Research Article

Methanol Aromatization over Zn and Ce Modified Hierarchical ZSM-5 Catalysts: Effect of Ce as a Promoter

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Zinc (Zn) and cerium (Ce) modified hierarchical ZSM-5 (HZ) catalysts were prepared by incipient wetness impregnation, and their catalytic performances in methanol to aromatics reaction were evaluated in a fixed-bed reactor operating at 400 °C under 0.1 MPa and WHSV of 1.0 h⁻¹. The structure, acidity, and state of Zn species of the Zn/Ce modified HZ catalysts were investigated via several characterization techniques, including XRD, NH₃-TPD, H₂-TPR, nitrogen adsorption, and XPS. The results showed that the aromatization activity of 2 wt% Zn-modified HZ (2% Zn/HZ) could be significantly enhanced by loading 0.6 wt% Ce, which was mainly attributed to the increase in surface ZnOH⁺ species. Moreover, it was found that Ce inhibited pore blockage caused by Zn. Consequently, compared to 2% Zn/HZ, 2% Zn-0.6% Ce/HZ exhibited higher aromatic selectivity and longer catalyst lifetime.

1. Introduction

Aromatics, as the important raw materials in the petrochemical industry, have achieved a growing demand in recent years, while the production of the traditional aromatics mainly depends on the oil thermal cracking and naphtha catalytic reforming [1]. As a result, it is anticipated that the availability of aromatics may be affected due to the consumption of the fossil oil [2]. It is, therefore, urgent to promote the exploration of new processes to increase aromatics production via coal-based resources.

Methanol to aromatics (MTA), as an alternative to petrochemical processes, is a promising process to achieve sustainable aromatic supply [3–5]. The MTA reaction is a complicated process including (1) the dehydration of methanol and achieving an equilibrium system, (2) the formation of the active “hydrocarbon pool” species, (3) producing light olefins, paraffins, and aromatics via the aromatic- and olefin-based cycles [2, 6–8]. ZSM-5 zeolites, the most widely studied catalyst for methanol-related processes, have been proved to be optimum for MTA reaction, due to their shape selectivity, hydrothermal stability, and tunable Bronsted acidity [2, 4]. Therefore, numerous researches about methanol aromatization were focused on this field, especially for the modification of ZSM-5, including a load of various metals aiming to achieve better catalytic performances. Among all the metal species studied, Zn and Ga have been proved to be the most effective in the enhancement of aromatization activity, which is ascribed to their superior dehydrogenation abilities over ZnOH⁺ or (GaO)⁺ sites, respectively [4, 9]. Due to the economic advantage of Zn, it is more suitable for large-scale industrial applications [10, 11]. Nevertheless, it remains a Herculean task for Zn species to fully realize its potential in the enhancement of catalytic stabilities, due to the inevitable deactivation caused by coking [4]. There have been abundant studies focusing on the improvement of stabilities over Zn-modified ZSM-5 (Zn/ZSM-5), in which the addition of
secondary metal species can feasibly achieve this purpose. Xin et al. [12] found that the addition of Sn was able to prolong the lifetime of Zn/ZSM-5 via the suppression of coke precursors. However, the as-synthesized Zn–Sn/ZSM-5 only exhibited a lifetime of 16 h, which is still far from the actual demand. Wang et al. [13] suggested that Zn/ZSM-5 prepared by the process of atomic layer deposition (ALD) presented a longer lifetime (about 36 h) than those prepared by the method of impregnation and ion exchange. Nevertheless, the ALD process was complicated and expensive, and the lifetime of the prepared catalysts was also not satisfactory. From the above-mentioned researches, it can be concluded that exploiting other di-metal decorated ZSM-5 is an effective way to solve the stability problems notwithstanding, from the perspective of either investment or labor costs.

In our previous work, hierarchical ZSM-5 zeolites obtained through the method of demetallation successfully exhibited a longer lifetime than the microporous ZSM-5 counterpart [3] while it is believed that the catalytic performance can be further improved to achieve even better performance. As has been reported, the introduction of Ce can fulfill the desired changes, namely, the regulation of the metallic state and acidity simultaneously [14–16], yet the influence of Ce on Zn-modified hierarchical ZSM-5 zeolites has not been investigated in MTA reaction. In consequence, hierarchical ZSM-5 zeolites are prepared by demetallation and utilized as support of active metal species (Zn/Ce), the catalytic performance of these as-synthesized catalysts is evaluated in MTA reaction, and a series of characterizations are employed to reveal the structure-performance relationship; in particular, the effects of Ce addition on the state of Zn and catalytic aromatization performance are well established. These findings are beneficial to the design of a more efficient catalyst and solve the common deactivation problems in MTA processes.

