Ni/HZSM-5 catalysts with and without γ -alumina. Even though there was no obvious characteristic diffraction peaks for Ni/HZSM-5 catalysts in the XRD characterizations, it can be

**Fig. 3** Nitrogen adsorption and desorption isotherms at -196°C for HZSM-5 samples. **a** HZSM-5 catalysts with and without γ -alumina. **b** 3.0 wt% Ni/HZSM-5 catalysts with and without γ -alumina**Table 2** Textural data for 3 wt% Ni/HZSM-5 catalysts with and without γ -alumina

| | Specific surface area (m^2/g) | Average pore diameter (nm) | Pore volume (cm^3/g) |
|---|---|----------------------------|--|
| HZSM-5 without γ -alumina | 118.4 | 6.56 | 0.19 |
| 3 wt% Ni/HZSM-5 without γ -alumina | 106.6 | 7.74 | 0.21 |
| HZSM-5 with γ -alumina | 172.1 | 4.46 | 0.19 |
| 3 wt% Ni/HZSM-5 with γ -alumina | 182.0 | 4.22 | 0.19 |

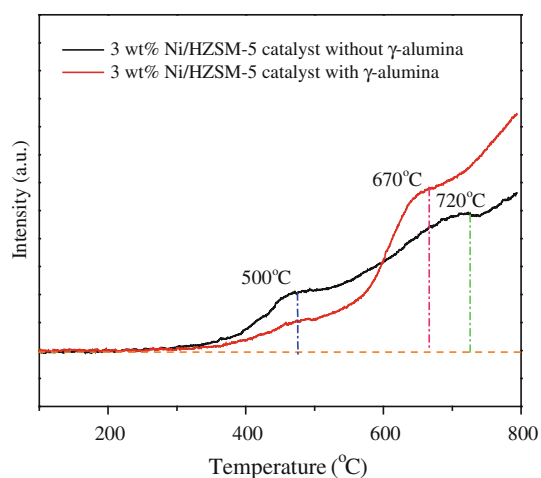


Fig. 4 H₂-TPR profiles for 3 wt% Ni/HZSM-5 catalysts with and without γ -alumina

seen clearly that there were mainly three kinds of reduction peaks within measuring range from H₂-TPR profiles, which indicated three possible existences of nickel species on the surface of the catalysts. Both catalysts had reduction peaks at around 500 and 700 °C. Masalska [29] has reported that reduction peaks at around 500 and 700 °C are ascribed to the interaction of nickel species with the support. The reduction of the amorphous overlayer of nickel oxide at around 700 °C interacts with the support stronger than does the amorphous overlayer of nickel oxide at around 500 °C. However, both reductions are not chemically bound. As for the third reduction peak over 700 °C, it is ascribed to the reduction of the Ni–Al spinels caused by the strong interactions between nickel oxide species and alumina.

By comparison, 3 wt% Ni/HZSM-5 catalyst with γ -alumina had slight differences in reduction temperatures and areas. It indicated that the addition of γ -alumina strengthened the interaction of amorphous overlayer of nickel oxide with support, which could be reflected by the increase in the reduction area at around 700 °C. In addition, because of the introduction of γ -alumina, Ni–Al spinels were prone to generate, which could be suspected by the initial reduction temperature of Ni–Al spinels (3 wt% Ni/HZSM-5 catalyst with γ -alumina began at 670 °C, 3 wt% Ni/HZSM-5 catalyst without γ -alumina began at 720 °C). Chang and Coworkers [30] have reported that Al species from alumina can transfer to HZSM-5 zeolite, therefore, nickel species on the surface of HZSM-5 zeolite tended to interact with Al species and in turn formed more Ni–Al spinels. At the reaction temperature investigated in this study, Ni/HZSM-5 catalysts with γ -alumina had a higher capability of keeping the nickel oxide from undergoing reduction.

