

金属氧化物改性的 HZSM-5 催化热解木质素定向制备对二甲苯

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摘要 对二甲苯是石化行业中一种重要的大宗化学品,而且生物质基对二甲苯的制备在学术和工业领域都具有重要意义.对木质素和甲醇在不同金属氧化物改性的 HZSM-5 催化剂作用下共催化热解一步法制备可再生的对二甲苯的过程进行了研究.研究表明,在 HZSM-5 催化剂中引入 La, Mg, Ce 和 Zn 元素可以调节催化剂的酸强度和强酸性位点,进而促进轻芳烃(如苯和甲苯)烷基化形成对二甲苯以及间/邻二甲苯向对二甲苯的异构化.木质素和甲醇的共催化热解显著地提高了对二甲苯的产率.在 20% La₂O₃/HZSM-5 催化剂作用下,木质素与 33 wt% 甲醇共催化热解获得的对二甲苯的最高收率为 13.9%,对二甲苯/二甲苯比率为 82.7%.并且基于产物的分析以及催化剂的表征,提出了由木质素制备对二甲苯的可能反应途径.

关键词 木质素;对二甲苯;催化热解;烷基化;异构化

Catalytic Pyrolysis of Lignin for Directional Production of *p*-Xylene over Metal Oxides-Modified HZSM-5 CatalystsJia, Qifang^a Zhu, Lijuan^a Fan, Minghui^b Li, Quanxin^{*,a}^(a) Department of Chemical Physics, Anhui Key Laboratory of Biomass Clean Energy, University of Science and Technology of China, Hefei 230026)^(b) Anhui Key Laboratory of Tobacco Chemistry, Anhui Tobacco Industrial. Co., Ltd., Hefei 230088)

Abstract Para-xylene (*p*-xylene) is an important bulk chemical in petrochemical industry, and the production of biomass-based *p*-xylene is of great significance in both academic and industrial arenas. This work proves the one step process for the production of *p*-xylene through the catalytic pyrolysis of lignin into the aromatic monomers, together with the alkylation of light aromatics and the isomerization of xylenes isomers into *p*-xylene over metal oxides-modified HZSM-5 catalysts. The modified catalysts by adding the La, Mg, Ce, and Zn elements into HZSM-5 promoted the alkylation of light aromatics (like benzene and toluene) into xylenes, and the isomerization of *m/o*-xylenes to *p*-xylene, due to the modulations of the acid strength and the strong acid sites. Co-catalytic pyrolysis of lignin and methanol significantly enhanced the production of *p*-xylene during the catalytic pyrolysis of lignin. The highest *p*-xylene yield of 13.9% with a *p*-xylene/xylenes ratio of 82.7% was obtained by the co-catalytic pyrolysis of lignin with 33 wt% methanol over the 20% La₂O₃/HZSM-5 catalyst. The reaction pathway for the formation of *p*-xylene from lignin was addressed based on the identified products and the characterization of catalysts.

Keywords lignin; *p*-xylene; catalytic pyrolysis; alkylation; isomerization

1 Introduction

Para-xylene (*p*-xylene), an important bulk chemical in petrochemical industry, has been used mainly in the production of terephthalic acid that is an important intermediate for the synthesis of resins and fibers.^[1] Industrially, various aromatic chemicals have been usually obtained

from the refining of petroleum. Para-xylene can be formed from various subsequent catalytic transformations such as aromatic disproportionation, alkylation, isomerization along with a series of separation processes.^[2-4] With the growing consumption of oil and the negative environmental impacts, there is considerable interest in producing commodity chemicals using renewable biomass re-

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sources.^[5,6]

Lignin, one of three principal components (namely lignin, cellulose, hemicellulose) in lignocellulosic biomass, contains 15~30 wt% weight and about 40% energy of biomasses.^[6] Lignin is an irregular polymer that can be biosynthesized by free radical polymerization of coumaryl, coniferyl and sinapyl alcohols.^[5] It is known that lignin contains phenol, 2-methoxy phenol (guaiacol), and 2,6-dimethoxy phenol (syringol) units, which are linked through the C—O and C—C bonds such as β -*o*-4, 4-*o*-5, 5-5, β -5, β -1 and β - β bonds.^[6] Lignin has been considered to be a potential feedstock for the production of bulk and fine chemicals (especially aromatic compounds), in view of its unique structure, abundant content of aromatic units and huge annual amount originated from pulping process or agriculture residue.^[5,6]