2. Experimental

2.1. Catalyst Preparation

2.1.1. Preparation of Hierarchical ZSM-5. Commercial ZSM-5 zeolites (named as Z, Si/Al = 25, Nankai University Catalyst Corporation) were calcined at 550°C for 6 h with an elevating rate of 2°C/min to remove the volatile organics before each test. Typically, 18 g ZSM-5 zeolites were stirred in 450 mL of NaOH solution (0.3 M) at 65°C for 45 min. Then, the slurry was cooled off, filtered, and dried to get hierarchical Na-ZSM-5. Finally, the hierarchical Na-ZSM-5 was subjected to ion exchange with NH4Cl solution (1.0 M) followed by calcination under the above-mentioned conditions, to obtain protonated hierarchical ZSM-5 (named as HZ).

2.1.2. Metal Modified Hierarchical ZSM-5. In our study, impregnation was used except additional explanations, and an incipient wetness impregnation method was employed. Typically, Zn(NO3)2•6H2O and Ce(NO3)3•6H2O purchased from Aladdin were used in analytically pure grade. Zn and Ce modified HZ (Zn–Ce/HZ) was prepared by coimpregnation method: HZ was impregnated in a mixed solution of Zn(NO3)2 and Ce(NO3)3. Additionally, Zn-modified HZ (Zn/HZ) was prepared by mixing HZ with a Zn(NO3)2 solution, and Ce modified HZ (Ce/HZ) was prepared by mixing HZ with a Ce(NO3)3 solution. All slurries were kept static at 25°C for 24 h. After that, the slurries were dried at 120°C for 12 h and then calcined at 540°C for 6 h. The resultant catalysts were named x% Zn–y% Ce/HZ, x% Zn/HZ, and y% Ce/HZ, where x and y represented the mass fraction of Zn and Ce loading, respectively.

2.2. Catalyst Characterization. A Japanese D/max 2550 VB/PC diffractometer with CuKα radiation (λ = 1.5418 Å) was employed to record XRD patterns. The relative crystallinity was obtained by comparing the intensity of the modified samples in the intense (021) reflection at 2θ with that of the parent ZSM-5 zeolites, assuming 100% crystallinity for the parent one.

A Micromeritics chemisorb 2720 was employed to conduct temperature-programmed desorption of ammonia (NH3-TPD). The samples were firstly treated in a He stream (30 mL/min) at 550°C for 1 h and then cooled off to 25°C followed by adsorbing 5% NH3–He in a saturated condition. The samples were then kept at 150°C to sweep away NH3 adsorbed by physical absorption. Finally, the temperature was increased at a rate of 10°C/min up to 700°C to desorb all ammonia adsorbed. The results were recorded by a thermal conductivity cell detector.

Temperature-programmed reduction of H2 (H2-TPR) measurements was conducted on a Micromeritics chemisorb 2720. Prior to reduction, the samples were degasified at 550°C for 2 h in a He stream (30 mL/min). The reduction was performed under a 5% H2/He stream (30 mL/min) with the temperature increasing from 25 to 960°C at a rate of 10°C/min. H2 consumption was recorded with a thermal conductivity cell detector after removing the water.

N2 adsorption-desorption measurements were operated at liquid nitrogen temperature on a Micromeritics ASAP-2020V3.00H apparatus with an accuracy of 0.15% of reading. Before the measurements, all samples were evacuated at 280°C for 12 h.

X-ray photoelectron spectroscopy (XPS) was recorded using an ESCALAB 250 spectrometer employing an Al Kα radiation source (hν = 1486.6 eV). C 1s peak at 284.8 eV was taken as a reference to calibrate the binding energy (BE) values. All peaks were fitted with a Gaussian Lorentzian shape (40: 60). The atomic ratios on the catalyst surface were calculated from the calibrated peak area by the sensitive factor [17].