Table 3 Part of product distributions for HZSM-5 catalysts with and without γ -alumina

| | HZSM-5 catalyst with γ -alumina | HZSM-5 catalyst without γ -alumina |
|--|--|---|
| Part of product distributions (wt%) | | |
| Conversion | 99.9 | 99.9 |
| Coke | 0.2 | 0.1 |
| C ₃ –C ₄ hydrocarbons | 11.3 | 9.5 |
| Propane | 2.9 | 1.0 |
| Propylene | 2.5 | 4.1 |
| Butane | 4.7 | 2.5 |
| Butylene | 1.3 | 1.8 |
| Gasoline yield | 26.5 | 26.4 |
| Aromatic yield | 18.2 | 14.4 |
| Selectivity for paraffins, olefins, naphthenes, and aromatics (PONA) in gasoline (wt%) | | |
| Paraffins | 22.1 | 21.5 |
| Olefins | 8.0 | 19.5 |
| Naphthenes | 3.2 | 3.9 |
| Aromatics | 66.7 | 55.1 |

3.2 Reaction Performance of HZSM-5 Catalysts With and Without γ -Alumina

According to the result in Table 3, the selectivity towards aromatics was totally different for the two catalysts. By comparison, the selectivity and yield for aromatics over HZSM-5 catalyst with γ -alumina were raised to 66.7 and 18.2 wt% from 55.1 and 14.4 wt% over HZSM-5 catalyst without γ -alumina, respectively. It is necessary to note that the above results were calculated on the basis of the mass of methanol. In theory, methanol can convert into 56.3 wt% water and 43.7 wt% hydrocarbons at a total conversion. Therefore, the above-mentioned effect of γ -alumina on the aromatization of methanol was very obvious.

Chang and coworkers [30] have shown that the introduction of alumina as one binder to HZSM-5 zeolite could increase the activity of HZSM-5 catalysts in the methanol to hydrocarbons. However, only the factor of Al transfer was mentioned, other detailed information about why alumina had binder activation was not given. In this study, nitrogen adsorption and desorption isotherms showed that HZSM-5 catalyst with γ -alumina possessed substantial mesopores. On one hand, mesopores provided more room for aromatics to form. On the other hand, mesopores were able to weaken the diffusion limit of aromatics desorbed from the catalyst surface and in turn were conducive to the increase in the yields of aromatics. Besides, the greatly enhanced specific surface area (listed in Table 2) caused by γ -alumina is another very important factor. The increased

Table 4 Aromatic yields for Ni/HZSM-5 catalysts with and without γ -alumina

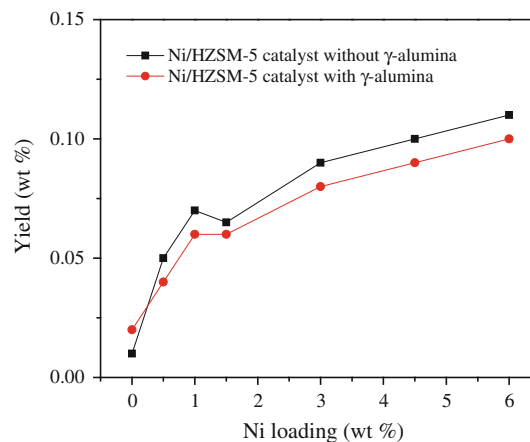
| Loading amount of nickel species (wt%) | Aromatic yield (wt%) | |
|--|----------------------------------|-------------------------------------|
| | Ni/HZSM-5 with γ -alumina | Ni/HZSM-5 without γ -alumina |
| 0.0 | 18.2 | 14.4 |
| 0.5 | 17.7 | 17.3 |
| 1.0 | 19.8 | 14.9 |
| 1.5 | 18.8 | 14.6 |
| 3.0 | 18.7 | 16.5 |
| 4.5 | 17.2 | 15.6 |
| 6.0 | 17.1 | 14.2 |

specific surface area increased the contact possibility between methanol molecules and active sites on the catalysts. Finally, acidity also played a critical role. NH_3 -TPD exhibited that the addition of γ -alumina increased the total acid amount of the catalysts. Meanwhile, together with the hydrophilic property of γ -alumina [31], methanol could adsorb much more easily on the surface of the catalyst, as a result, which greatly increased the possibility of contact between methanol and active sites.

In addition, besides the decrease in the selectivity for olefins in gasoline, it can be also observed that the light alkenes, such as propylene and butylene, reduced because of the addition of γ -alumina. Accordingly, we can rationally deduce that γ -alumina might promote the subsequent aromatization of alkenes, which could account for both the decrease in the alkenes and the increase in the aromatics.

