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Zn-P Co-Modified Hierarchical ZSM-5 Zeolites Directly Synthesized via Dry Gel Conversion for Enhanced Methanol to Aromatics Reaction

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Abstract: A unique method to prepare Zn-P co-modified hierarchical ZSM-5 zeolites was developed. The ZSM-5 zeolite was directly synthesized by a dry gel conversion without adding any templates or seeds. Afterwards, the hierarchical structure was endowed to the ZSM-5 zeolite by the sequential desilication-dealumination. Zn and P species were then introduced into the hierarchical ZSM-5 zeolites by the impregnation method and their activity in methanol to aromatics process was investigated. It was found that the Zn-P co-modified hierarchical ZSM-5 zeolites possessed more Zn-related Lewis acid sites, and the ratio of $\text{Zn}(\text{OH})^+/\text{ZnO}$ was increased. The catalytic evaluation results revealed that the benzene, toluene and xylene (BTX) and aromatics selectivity were significantly improved from 20.59% and 29.41% of pristine ZSM-5 zeolite to 28.12% and 41.88% of Zn-P co-modified hierarchical counterpart (1.5Zn0.3P/HZSM-5), respectively. Owing to the introduced highly stable Zn-P co-modified hierarchical structures, the lifetime (conversion not less than 99%) of ZSM-5 zeolite during methanol to aromatics reaction was increased from 6 h to 18 h.

Keywords: methanol to aromatics; hierarchical ZSM-5; dry gel conversion; Zn-P co-modified

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1. Introduction

During the past decade, market demand for aromatics, especially benzene (B), toluene (T) and xylene (X), has surged due to the growth of the polymer and fine chemical industries [1]. Thanks to the wide range of non-petroleum origins of methanol including coal, biomass and natural gas, the methanol to aromatics (MTA) process has been successfully developed as a promising source for enlarging aromatics supply [2]. Owing to the suitable acidity and shape-selective generated from the unique framework structures, ZSM-5 (MFI topology) zeolite has attracted extensive attention as the catalyst for methanol to aromatics [3].

ZSM-5 zeolites are typically synthesized by the hydrothermal method in the presence of ammonium-related organic templates [3,4]. However, the high cost and environmental pollution of ammonium-related organic templates during their thermal decomposition are the limiting problems for the synthesis of ZSM-5 at industrial scale [4,5]. Alternatively, a dry gel conversion (DGC) method, which generates high zeolite yield and low environmental pollution [6,7], is regarded as a green, cheap and efficient synthesis route. Xiao et al. reported a combined strategy of both organotemplate- and solvent-free conditions to synthesize aluminosilicate zeolites Beta and ZSM-5 [8,9]. However, usage of the mineralizing agent such as NH_4F or NH_4Cl limits the industrial production of zeolites at a large scale because of their toxicity to the environment [5]. Recently, a dry gel conversion (DGC) method has attracted widespread attention due to its advantages such as high

zeolite yield and low environmental pollution [10,11]. However, direct synthesis of ZSM-5 zeolite without an organic template or seed crystals via dry gel conversion has rarely been reported to date.

Generally, the conventional MTA pathway consists of methanol-to-olefins (MTO) and olefins-to-aromatics (OTA) reactions [10]. In the OTA reaction, olefins need to be cyclized to cycloalkanes and then dehydrogenated to aromatics [3]. Meanwhile, the side reaction of olefins hydrogenation to alkanes is inevitable. Therefore, transitional metals such as Zn, Ga, Ag, Mo, etc. are required to improve the dehydrogenation or hydrogen transfer capability of ZSM-5 and then promote the yield of aromatics in the OTA reaction [11–13]. Among all introduced metal species, Zn has been recognized as one of the most attractive components due to its excellent dehydrogenation ability, the high selectivity of BTX and low cost [14–16]. Ono et al. firstly reported the significant promotion of aromatic selectivity in the MTA reaction by modifying ZSM-5 zeolite with Zn metal [17]. In addition, Kolyagin et al. found that three types of zinc species were involved in Zn/HMFI zeolite prepared by impregnation with an aqueous solution of $\text{Zn}(\text{NO}_3)_2$, i.e., small ZnO clusters inside the pores, large ZnO clusters on the external surface, and zinc cations (Zn^{2+} or ZnOH^+) [18]. In particular, ZnOH^+ species are reported to be the active sites to catalyze dehydrogenation or hydrogenation, which are formed by coordinating Zn^{2+} cations to the framework aluminate site, and serve as the Lewis (L) acid sites with medium-strong acidity [19]. Therefore, the introduction of Zn into ZSM-5 zeolite decreases the Brønsted (B) acid sites and increases the proportion of medium-strong acid sites due to the formation of ZnOH^+ species. Recently, the multiple-oxides-modified ZSM-5 zeolites were demonstrated to be a class of efficient catalysts for selective methanol conversion to p-xylene [20,21]. The primary metal modification, typically the low cost and non-toxic Zn species, is aimed to enhance the dehydro-cyclization and MTA reactivity [22,23]. Subsequent modification with the other oxides such as Mg [24], P [25], Si [26], B [27], etc. not only narrows the micropore openings and thus improves the zeolite shape-selectivity, but also effectively passivates the external acidity.