2.3. Catalytic Test. Catalytic performance was tested in a fixed-bed stainless steel reactor with a whole length of 600 mm and an inner diameter of 10 mm. 2.4 g catalyst (40–60 mesh) was mixed with an equal volume of silica sand and then packed in the center zone of the reactor. The pure methanol (0.05 mL/min) was pumped through a preheater maintained at 150°C with an N2 flow of 5 mL/min and
reacted at a temperature of 400°C and a total pressure of 0.1 MPa. And then the products were analyzed online by a GC 6890 equipped with an FID detector and an SPB-5 capillary column. The methanol conversion and selectivity for different products were calculated based on carbon balance.

### 3. Results and Discussion

#### 3.1. Catalytic Performance

Table 1 shows the initial product distributions on various catalysts, the methanol conversions for all catalysts are 100%, and products are categorized into 5 classes, which are olefins, paraffins, aromatics, and others, with aromatics and paraffins as primary products. Since the variations in the selectivity toward olefins, C₅⁺, and others are not much, aromatic and paraffin selectivity will be discussed in priority. As can be seen, HZ exhibited higher selectivity for aromatics (43.5%) than the parent Z counterpart (38.7%). In the previous report, the better performance was attributed to the accelerated hydrogen transfer reaction over hierarchical ZSM-5 zeolites [3]. After Zn modification, it can be seen that the aromatic selectivity increased at the initial stage, which rose to 52.8% in 1% Zn/HZ and reached the vertex of 64.0% in 2% Zn/HZ; then, this value underwent a decline to 55.4% in 3% Zn/HZ. Unlike Zn, modification of HZ with single Ce displayed a negligible effect on the aromatization activity compared with HZ, presenting a similar aromatic selectivity of 42.9%. However, significant promotions can be found in aromatic selectivity when Ce was introduced into 2% Zn/HZ. With the help of 0.3 wt% Ce, the aromatic selectivity in 2% Zn-0.3% Ce/HZ rose from 64% to 70.5%, further achieving the maximum value of 75.9% in 2% Zn-0.6% Ce/HZ, and then fell back to 66.4% in 2% Zn-0.9% Ce/HZ. On the contrary, the paraffin selectivity demonstrated a reverse trend compared with that of aromatics, implying a mutual transformation process effected by Zn and Ce between the two products.

The time-on-stream (TOS) data are depicted in Figure 1. All catalysts displayed near 100% methanol conversions initially as shown in Figure 1(a). As the reaction processing, Z displayed a breakthrough (99% conversion) in methanol conversions [18] after 30 h, while no signs of deactivation could be found for HZ until 60 h, evidencing enhanced stability of HZ, which possibly benefits from the introduction of mesopores [3, 19]. Ce modification imposed little effect on the catalyst stability of HZ, expressing that 0.6% Ce/HZ had a nearly identical TOS curve compared with HZ. Meanwhile, 2% Zn/HZ also failed to keep the 99% conversion at 60 h, but the conversion decreased more significantly thereafter, denoting a more rapid deactivation. It should be emphasized that, even though methanol breakthrough over 2% Zn-0.6% Ce/HZ was detected at 60 h, just like others, it displayed a lower descent speed and the TOS curve recovered to the same level of HZ. Figure 1(b) displays the aromatic selectivity as a function of TOS. Aromatic selectivity gradually declined for all catalysts with the increase of TOS; the slopes of 2% Zn-0.6% Ce/HZ and 2% Zn/HZ were similar, which seemed to be a little higher than the other three samples. Notably, 2% Zn-0.6% Ce/HZ exhibited the highest aromatic selectivity among all selected catalysts within 85 h on stream. These reactivity results suggested that 2% Zn-0.6% Ce/HZ was the most promising one for catalytic applications.

#### 3.2. Characterization of Catalysts

To determine the topology and crystallinity of the as-prepared catalysts, X-ray diffraction (XRD) was performed as shown in Figure 2. All samples presented diffraction peaks within 2θ = 7–9°, and 22–25°, which were the typical structure of ZSM-5 (JCPDS Card no. 00-037-0361). Moreover, the peaks assigned to ZnO or CeO₂ were not found in either sample, indicating their well dispersion on zeolites [16, 20–24]. However, decreases in crystallinities were detected for all modified zeolites, which was owing to the demetallation and higher absorption coefficient of loading metals [25–27].