3.3 Reaction Performance of Ni/HZSM-5 Catalysts With and Without γ -Alumina

Above-mentioned result proved that γ -alumina was beneficial for MTA. The follow-up work was focused on the modified HZSM-5 catalysts with nickel species. Table 4 gives the aromatic yields for Ni/HZSM-5 catalysts with γ -alumina and without γ -alumina. Methanol over Ni/HZSM-5 catalysts with γ -alumina and without γ -alumina was reacted at a nearly full conversion. By comparison with HZSM-5 catalysts with γ -alumina and without γ -alumina, appropriate incorporation of nickel species increased the aromatic yields regardless of γ -alumina. However, the formations of aromatics had no positive relationship with the adding amount of nickel species. It can be also found that Ni/HZSM-5 catalysts with γ -alumina had a higher aromatic yield compared with Ni/HZSM-5 catalysts without γ -alumina when the loading amount of nickel species was the same. It indicated the significant importance of γ -alumina in the aromatization of methanol. As has been shown in Fig. 4, the interaction

**Fig. 5** Hydrogen yield over Ni/HZSM-5 catalysts with and without γ -alumina

between nickel species and γ -alumina might also play a critical role in the aromatization of methanol.

It is usually recognized that the final formations of aromatics over HZSM-5 catalyst are obtained through hydrogen transfer reaction of naphthenes. However, the addition of nickel species seemed to alter the aromatization paths. Figure 5 exhibits the hydrogen yields over the Ni/HZSM-5 catalysts with and without γ -alumina, which proved the high capability for dehydrogenation of nickel species in the MTA reaction. Accordingly, there is a strong likelihood to shift the aromatization paths from hydrogen transfer aromatization to dehydrogenation aromatization.

It is very interesting to note (listed in Table 3) that the aromatic yields first showed a downward trend followed by an upward trend and a downward trend over the Ni/HZSM-5 catalysts without γ -alumina. In the beginning, the hydrogen transfer aromatization was suppressed because of the addition of nickel species. Meanwhile, the dehydrogenation aromatization had little contributions to the formations of aromatics. Subsequently, with the increasing loading amount of nickel species, the dehydrogenation aromatization started to be in a dominant position, which thus gave rise to the increase in the aromatic yields. However, it does not mean that more nickel species imply more aromatics. Besides of the strong ability of dehydrogenation, nickel species also have a high capability of cracking C–C bond [32]. Therefore, the cracking degree of higher molecular weight hydrocarbons got strengthened when the loading amount of nickel species was too large, which resulted in the reduction of the total liquid yield and in turn decreases the aromatic yields.

Slightly different from the variations of aromatics over the Ni/HZSM-5 catalysts without γ -alumina, the aromatics over the Ni/HZSM-5 catalysts with γ -alumina exhibited an increase first followed by a reduction. The coexistence of