As the MTA reaction progresses, bulky by-products such as polyaromatic hydrocarbons and coke are inevitably formed accompanied with the targeted BTX products within ZSM-5 framework. These by-products are too bulky to diffuse through the narrow micropore walls of ZSM-5 (0.54 nm) resulting in a deactivation and reduced catalyst life span [28,29]. Therefore, increasing diffusion and catalyst efficiency via developing hierarchical ZSM-5 zeolites is of significance for MTA reaction [30]. Hitherto, reported strategies for making hierarchical ZSM-5 zeolites can be divided into constructive and destructive methods [31]. Although most of these constructive methods successfully acquire mesoporosity and improve performance in catalytic reactions, the costs and environmental issues raised by the substantial usage of templates require further evaluation for industrialization [32]. In contrast, destructive methods, including desilication and dealumination, are relatively easier to implement on an industrial scale [33]. As reported in our previous study, the introduction of mesopores by the alkaline-mediated leaching of framework Si has been regarded as a promising method due to the low cost and high efficiency [34]. The sequential dealumination will remove the non-framework aluminate and thereby reduce the diffusion resistance in the ZSM-5.

Herein, firstly, the pure phase ZSM-5 zeolite was directly synthesized without adding any templates and seeds via a dry gel conversion method. Secondly, the hierarchical ZSM-5 zeolites were prepared using the as-synthesized ZSM-5 zeolite as the raw material by sequential desilication-dealumination to reduce the diffusion resistance. Then, Zn and P were introduced into the hierarchical ZSM-5 zeolite by an impregnation method to adjust its acidity, and the differences of acid properties and MTA reaction performance between Zn modified and Zn-P co-modified ZSM-5 zeolite were compared.

2. Results and Discussions

2.1. Sample Characterizations

The XRD patterns of ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples are presented in Figure 1. The zoom areas have been shown in Figures S1 and S2. All the samples exhibited typical diffraction peaks in the 2θ range of $8\text{--}10^\circ$ and $22\text{--}25^\circ$ corresponding to the MFI structure. For ZSM-5 zeolite by the DGC method, low Zn and P loading cases (Zn loading is less than 2.0 wt% and P loading is less 1.0 wt%), intensities of the samples are not apparently changed. This indicates that the framework structure of ZSM-5 zeolites is not affected by Zn and P species introduction. With the increase of Zn loadings, the intensity of diffraction peaks is slightly decreased (Figure 1a). This may be due to deposited of amorphous Zn species on the surface or in the pores of hierarchical ZSM-5 zeolites [35]. In contrast, when the P loading is 1.0 wt%, the intensity of diffraction peaks is dramatically decreased as displayed in Figure 1b. This is because P species exist as oxides on the surface and/or in the pores of ZSM-5 zeolites due to the excessive treatment by the phosphoric acid solution in the impregnation method [36].

Figure 1. X-ray diffraction (XRD) patterns of ZSM-5, HZSM-5, Zn modified (a) and Zn-P co-modified (b) samples.