The acidic properties (density and strength) are determined by NH₃-TPD, as shown in Figure 3 and Table 2. The broad TCD signal was deconvoluted into three subpeaks for each sample according to the desorption temperatures, namely, l-peak (150–250 °C), m-peak (260–360 °C), and h-peak (420–500 °C), respectively. Generally, the m-peak and h-peak were ascribed to NH₃ chemisorbed on medium and strong acid sites, respectively [28, 29]. The l-peak was ascribed to NH₃ physically adsorbed on weak acid sites (WAS), possibly stemming from the terminal silanols, which were believed to be inactive in MTA reaction [19, 30]. It can be seen in Table 2 that all samples except Z exhibited close weak acid densities or strengths. Hence, further investigation should be mainly taken with the changes of medium and strong acid sites in this work [19].

Clearly, HZ possessed a lower density of all acid sites than Z, which was proved to be caused by the removal of framework Al [31]. However, the temperature maximum (T_max) of all desorption peaks was almost unchanged after demetallation, indicating that demetallation exerted no effect on the strength of acid sites. The introduction of Ce into HZ brought about a slight increase in the density of medium acid sites while leaving other acidic properties nearly intact. It has been proposed that the impregnated Ce predominantly interacted with the isolated silanols on the external surface of zeolites instead of protonic acid sites [16]. Therefore, the medium acid sites were formed by the interaction between metallic oxide and silanols groups without the expense of strong acid sites (protonic acid sites), which can also be confirmed by the well-reserved SAS. By comparison, Zn incorporated into HZ led to an increase of medium acid sites at the expense of strong acid sites. Niu et al. [4] reported that Zn-Lewis acid sites with medium strength originated from Zn species interacted with the strong protonic acid sites, which may be the explanation for this phenomenon. For the same reason, the strength of medium and strong acid sites also decreased by impregnation of Zn. In comparison with the sole impregnation of Zn, the coimpregnation of Zn and Ce created more medium acid sites with less damage to strong acid sites, due to the compensation interactions of Zn and Ce on the acidities.
Table 3 displays the textural properties of different catalysts. Surely, mesopores were introduced into Z by demetallation, which was mainly due to desilication. Introducing Ce into HZ induced a slight decrease in external surface area (Sext) and had no effect on micropores. It indicates that Ce was located predominantly on the external surface, and the micropores of zeolites were well maintained. However, Zn loaded with HZ led to a comparatively marked decrease of Sext and micropore volume (Vmicro), which should be attributed to the pore blockage caused by the impregnated Zn [32]. Notably, bimetallic 2% Zn-0.6% Ce/HZ showed less loss of Sext and Vmicro than 2% Zn/HZ. It suggested that Ce inhibited the pore blockage caused by Zn. Generally speaking, the effect of metal loadings on the texture properties of zeolites is limited since the total metal content is not very high.

XPS analyses were performed to investigate the state and distribution of surface Zn species. The Zn 2p3/2 spectra of 2% Zn/HZ and 2% Zn-0.6% Ce/HZ are displayed in Figure 4. Two peaks centering at 1022.6 eV and 1023.2 eV denoting ZnO cluster and ZnOH+ species on the zeolite surface were resolved for each sample, respectively [4]. For 2% Zn/HZ, the content of surface ZnO species was higher than that of surface ZnOH+ species. However, for 2% Zn-0.6% Ce/HZ, the majority of surface Zn species were interpreted as ZnOH+ species. The XPS results suggested that Ce could promote the formation of surface ZnOH+ species.

Figure 5 shows the TPR profiles of the selected catalysts. For 2% Zn/HZ and 2% Zn-0.6% Ce/HZ, a negative peak below 300°C was observed, belonging to the H2 uptake caused by heterolytic dissociation of H2. Notably, the introduction of Ce into 2% Zn/HZ rendered the peak more intense. Previous research studies proposed that the heterolytic dissociation of H2 might only occur at isolated Zn2+ sites [23, 33]. Hence, it can be inferred that Ce promoted the dispersion of Zn and ameliorated the formation of isolated Zn2+. For 2% Zn/HZ, two obvious reduction peaks were observed at around 370 and 610°C. The low-temperature

Table 1: Production distribution of MTA reaction over different catalysts.