Among various routes for the production of lignin-based chemicals, fast pyrolysis^[5~10] and catalytic fast pyrolysis of lignin^[12~17] have received considerable interest. Fast pyrolysis of lignin generates organic liquid products (mainly phenolic compounds) along with solid char and gas.^[5] In general, various kinds of oxygenates are formed through the scission of the C—C and C—O bonds along with elimination of various functional groups (like methoxy and methyl groups) during the thermal decomposition of lignin, resulting in a wide compositional distribution and high oxygen content in lignin-derived bio-oil.^[6]

Unlike pyrolysis, catalytic fast pyrolysis (CFP) of lignin has been proved to be an effective method for production of aromatic chemicals.^[11~17] Generally, the CFP of lignin involves two cascade processes, pyrolysis of lignin and subsequent upgrading of lignin pyrolysis vapor in the same reactor. The main reaction pathway for the CFP of lignin with a zeolite catalyst involves the formation of phenols and other oxygenates by the thermal depolymerization of lignin, followed by the formation of aromatics (like benzene, toluene and xylenes) through further catalytic cracking, deoxygenation (dehydration, decarboxylation, and decarbonylation), aromatization and oligomerization over zeolites.^[16] Up to now, there are many reports on the production of lignin-based chemicals (especially aromatic chemicals) by catalytic pyrolysis of lignin with various catalysts including zeolite catalysts and metal oxide catalysts.^[11,17] The distribution of products and the yield of a specific hydrocarbon strongly depend on the characteristics of zeolite catalysts, the modes of catalytic pyrolysis, the reactor designs and reaction conditions.^[11~17] For example, Jackson *et al.*^[11] compared the CFP performance of Asian lignin with five catalysts including HZSM-5, KZSM-5, Al-MCM-41, solid phosphoric acid and Co/Mo/Al₂O₃. They pointed out HZSM-5 was the best catalyst for producing aromatics, while the Co/Mo/Al₂O₃ catalyst yielded 75% oxygenated aromatics. Ma *et al.*^[12] catalytically pyrolyzed alkaline lignin in the presence of zeolite catalysts with various acidity and pore size and reported 30% carbon yield of aromatic hydrocarbons with HZSM-5. Wang *et al.*^[14] investigated the CFP of cellulose, hemicellulose and

lignin over HZSM-5, and found that the yield of aromatic hydrocarbons decreased in the following order: cellulose > hemicellulose > lignin. To increase aromatics yields and reduce coke yield, there are several reports on the production of aromatic chemicals by co-CFP of biomass and additives.^[19,20]

Recently, the production of biomass-derived *p*-xylene has received a large amount of interest.^[21] Several different routes to produce bio-based *p*-xylene have been proposed, including synthesis of *p*-xylene from bio-ethanol based ethylene,^[1] conversion of bio-based isobutanol to *p*-xylene^[22] and CFP of biomass to *p*-xylene containing aromatics.^[23] However, the biggest challenge for the production of bio-based *p*-xylene using lignin or biomass is how to improve the yield and selectivity of the target product, along with reducing coke and catalyst deactivation. As far as we know, there is few work regarding selective production of *p*-xylene using lignin.^[24] Thus, further study on the optimizations of catalysts and controlling reaction pathways is required to improve the *p*-xylene yield.

In our previous work, we have investigated using lignin as a potential feedstock for the production of aromatic chemicals like benzene, ethylbenzene, cumene and C(8)—C(15) cycloparaffins.^[25~28] In this work a one-pot process that lignin could be directionally converted into *p*-xylene by coupling the catalytic pyrolysis of lignin into aromatic monomers, the alkylation of light aromatics to xylenes and the isomerization of *m/o*-xylenes to *p*-xylene over the metal oxides-modified HZSM-5 catalysts, is developed. The influences of the catalysts acidity, methanol additive and reaction temperature on the selectivity and yield of *p*-xylene were investigated in detail.

2 Results and discussion

2.1 Screening of catalysts for production of lignin-based xylenes

Figure 1 shows the performance of the catalytic pyrolysis of lignin cofeeding with methanol over the different metal oxides modified HZSM-5 catalysts at 450 °C. It was found that the introduction of the metal oxides (La₂O₃, MgO, CeO₂, or ZnO) into the HZSM-5 zeolite system improved the organic liquid products during the catalyst pyrolysis of lignin. Compared with HZSM-5, the yields of xylenes (especially *p*-xylene) over the metal oxides-modified zeolite catalysts were significantly enhanced, accompanied by the decrease in the yields of benzene, toluene and polycyclic aromatics such as naphthalene, methyl-naphthalene and indene. This implies that adding the La, Mg, Ce, or Zn element into HZSM-5 promoted the alkylation of benzene and toluene to form xylenes, and the isomerization of *m*-xylene and *o*-xylene to *p*-xylene. The selectivity of *p*-xylene using the different metal oxides-modified HZSM-5 catalysts decreased in the following order: 20% La₂O₃/HZSM-5 > 20% MgO/HZSM-5 > 20% ZnO/HZSM-5 > 20% CeO₂/HZSM-5 > HZSM-5. Among the tested catalysts, the 20% La₂O₃/HZSM-5 catalyst shows

the highest selectivity of xylenes (65.9%) and the highest *p*-xylene/xylenes ratio of 82.7%.