N_2 adsorption-desorption isotherms and pore size distribution of ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples are in Figure 2. Textural properties derived from different catalysts are summarized in Table 1. ZSM-5 presents a type I isotherm indicating that there are mainly micropores existed in ZSM-5 zeolites synthesized by the dry gel conversion method. After sequential desilication-dealumination, the BET surface area was increased from $262 \text{ m}^2/\text{g}$ to $311 \text{ m}^2/\text{g}$ in HZSM-5 zeolite as shown in Table 1. In addition, the adsorption isotherm changed into type IV isotherm with a hysteresis loop at $P/P_0 = 0.4\text{--}1.0$, reflecting the mesopores in ZSM-5 zeolites introduced by sequential desilication-dealumination. Zn-modified and Zn-P co-modified samples exhibited a similar isotherm type and hysteresis loop shape compared to HZSM-5 since introducing Zn and/or P species do not change the pore structure of synthesized HZSM-5 zeolites. With the increase of Zn loadings, the total surface area is slightly decreased due to Zn species deposited in the pores of ZSM-5 zeolites [37]. This is further proved by the pore size distribution as displayed in Figure 2a. In contrast, the BET surface area was increased after phosphorus modification, especially when the phosphorus loading was 1.0 wt%, the BET surface area was largely increased to $363 \text{ m}^2/\text{g}$ in Table 2. In addition, the pore size distribution was broadened, attributed to the etching effect of phosphoric acid, which is consistent with the XRD results.

Figure 2. N₂ absorption-desorption isotherms and pore size distribution (insert image) of ZSM-5, HZSM-5, Zn modified (a) and Zn-P co-modified (b) samples.

Table 1. Textural properties of ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples.

	Relative Crystallinity	S _{BET} ^a	S _{micro} ^b	S _{meso} ^c	V _{total} ^b	V _{micro} ^b	V _{meso} ^d
	(%)	(m ² /g)	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)	(cm ³ /g)
ZSM-5	100%	262	206	56	0.182	0.108	0.079
HZSM-5	49.9	311	167	144	0.311	0.088	0.244
0.5Zn/HZSM-5	52.1	297	164	133	0.302	0.086	0.238
1.0Zn/HZSM-5	52.5	289	160	129	0.293	0.084	0.229
1.5Zn/HZSM-5	54.8	282	154	128	0.294	0.081	0.235
2.0Zn/HZSM-5	52.2	271	154	117	0.280	0.081	0.219
1.5Zn0.1P/HZSM-5	50.5	299	144	155	0.312	0.076	0.258
1.5Zn0.3P/HZSM-5	49.5	314	159	155	0.321	0.084	0.259
1.5Zn0.6P/HZSM-5	49.5	332	167	163	0.329	0.088	0.262
1.5Zn1.0P/HZSM-5	32.2	363	169	194	0.348	0.089	0.277

^a BET surface area. ^b Calculated by t-plot method. ^c S_{meso} = S_{BET} − S_{micro}. ^d Calculated by BJH adsorption data.

Table 2. Acid amounts of Zn modified and Zn-P co-modified samples.

Samples	Py-IR (μmol/g)				NH ₃ -TPD (μmol/g)		
	Bronsted ^a	Lewis ^a	L/B ^b	Total ^c	Strong ^d	Medium ^d	Weak ^d
HZSM-5	262	114	0.44	761.6	212.7	174.3	374.7
0.5Zn/HZSM-5	246	204	0.83	807.1	180.9	223.8	402.4
1.0Zn/HZSM-5	164	222	1.35	799.3	173.5	240.1	385.7
1.5Zn/HZSM-5	161	252	1.57	816.5	177.3	245.2	394.0
2.0Zn/HZSM-5	159	278	1.75	818	152.6	257.9	407.5
1.5Zn0.1P/HZSM-5	153	303	1.98	834.3	173.3	254.3	406.7
1.5Zn0.3P/HZSM-5	146	319	2.19	966.2	244.9	266.2	455
1.5Zn0.6P/HZSM-5	141	300	2.13	846.2	180.4	223.4	442.4
1.5Zn1.0P/HZSM-5	134	284	2.12	782.7	175.1	208.9	398.7

^a Determined by Py-IR. ^b The ratio of Lewis acid amount to Brønsted acid amount. ^c Determined by NH₃-TPD. ^d Calculated by integrating the NH₃-TPD profiles in different temperature intervals.