| Catalysts  | XMeOH (%) | Olefins (%) | Paraffins (%) | C5+ (%) | Others (%) |
|------------|-----------|-------------|---------------|--------|------------|
| Z          | 100       | 8.5         | 43.7          | 8.3    | 38.7       | 0.8        |
| HZ         | 100       | 5.1         | 39.7          | 11.2   | 43.5       | 0.5        |
| 1% Zn/HZ   | 100       | 6.7         | 32.4          | 7.5    | 52.8       | 0.6        |
| 2% Zn/HZ   | 100       | 6.5         | 22.7          | 5.9    | 64.0       | 0.9        |
| 3% Zn/HZ   | 100       | 9.0         | 26.5          | 9.2    | 55.4       | 0.7        |
| 0.6% Ce/HZ | 100       | 8.2         | 38.9          | 11.7   | 42.9       | 0.7        |
| 2% Zn-0.3% Ce/HZ | 100 | 6.6 | 16.4 | 6.1 | 70.5 | 0.4 |
| 2% Zn-0.6% Ce/HZ | 100 | 5.5 | 12.4 | 5.6 | 75.9 | 0.6 |
| 2% Zn-0.9% Ce/HZ | 100 | 8.8 | 17.0 | 7.2 | 66.4 | 0.6 |

*a* The data was obtained at 0.5 h of time on stream. Reaction conditions: P = 0.1 MPa, T = 400°C, WHSV = 1.0 h⁻¹. Including C1–C4 olefins. Including C1–C4 paraffins. Including all the olefins and paraffins with more than five carbon atoms. Including CO, CO2, and coke.
peak might be caused by the highly reactive Zn$^{2+}$ ions, while the high-temperature peak has been suggested to be caused by oxygenated Zn aggregates [23, 34]. The TPR profile of 0.6% Ce/HZ contained two peaks: the first peak located at 480°C was attributed to the reduction of oxygenated Ce species at the charge-alternating sites of ZSM-5 zeolite, and the second peak at 670°C originated from the reduction of CeO$_2$ aggregates [35, 36]. In contrast, for 2% Zn-0.6% Ce/HZ, the reduction peaks of Zn and Ce species shifted to higher temperatures; this could be ascribed to the electron transfer from Zn to Ce as evidenced by XPS which also evidenced the strong interaction between Zn and Ce.

3.3. Effects of Catalyst Properties on the Catalytic Performance. Based on the above discussions, a mutual interaction between Zn, Ce, and HZ was demonstrated, which modified the texture and acidic properties of HZ along with the
electron and the existing state of Zn and Ce, which accordingly influenced its catalytic performance.

The synergistic effect is well accepted to occur between metal sites and acid sites of zeolites in MTA reaction [4, 32]. According to the results obtained in this work and previous contributions [6, 7, 37], the possible transformation pathways of MTA reaction are proposed and shown in Scheme 1. Methanol is dehydrated into dimethyl ether (DME), and the process quickly achieves chemical equilibrium. Furthermore, methanol can also generate low carbon alkanes via the hydrogen transfer reaction. Low carbon olefins (C_3-C_6 olefins) are formed from olefin methylation with methanol or DME or the dehydrogenation of low carbon alkanes, which undergo further methylation and oligomerization to generate C_4-C_9 olefins. Moreover, low carbon olefins and alkanes are also generated by the cracking of C_4-C_9 olefins. Notably, aromatics, as the target product, can be obtained through two routes: (1) aromatics and alkanes are formed from (CH_2)_n species via hydrogen transfer reaction on strong acid sites (Reaction 1) [6]; (2) aromatics are obtained by dehydrogenation of (CH_2)_n species, which also occurs on strong acid sites and has been proposed to be facilitated by the medium acid sites such as ZnOH^+ species (Reaction 2) [4, 9].

The introduction of Ce into HZ imposed little effect on strong acid sites, which, in turn, hardly influenced the aromatization activity. Nevertheless, Zn promoted Reaction 2 due to the formation of ZnOH^+ species. Hence, catalyst 2% Zn/HZ showed higher selectivity for aromatics than catalyst HZ. Notably, it has been proposed that the enhancement of aromatization activity is linearly related to the amount of surface ZnOH^+ species [4, 38]. For catalyst 2% Zn-0.6% Ce/HZ, Ce could increase the number of surface ZnOH^+ species, which was also reflected in the enhanced dehydrogenation of (CH_2)_n species to aromatics. Therefore, compared with 2% Zn/HZ, it exhibited higher aromatization activity.