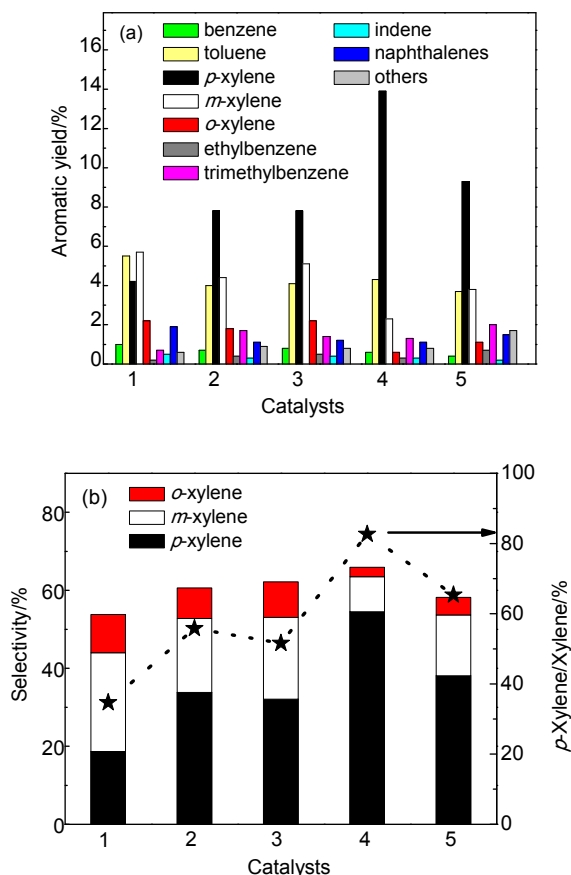


Figure 1 Catalytic pyrolysis of lignin into *p*-xylene over the different metal oxides-modified HZSM-5 catalysts

(1) HZSM-5; (2) 20% ZnO/HZSM-5; (3) 20% CeO₂/HZSM-5; (4) 20% La₂O₃/HZSM-5; (5) 20% MgO/HZSM-5. Reaction condition: *T* = 450 °C, *m*(lignin) : *m*(methanol) = 2 : 1 and catalyst/lignin = 2 : 1.

Figure 2(a) shows the XRD patterns of the unmodified and modified HZSM-5 catalysts. Five catalysts exhibited similar characteristic diffraction peaks of MFI structure,^[2] indicating that the crystal structure of the modified HZSM-5 catalysts was retained during the modification process. However, the crystallinity for the modified HZSM-5 catalysts was obviously reduced, which was also observed in the previous work.^[3] In addition, the weaker characteristic diffraction peaks of ZnO and CeO₂ were observed for 20% ZnO/HZSM-5 and 20% CeO₂/HZSM-5, respectively. No obvious diffraction peaks corresponding to MgO and La₂O₃ were detected in the XRD spectra from 20% MgO/HZSM-5 and 20% La₂O₃/HZSM-5 respectively, suggesting that MgO and La₂O₃ might be highly dispersed on the surface of HZSM-5.

In order to investigate the changes of the acidity and acid sites, the NH₃-TPD analyses were performed for the unmodified HZSM-5 and modified HZSM-5 catalysts with different metal oxides. The NH₃-TPD profiles were shown in Figure 2(b), and the acidic properties of the catalysts were summarized in Table 1. Total acidity was determined