Morphologies of ZSM-5, HZSM-5 and Zn-modified HZSM-5 zeolites were characterized by TEM (Figure 3). ZSM-5 zeolites directly synthesized by the dry gel conversion method (ZSM-5) exhibited a rectangular or hexagonal structure with a smooth surface as shown in Figure S3. After sequential desilication-dealumination, HZSM-5 zeolites can still maintain the original morphologies due to the post-treatment just slightly affecting the

external surface of zeolites. In addition, an obvious mesoporous structure in HZSM-5 can be observed in Figure 3b. After the introduction of Zn species into hierarchical ZSM-5 zeolites, all the catalysts exhibited a similar morphology with intercrystalline mesopores. No obvious Zn particles are aggregated on the surface of HZSM-5 zeolites indicating a good dispersion of Zn species, which is in agreement with the XRD results.

Figure 3. TEM images of Zn modified samples: (a) ZSM-5, (b) HZSM-5, (c) 0.5Zn/HZSM-5, (d) 1.0Zn/HZSM-5, (e) 1.5Zn/HZSM-5, (f) 2.0Zn/HZSM-5.

The TEM images and EDX mappings of Zn-P co-modified samples are shown in Figure 4. It is found that the morphology of Zn-P co-modified samples still maintains a similar structure to the HZSM-5 and obvious intercrystalline mesopores can be observed in Figure 4. With the increase of P loadings, the mesoporous structure was enhanced as shown in Figure 4d. This is consistent with the XRD results that the intensity was decreased when the P loading is 1.0 wt%. In addition, no particles belonging to zinc oxide or phosphorus oxide in TEM images indicating that Zn and P exhibited a good dispersion in HZSM-5 zeolites and the introduction of P species did not cause Zn species to fall off.

Figure 4. TEM images and energy-dispersive X-ray spectroscopy (EDX) mappings of Zn-P co-modified samples: (a) 1.5Zn0.1P/HZSM-5, (b) 1.5Zn0.3P/HZSM-5, (c) 1.5Zn0.6P/HZSM-5, (d) 1.5Zn1.0P/HZSM-5, (e) high angle annular dark-field (HAADF) and EDX mappings of 1.5Zn0.3P/HZSM-5.

Figure 5a,b show the UV-vis spectra of the Zn-modified and Zn-P co-modified catalysts. Both two absorption bands at 207 nm (ZnOH^+ species caused by the interaction of Zn species and framework O^{2-}) and 275 nm (the ZnO cluster around 1 nm) appears in all the Zn-modified and Zn-P co-modified samples, indicating the coexistence of ZnOH^+ and ZnO clusters in the synthesized samples [37,38]. The chemical state of the Zn species on the surface of the zeolite was determined by X-ray photoelectron spectroscopy (XPS)

analysis in Figure 5c. Peaks shown at 1023.3 eV and 1024.2 eV should be attributed to ZnO and ZnOH⁺ species, respectively [39]. The portion of surface ZnOH⁺ species in 1.5Zn0.3P/HZSM-5 (about 60%) is higher than that of 1.5Zn/HZSM-5 (about 53%), indicating that the introduction of P species will further enhance the distribution of Zn species.

Figure 5. Ultraviolet-visible (UV-vis) spectra of Zn modified (a) and Zn-P co-modified (b) samples and X-ray photoelectron spectroscopy (XPS) spectra of Zn 2P_{3/2} for 1.5Zn/HZSM-5 and 1.5Zn0.3P/HZSM-5 (c).