The unsaturated species including alkenes, aromatics, and cyclic alkenes are transformed into coke through deep dehydrogenation and condensation occurring on strong acid sites [39]. Coke, trapped inside the cavity and deposited on the outer surface of catalysts, is widely accepted to result in catalyst deactivation [30]. To solve the issue, effective methods have been found to improve diffusion limitations by applying hierarchical zeolites or reducing the number of strong acid sites by dealumination [40, 41]. For HZ, it exhibited improved catalyst stability due to the construction of mesopores [3, 42]. However, the loaded Zn deteriorated the stability of HZ as they resulted in pore blockage, as shown in the texture properties [4]. Moreover, it has been

### Table 2: Acidic properties of different catalysts.

| Samples   | Acidity by strengtha (mmol/g) | SAS  | MAS  | WAS  | Totalb |
|-----------|-------------------------------|------|------|------|--------|
| Z         | 0.208                         | 0.333| 0.364| 0.905|
| HZ        | 0.114                         | 0.129| 0.264| 0.507|
| 0.6% Ce/HZ| 0.118                         | 0.152| 0.236| 0.506|
| 2% Zn/HZ  | 0.079                         | 0.141| 0.270| 0.490|
| 2% Zn-0.6% Ce/HZ | 0.091 | 0.165| 0.285| 0.541|

a The density of strong acid sites (SAS), medium acid sites (MAS), and weak acid sites (WAS) by deconvolution of the NH_3-TPD profile with Gaussian peaks (R^2 > 0.95). b Total represents the sum of strong, medium, and weak acid sites.

### Table 3: Textural properties of different catalysts.

| Zeolites   | S_BETa (m²/g) | S_etb (m²/g) | V_totalc (cm³/g) | V_microb (cm³/g) | V_meso d (cm³/g) |
|-----------|---------------|-------------|-----------------|-----------------|-----------------|
| Z         | 255           | 52          | 0.17            | 0.11            | 0.06            |
| HZ        | 297           | 116         | 0.24            | 0.10            | 0.14            |
| 0.6% Ce/HZ| 293           | 107         | 0.23            | 0.10            | 0.13            |
| 2% Zn/HZ  | 207           | 83          | 0.18            | 0.07            | 0.11            |
| 2% Zn-0.6% Ce/HZ | 241 | 92           | 0.21            | 0.09            | 0.12            |

a BET method. b t-plot method. c Calculated from the adsorption branch at p/p_0 = 0.99. d V_meso = V_total - V_micro.

![Figure 4: XPS spectra of Zn 2p_{3/2} for 2% Zn/HZ and 2% Zn-0.6% Ce/HZ.](image)

![Figure 5: Temperature-programmed reduction (TPR) profiles of selected 2% Zn/HZ, 0.6% Ce/HZ, and 2% Zn-0.6% Ce/HZ.](image)
proposed that Zn also resulted in the formation of heavy coke leading to rapid deactivation [4, 12]. By contrast, Ce maintained the micropores and did not reduce the number of strong acid sites. The Ce was selectively loaded on the external surface of zeolites due to the large molecular size and effectively avoided covering the strong acid sites in the micropores. Thereby, the addition of Ce induced little effect on the stability of catalyst HZ. However, Ce could inhibit the micropores blockage caused by Zn. It should be noted that the strong acid sites, as active sites for MTA reaction, were mainly located in microporosity. The fewer pore blockages resulted in more accessibility to active sites, which was directly reflected in the improved capability to catalytically convert methanol. Furthermore, it has been reported that the pore blockage was the main reason for fast deactivation [39, 43]. As the Ce was majorly located at the external surface of ZSM-5 and exerted a strong interaction with Zn, it is believed that Ce also played a role as an anchor site for Zn, which was able to immobilize the Zn tightly with itself on the external surface in the state of ZnOH⁺. Thus, Ce modified Zn/HZ catalyst exhibited better stability due to the ameliorated pore-blockage phenomenon generated by the anchor effect from Ce, which held most Zn at the external surface, and a higher aromatic selectivity due to enhanced dehydrogenation abilities brought by more surface ZnOH⁺ species.

4. Conclusions

In summary, the introduction of Zn and Ce into HZ by coimpregnation was an effective method to prepare the catalyst with superior stability and enhanced selectivity for aromatics. The Zn/Ce modified HZ catalysts were studied via several characterization methods, and their catalytic performances in MTA reactions were evaluated.