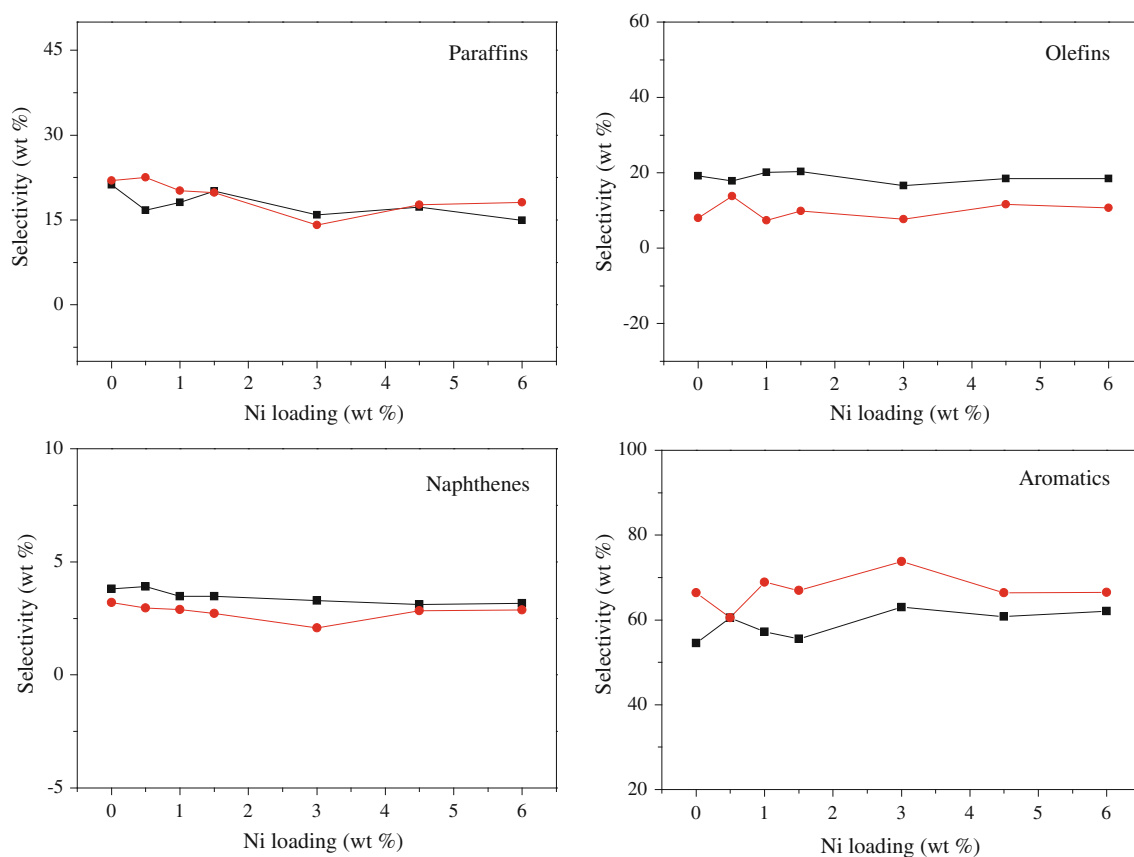


Fig. 6 Selectivity for PONA in gasoline over Ni/HZSM-5 catalysts with and without γ -alumina. Filled square Ni/HZSM-5 catalysts without γ -alumina. Red coloured circle Ni/HZSM-5 catalysts with γ -alumina

nickel species and γ -alumina made the dehydrogenation aromatization dominant despite of low loading amount of nickel species in the beginning. Subsequently, similar to the variations of aromatics over the Ni/HZSM-5 catalysts without γ -alumina, the yields of aromatics began to reduce. It can be observed that the maximum aromatic yield was 19.8 wt% over the 1.0 wt% Ni/HZSM-5 catalysts with γ -alumina in this study.

In order to further investigate the effect of nickel species and γ -alumina on the formations of aromatics, the selectivity for PONA over the Ni/HZSM-5 catalysts with and without γ -alumina is given in Fig. 6. By observation, nickel species alone gave rise to a slight reduction in the selectivity for olefins and naphthenes, and a rise in the selectivity for aromatics with the increasing loading amount of nickel species. The addition of nickel species was bound to enhance the dehydrogenation aromatization. Moreover, by comparison with the two groups of experiments, the selectivity for aromatics had a higher value over the Ni/HZSM-5 catalysts with γ -alumina as a whole while the selectivity for both olefins and naphthenes showed a lower value. The above-mentioned result further verified

that γ -alumina could enhance the aromatization of olefins and naphthenes. Above all, the synergistic effect of nickel species and γ -alumina contributed to the final aromatization of methanol.

4 Conclusion

Ni/HZSM-5 catalysts with γ -alumina were prepared by the sol-gel method. The introduction of nickel species and γ -alumina increased the total acidity of Ni/HZSM-5 catalysts with γ -alumina. Furthermore, γ -alumina gave rise to the increase of mesopores. H_2 -TPR showed that nickel species in the HZSM-5 catalysts with γ -alumina were much more stable than those in the ones without γ -alumina. In addition, nickel species might alter the aromatization path from hydrogen transfer aromatization to dehydrogenation aromatization. Both nickel species and γ -alumina contributed to the aromatization of methanol.

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