The type and concentration of Brønsted and Lewis acid sites for Zn-modified and Zn-P co-modified samples were determined by Fourier-transformed infrared spectrum of pyridine adsorption (Py-IR) characterization and the results are shown in Figure 6a,b, respectively. The detailed acid amounts and acid distributions are summarized in Table 2. Vibration peaks at 1547 and 1454 cm^{−1} are assigned as the adsorption of pyridine on Brønsted and Lewis acid sites, respectively, while the vibration peaks at 1490 cm^{−1} are results of the co-effects of both Brønsted and Lewis acid sites [38]. Compared to the hierarchical ZSM-5 zeolite (HZSM-5), the total acid amount was slightly changed after the Zn modification. With the increase of Zn loadings, the intensity of Brønsted acid was decreased, while the intensity of Lewis acid was increased as shown in Figure 6a. Thus, the ratio of Lewis acid to Brønsted acid was largely increased from 0.44 of HZSM-5 to 1.75 of 2.0Zn/HZSM-5 in Table 2. This indicates that the introduced Zn species covered the Brønsted acid sites firstly, and then interacted with Brønsted acid sites to generate new Lewis acid sites [3]. Compared to the Zn modified samples, the intensity of Brønsted acid was further decreased, while the intensity of Lewis acid was increased firstly and then decreased with the increase of P loadings as shown in Figure 6b. Therefore, the ratio of Lewis acid to Brønsted acid was firstly increased from 1.57 of 1.5Zn/HZSM-5 to 2.19 of 1.5Zn0.3P/HZSM-5 and then decreased to 2.12 of 1.5Zn1.0P/HZSM-5 in Table 2. Therefore, the introduction of P species

leads to two consequences: (1) exclusively poisoning the Brønsted acid sites; (2) promoting the Zn species dispersion and generating more Zn-Lewis acid sites [25].

Figure 6. Fourier-transformed infrared spectrum of pyridine adsorption (Py-IR) spectra ((a) Zn modified, (b) Zn-P co-modified) and NH_3 -TPD profiles ((c) Zn modified, (d) Zn-P co-modified) of catalysts.

The acid properties of the samples were measured by NH_3 -TPD, and the results are shown in Figure 6c,d. The desorption peaks in NH_3 -TPD profiles consist of low-temperature peaks (100–300 °C) and high-temperature peaks (300–550 °C). For low-temperature peaks, it represents weak acid sites (120–200 °C) and medium acid sites (200–300 °C) [3], while the high-temperature peaks (300–550 °C) correspond to the strong acid sites. It is found that the intensity of strong acid sites was dramatically decreased, while the intensity of weak and medium acid sites was increased and expanded towards the high temperatures. As shown in Table 2, the amount of strong acid was decreased from 212.7 $\mu\text{mol/g}$ of HZSM-5 to 152.6 $\mu\text{mol/g}$ of 2.0Zn/HZSM-5, while the amounts of weak and medium acid were increased from 374.7 $\mu\text{mol/g}$ and 174.3 $\mu\text{mol/g}$ of HZSM-5 to 407.5 $\mu\text{mol/g}$ and 257.9 $\mu\text{mol/g}$ of 2.0Zn/HZSM-5, respectively. The generated weak and medium acid sites are attributed to the interaction between the introduced Zn species and strong acid sites. With the increasing amount of P species into the zeolites, the amounts of weak, medium and strong acid sites were increased firstly and then decreased (Figure 6d and Table 2) because a small amount of P modification enhances the distribution of Zn species in zeolites and generates more Zn-Lewis acid sites, while a large amount of P modification covers the acid site in zeolites.

2.2. Catalytic Performance in Methanol to Aromatics (MTA) Reaction

The catalytic performance of ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples was evaluated in the MTA reaction, and the distribution of aromatic products is shown in Figure 7a,b. The detailed product distribution is summarized in Table 3. The

selectivity of BTX and aromatics of ZSM-5 was 20.59% and 29.41%, respectively. After introducing hierarchical pores into ZSM-5 zeolites via the post-treatment method, the selectivity of BTX was decreased from 20.59% to 18.03%. The selectivity of aromatics was increased from 29.41% to 30.56%, which agrees with the increase of C_9^+ from 8.82% to 12.53% in Table 3. The introduction of a large number of mesopores after sequential desilication-dealumination provides space for the further reaction of macromolecular products, resulting in a decrease in the selectivity of light aromatics and a significant increase in the selectivity of C_9^+ .

Figure 7. Aromatic product distribution (a,b) and conversion of methanol versus time (c,d) over ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples.