The results demonstrated that monometal modification of Zn could enhance the aromatization activity but deteriorate the catalyst stability, while that of Ce imposed little effect on MTA reaction. Meanwhile, bimetal modification achieved by coimpregnation with Zn and Ce was capable of generating a synergistic effect to enhance the aromatic selectivity and catalytic stability. As a result, 2% Zn-0.6% Ce/HZ displayed high aromatic selectivity of 75.9% and kept 100% methanol conversion for about 60 h on stream. This could be attributed to the increased amount of surface ZnOH⁺ species and the micropores blockage improved by the presence of Ce.

Data Availability

All data used to support the findings of this study are currently under embargo while the research findings are commercialized. Requests for data, 12 months after publication of this article, will be considered by the corresponding author.

Conflicts of Interest

The authors declare no competing financial interests.

Authors’ Contributions

Zhenhao Wei contributed to the conceptualization, investigation, methodology, and writing the original draft; Yufan Ji, investigation and writing the original draft; Yiping Huang, funding acquisition and reviewing and editing of the manuscript; Jingjing Huang, formal analysis and methodology; Yunguo Huang, funding acquisition; Changhai Yue, data curation and methodology; Junzhu Li, data curation; Mingwei Tang, validation; Yufang Liu, validation; Hanfei Liu, Hao Zhu, Kai Zhu, and Fan Yang, reviewing and editing of the manuscript; Xuedong Zhu, project administration, supervision, and reviewing and editing of the manuscript.

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References

[1] M. A. Fahim, T. A. Alsahhaf, and A. Elkilani, Chapter 6 - Thermal Cracking and Coking, Fundamentals of Petroleum Refining, Elsevier, Amsterdam, Nederland, pp. 123–152, 2010.
[2] U. Olsbye, S. Svelle, M. Bjørgen et al., “Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity,” Angewandte Chemie International Edition, vol. 51, no. 24, pp. 5810–5831, 2012.
[3] Z. Wei, T. Xia, M. Liu et al., “Alkaline modification of ZSM-5 catalysts for methanol aromatization: the effect of the alkaline concentration,” Frontiers of Chemical Science and Engineering, vol. 9, no. 4, pp. 450–460, 2015.
[4] X. Niu, J. Gao, Q. Miao et al., “Influence of preparation method on the performance of Zn-containing HZSM-5 catalysts in methanol-to-aromatics,” Microporous and Mesoporous Materials, vol. 197, pp. 252–261, 2014.
[5] Y. Gao, B. Zheng, G. Wu, F. Ma, and C. Liu, “Effect of the Si/Al ratio on the performance of hierarchical ZSM-5 zeolites for methanol aromatization,” RSC Advances, vol. 6, no. 87, Article ID 83588, 2016.
[6] S. Ilias and A. Bhan, “Mechanism of the catalytic conversion of methanol to hydrocarbons,” ACS Catalysis, vol. 3, no. 1, pp. 18–31, 2012.
[7] M. Bjorgen, S. Svelle, F. Jøensen et al., “Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: the role of the oléfinic species,” Journal of Catalysis, vol. 249, no. 2, pp. 195–207, 2007.
[8] Z. Wen, T. Xia, M. Liu, K. Zhu, and X. Zhu, “Methane formation mechanism in methanol to hydrocarbon process: a periodic density functional theory study,” Catalysis Communications, vol. 75, pp. 45–49, 2016.
[9] P.-C. Lai, C.-H. Chen, H.-Y. Hsu, C.-H. Lee, and Y.-C. Lin, “Methanol aromatization over Ga-doped desilicated HZSM-5,” RSC Advances, vol. 6, no. 71, Article ID 67371, 2016.
[10] Y. Ono, H. Adachi, and Y. Senoda, “Selective conversion of methanol into aromatic hydrocarbons over zinc-exchanged ZSM-5 zeolites,” Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases, vol. 84, no. 4, pp. 1091–1099, 1988.
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[11] Y. Bi, Y. Wang, X. Chen, Z. Yu, and L. Xu, "Methanol aromatization over HZSM-5 catalysts modified with different zinc salts," *Chinese Journal of Catalysis*, vol. 35, no. 10, pp. 1740–1751, 2014.

[12] Y. Xin, P. Qi, X. Duan, H. Lin, and Y. Yuan, "Enhanced performance of Zn-Sn/HZSM-5 catalyst for the conversion of methanol to aromatics," *Catalysis Letters*, vol. 143, no. 8, pp. 798–806, 2013.

[13] F. Wang, W. Xiao, L. Gao, and G. Xiao, "The growth mode of ZnO on HZSM-5 substrates by atomic layer deposition and its catalytic property in the synthesis of aromatics from methanol," *Catalysis Science & Technology*, vol. 6, no. 9, pp. 3074–3086, 2016.

[14] Y. Chen, T. Liu, C. Chen et al., "Synthesis and characterization of CeO2 2 nano-rods," *Ceramics International*, vol. 39, no. 6, pp. 6607–6610, 2013.

[15] Y. Zhang, M. Xue, Y. Zhou et al., "Propane dehydrogenation over Ce-containing ZSM-5 supported platinum-tin catalysts: Ce concentration effect and reaction performance analysis," *RSC Advances*, vol. 6, no. 35, Article ID 29422, 2016.

[16] H.-G. Jang, K. Ha, J.-H. Kim, Y. Sugi, and G. Seo, "Ceria and lanthana as blocking modifiers for the external surface of MFI zeolite," *Applied Catalysis A: General*, vol. 476, pp. 175–185, 2014.

[17] J. E. Castle, "Practical surface analysis by Auger and X-ray photoelectron spectroscopy," *Surface and Interface Analysis*, vol. 6, no. 6, p. 302, 1984.

[18] F. Bleken, W. Skistad, K. Barbera et al., "Conversion of methanol over 10-ring zeolites with differing volumes at channel intersections: comparison of TNU-9, IM-5, ZSM-11 and ZSM-5," *Physical Chemistry Chemical Physics*, vol. 13, no. 7, pp. 2539–2549, 2011.

[19] X. Wang, J. Zhang, T. Zhang et al., "Mesoporous ZnZSM-5 zeolites synthesized by one-step desilication and reassembly: a durable catalyst for methanol aromatization," *RSC Advances*, vol. 6, no. 28, Article ID 23437, 2016.

[20] W. Zeng, T. Liu, and Z. Wang, "Impact of Nb doping on gas-sensing performance of TiO2 thick-film sensors," *Sensors and Actuators B: Chemical*, vol. 166–167, pp. 141–149, 2012.

[21] Z. Wang, W. Zeng, L. Gu, M. Saito, S. Tsukimoto, and Y. Ikuhara, "Atomic-scale structure and electronic property of the LaAlO3/TiO2 interface," *Journal of Applied Physics*, vol. 108, no. 11, Article ID 113701, 2010.

[22] H. Xue, X. Guo, T. Meng, D. Mao, and Z. Ma, "NH3-SCR of NO over M/ZSM-5 (M = Mn, Co, Cu) catalysts: an in-situ DRIFTS study," *Surfaces and Interfaces*, vol. 29, Article ID 101122, 2022.

[23] S. M. T. Almutairi, B. Mezari, P. C. M. M. Magusin, E. A. Pidko, and E. J. M. Hensen, "Structure and reactivity of Zn-modified ZSM-5 zeolites: the importance of clustered cationic Zn complexes," *ACS Catalysis*, vol. 2, no. 1, pp. 71–83, 2011.

[24] A. Susarrey-Arce, M. A. Hernández-Espinosa, F. Rojas-González, C. Reed, V. Petranovskii, and A. Licea, "Inception and trapping of ZnO nanoparticles within desilicated mordenite and ZSM-5 zeolites," *Particle & Particle Systems Characterization*, vol. 27, no. 3-4, pp. 100–111, 2010.

[25] D. Verboekend, S. Mitchell, M. Milina, J. C. Groen, and J. Pérez-Ramírez, "Full compositional flexibility in the preparation of mesoporous MFI zeolites by desilication," *Journal of Physical Chemistry C*, vol. 115, no. 29, Article ID 14203, 2011.
[41] L. R. Aramburo, S. Teketel, S. Svelle et al., "Interplay between nanoscale reactivity and bulk performance of H-ZSM-5 catalysts during the methanol-to-hydrocarbons reaction," *Journal of Catalysis*, vol. 307, pp. 185–193, 2013.

[42] Y. Wang, W. Chen, Y. Chen et al., "Carbon-based catalysts by structural manipulation with iron for oxygen reduction reaction," *Journal of Materials Chemistry*, vol. 6, no. 18, pp. 8405–8412, 2018.

[43] M. Guisnet, L. Costa, and F. R. Ribeiro, "Prevention of zeolite deactivation by coking," *Journal of Molecular Catalysis A: Chemical*, vol. 305, no. 1-2, pp. 69–83, 2009.