After the HZSM-5 zeolites were modified with Zn species, the selectivity of BTX and aromatics was largely increased when the Zn loadings were 0.5 wt%, 1 wt% and 1.5 wt% as shown in Figure 7a. This is because the introduction of Zn species interacts with the Brønsted acid sites and generates dehydrogenation sites, which improved the efficiency of the dehydrogenation step in the aromatization process resulting in an increase in aromatic selectivity. Thus, 1.5Zn/HZSM-5 reached the highest selectivity of BTX (25.40%) and aromatics (15.11%). By further increasing Zn loading to 2.0 wt%, the selectivity of BTX and aromatics was decreased to 20.19% and 13.04%, respectively. It is inferred that only introducing appropriate Zn species into ZSM-5 zeolites generates enough Brønsted acid sites to ensure the processes of dehydration, cyclization and aromatization. At the same time, the Zn species can also provide enough $Zn(OH)^+$ active sites for dehydrogenation. However, if a large amount of Zn species is introduced into ZSM-5 zeolites, Brønsted acid sites are reduced and the process of methanol dehydration to produce dimethyl ether is retarded. Therefore, the steps of olefin cyclization and aromatization will be affected, resulting in a decrease in aromatic selectivity.

Table 3. Distribution of methanol to aromatics (MTA) products over Zn modified and Zn-P co-modified samples.

Sample	B (%)	T (%)	X (%)	BTX (%)	C ₉ ⁺ (%)	Aromatics (%)
ZSM-5	1.01	6.41	13.17	20.59	8.82	29.41
HZSM-5	0.25	3.59	14.19	18.03	12.53	30.56
0.5Zn/HZSM-5	0.36	4.72	14.75	19.83	13.02	32.85
1.0Zn/HZSM-5	0.32	5.17	16.57	22.06	14.49	36.55
1.5Zn/HZSM-5	0.39	5.84	19.17	25.40	15.11	40.51
2.0Zn/HZSM-5	0.29	4.75	15.15	20.19	13.04	33.23
1.5Zn0.1P/HZSM-5	0.47	6.03	19.15	25.65	15.04	40.69
1.5Zn0.3P/HZSM-5	0.53	6.62	20.97	28.12	13.76	41.88
1.5Zn0.6P/HZSM-5	0.49	5.56	19.61	25.66	11.97	37.63
1.5Zn1.0P/HZSM-5	0.50	5.87	18.62	24.99	9.13	34.12

After Zn, P co-modification, the aromatic product distribution of ZSM-5 zeolites exhibited a huge difference as shown in Figure 7b. For example, compared to Zn modified ZSM-5 zeolites, the selectivity of BTX and aromatics of Zn, P co-modified ZSM-5 zeolites increase firstly and then decrease, while the selectivity of C₉⁺ was decreased with the increase of P loadings. When the P loading is 0.3 wt%, the selectivity of BTX is increased from 25.4% of 1.5Zn/HZSM-5 to 28.12% of 1.5Zn0.3P/HZSM-5. This phenomenon should be contributed to two reasons: (1) the introduction of P species reduces the amount of Brønsted acid sites, retards the further reaction of light aromatics, and reduces the selectivity of C₉⁺; (2) the introduction of P species will promote the dispersion of Zn species and part of P species will exist as the phosphorus oxide deposited on the pores of ZSM-5 zeolites. An appropriate amount of introduced P species into the Zn modified ZSM-5 zeolites can lead to a synergistic effect with Zn species. However, excessive phosphorus species into Zn modified ZSM-5 zeolites can dramatically decrease the amount of Brønsted acid sites and sequentially reduce the selectivity of aromatics and BTX.

Figure 7c,d show the conversion of methanol versus time over ZSM-5, HZSM-5, Zn modified and Zn-P co-modified samples. It is found that ZSM-5 exhibited a short lifetime of 6 h due to the large crystal size and narrow microporous channels, which led to coke deposition after multiple reactions [39]. The lifetime of hierarchical ZSM-5 zeolites was dramatically increased to 14 h due to a large amount of mesopores being introduced by sequential desilication-dealumination and the diffusion properties were enhanced. However, after introducing Zn species into hierarchical ZSM-5 zeolites, the lifetime was decreased as shown in Figure 7c, which is attributed to the following two aspects. On the one hand, the introduction of Zn species will enhance the dehydrogenation capacity of catalysts, promote the formation of macromolecular aromatics, and aggravate the coke deposition in the pores of ZSM-5 zeolites. The coke not only blocks the pores of ZSM-5 zeolites but also covers the active sites, resulting in the unable interaction between reactants and acid sites; on the other hand, the introduced Zn species exist in the form of oxides on the surface and in the pores of ZSM-5 zeolites, which retard the diffusion properties of the catalysts.

Compared to the Zn modified ZSM-5 zeolites, the lifetime of Zn-P co-modified ZSM-5 zeolites was improved as shown in Figure 7d. For example, the lifetime was increased from 11 h of 1.5Zn/HZSM-5 to 18 h of 1.5Zn0.3P/HZSM-5. Three reasons are responsible for the enhanced lifetime. Firstly, the amount of Brønsted acid sites was decreased after Zn-P co-modification, which retards the coke formation during the catalytic reaction. Secondly, the specific surface area and pore volume were increased due to the etching effect of phosphoric acid. The diffusion properties and anti-coking abilities were increased. Thirdly, the presence of P species can stabilize the framework aluminate of zeolites and improve the hydrothermal stability of the catalysts [21]. Therefore, the Zn-P co-modified ZSM-5 zeolites exhibited a much longer lifetime.

3. Materials and Methods

3.1. Catalyst Preparation

3.1.1. The Preparation of ZSM-5 Zeolites via Dry Gel Conversion (DGC)

Commercial basic silica sol (Qingdao Haiyang Co., Ltd., Qingdao, China, 30 wt% SiO₂) and sodium aluminate (Sinopharm Co., Ltd., Beijing, China, 41 wt% Al₂O₃) were adopted as silicon source and aluminate source, respectively, without further treatment. A typical direct synthesis process of ZSM-5 zeolite by dry gel conversion is as follows: 1.025 g of sodium aluminate and 1.675 g sodium hydroxide were added to 100 mL deionized water at room temperature and stirred for 0.5 h. After that, 50 g silica sol was dropped into the mixture and continuously stirred for 6 h. The mixture obtained was dried at 110 °C to form a dry gel and then put into 250 mL reactor partition. 25 mL deionized water was added to the bottom of a stainless-steel autoclave and put into the oven at 170 °C for 48 h. The crystallized products were ion-exchanged three times in 1 mol/L NH₄Cl solution (0.1 g ZSM-5/mL NH₄Cl solution) and calcined at 550 °C for 4 h to obtain H-type ZSM-5 zeolites (ZSM-5).

3.1.2. The Preparation of Hierarchical ZSM-5 Zeolites via the Destructive Method

Typically, 1 g of H-type ZSM-5 zeolites are dissolved in 10 mL 0.6 mol/L aqueous NaOH solution (0.1 g ZSM-5/mL NaOH solution) and stirred at 80 °C for 1 h. Then the product was collected by filtration followed by washing with deionized water and drying at 80 °C overnight. The alkali-treated zeolites were transferred into 0.1 mol/L HCl aqueous solution (5 g zeolite per 50 mL of solution) and reacted for 5 h at 80 °C, followed by filtration, washing with deionized water and finally dried at 80 °C overnight. The obtained zeolites were ion-exchanged three times in 1 mol/L NH₄Cl solution and calcined at 550 °C for 4 h to obtain H-type hierarchical ZSM-5 zeolites (HZSM5).

3.1.3. The Preparation of Zn-Modified or Zn-P Co-Modified Hierarchical ZSM-5 Zeolites via Impregnation Method

The Zn-modified or Zn-P co-modified hierarchical ZSM-5 zeolites were prepared by the wet impregnation method. Typically, a predetermined amount of Zn(NO₃)₂ and phosphoric acid was dissolved in the deionized water and then added into the synthesized hierarchical ZSM-5 zeolites. The mixture was stirred for 24 h at room temperature, followed by drying at 110 °C overnight and calcination at 550 °C for 4 h in a muffle furnace. The obtained products were designated as xZn/HZSM-5 or xZn_yP/HZSM-5 (x and y are the weight percentages of introduced Zn and P species, respectively).

3.2. Characterization

Phases of synthesized zeolites were characterized by the X'Pert Pro MPD polycrystalline powder X-ray diffractometer (XRD, PANalytical) with Cu K α radiation at 40 kV and 400 mA. The data was collected when the 2 Theta ranging from 5–60° and the scanning speed was 10°/min. The N₂ adsorption-desorption isotherms were measured at −196 °C using a Micromeritics Tristar 3020 physical adsorption instrument. The total surface area and micropore volume were calculated using Brunauer–Emmett–Teller (BET) equation and t-plot method, respectively. The Barrett–Joyner–Halenda (BJH) method was used to determine the mesopore volume and pore size distribution. The morphology was investigated by a transmission electron microscope (TEM, JEM-2100UHR). The samples were ultrasonically dispersed in absolute ethanol and dropped cast on carbon-coated Cu grids. High-angle annular dark-field (HAADF) images were carried out using a scanning transmission electron microscope (STEM, FEI Titan3 Themis 300) operating at 300 kV with FEI Super-X 4-detector EDX system. Temperature-programmed desorption of ammonia (NH₃-TPD) was conducted by an AutoChem II 2920 (Micromeritics). Typically, 100 mg of samples were pretreated at 550 °C for 30 min in He, and then NH₃ was injected at 80 °C for 40 min. After that, the reactor was purged by He at the same temperature for 60 min. Desorption of NH₃ was conducted at a temperature window ranging from 70

to 650 °C at a rate of 10 °C/min. A Thermo Nicolet NEXUS spectrometer was used for the Fourier-transformed infrared spectrum of pyridine adsorption (Py-IR). Firstly, all the samples were dried in a vacuum at 300 °C for 3 h before analysis and then the pyridine adsorption was conducted for 24 h after cooling to room temperature. Then the samples were vacuumed for 3 h at 150 °C to remove the physically adsorbed pyridine. The UV-visible absorption spectra were measured by a Shimadzu UV-2450 spectrophotometer. The elemental contents of samples were determined by an X-ray fluorescence spectrometer (AXIOS-Petro, PANalytical, Netherlands). X-ray photoelectron spectroscopy (XPS) was measured by a Thermo Fisher's Escalab 250 Xi instrument, and all samples were dried and compressed before analysis.

3.3. MTA Catalytic Tests

0.5 g of catalyst (20–40 mesh) was loaded into a fixed bed reactor (inner diameter: 10 mm, length: 50 cm) and the catalyst was fixed by the quartz. First, the catalyst was activated in N₂ (20 sccm) at 400 °C for 1 h. After that, methanol was injected by an injection pump with a weight hourly space velocity (WHSV) of 2.1 h^{−1}. The reaction products were analyzed online using gas chromatograph (SCION-436GC). The selectivity of the product (S_i) was calculated by Equation (1):

$$S_i = \frac{(\text{mass of product } i)}{(\text{total mass in the feed})} \times 100\% \quad (1)$$

When the methanol conversion rate is less than 99%, the catalyst is considered to be deactivated.

4. Conclusions

Using ZSM-5 zeolite directly synthesized by a dry gel conversion method without adding any template or seed crystals as the raw material, hierarchical ZSM-5 zeolites were prepared based on the synthesized ZSM-5 via sequential desilication-dealumination. Zn and P species were successfully introduced into the hierarchical ZSM-5 zeolite by the impregnation method. The effects of Zn and P loadings on the physiochemical properties of hierarchical ZSM-5 zeolites and MTA reaction performance were investigated. The results show that after Zn, P co-modification, the BTX and aromatics selectivity of 1.5Zn0.3P/HZSM-5 was significantly increased to 28.12% and 41.88%, respectively. The lifetime was extended from 6 h of ZSM-5 to 18 h of 1.5Zn0.3P/HZSM-5. This is attributed to the introduction of Zn and P species generating more new Zn-Lewis acid sites and the ratio of Zn(OH)⁺/ZnO being increased.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111388/s1>, Figure S1: XRD patterns (zoom area) of ZSM-5, HZSM-5, Zn modified, Figure S2: XRD patterns (zoom area) of Zn-P co-modified samples, Figure S3: SEM image of synthesized ZSM-5.

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