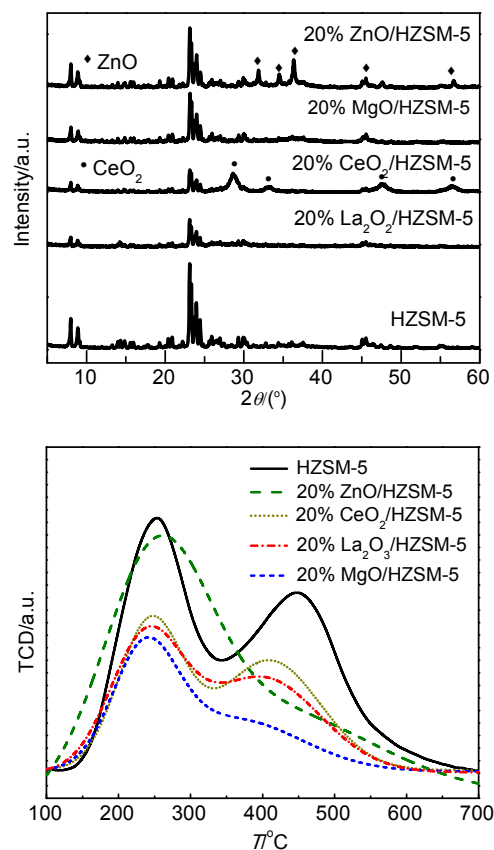


Figure 2 (a) XRD characterizations, and (b) NH₃-TPD profiles for five catalysts

by the amounts of ammonia desorbed from the catalyst surface. Compared with HZSM-5, the acidities of all modified HZSM-5 catalysts were significantly reduced by adding the metal oxides into HZSM-5. For example, the acidity of HZSM-5 was 335.7 μmol NH₃/gcatalyst, and the acidity of 20% La₂O₃/HZSM-5 decreased to 194.1 μmol NH₃/gcatalyst. As can be seen from Figure 2(b), HZSM-5 exhibited two desorption peaks near 250 and 450 °C, corresponding to ammonia desorbed from the weak acid site and strong acid site, respectively.^[29] Similar double peaks in the NH₃-TPD profiles were also observed for 20% La₂O₃/HZSM-5 and 20% CeO₂/HZSM-5, while the high-temperature desorption peak corresponding to the strong acid site was significantly decreased for 20% MgO/HZSM-5 and 20% ZnO/HZSM-5. Furthermore, the ratio of strong acid site to the weak acid site (S/W ratio) can be determined by fitting the NH₃-TPD patterns into two Gaussian components.^[29] Notably, the S/W ratios were reduced remarkably for the metal oxides-modified HZSM-5 catalysts. The S/W ratio for HZSM-5 was 1.14, and the values for the catalysts modified by the metal oxides of La₂O₃, MgO, CeO₂, and ZnO decreased to 0.73, 0.40, 1.08 and 0.45 respectively. Accordingly, the increase in the yield and selectivity of *p*-xylene using the metal oxides-modified HZSM-5 catalysts should be in association with the alteration of the acid strength and the strong acid sites. In addition, the Influence of the La₂O₃ content on the

Table 1 Main properties of the catalysts^a

Catalysts	Si/Al	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	$V_p/(\text{cm}^3 \cdot \text{g}^{-1})$	S/W	Total acidity ($\mu\text{mol} \cdot \text{NH}_3 \cdot \text{g cat}^{-1}$)
HZSM-5	50	356.3	0.22	1.14	335.7
10% $\text{La}_2\text{O}_3/\text{HZSM-5}$	50	292.5	0.16	0.56	259.3
20% $\text{La}_2\text{O}_3/\text{HZSM-5}$	50	220.6	0.14	0.73	194.1
30% $\text{La}_2\text{O}_3/\text{HZSM-5}$	50	148.9	0.13	0.70	127.2
20% $\text{CeO}_2/\text{HZSM-5}$	50	282.1	0.20	1.08	217.8
20% $\text{MgO}/\text{HZSM-5}$	50	165.8	0.15	0.40	140.6
20% $\text{ZnO}/\text{HZSM-5}$	50	146.7	0.11	0.45	262.6

^a Symbols meanings: Si/Al: the ratio of silicon to aluminum in the zeolites, S_{BET} : Brunauer-Emmett-Teller surface area, V_p : pore volume, and S/W : the ratio of strong acid sites to the weak acid sites estimated by the Gaussian fitting of NH_3 -TPD profiles.

production of *p*-xylene by the co-catalytic pyrolysis of lignin/methanol was added in the revision. Increasing the La_2O_3 content reduced the yield of total aromatics. However, the yield and selectivity of *p*-xylene were much improved with increasing the La_2O_3 content from 0 to 20%. This could be attributed to the decrease in the acidity and the pore volume (Table 1).

2.2 Effect of adding methanol on transformation of lignin into *p*-xylene

To improve the yield and selectivity of *p*-xylene, co-catalytic pyrolysis of lignin and methanol was conducted using the selected 20% $\text{La}_2\text{O}_3/\text{HZSM-5}$ catalyst with a varied methanol content in the mixture of lignin and methanol. As shown in Figure 3, co-feeding lignin with methanol significantly enhanced the yield of the organic liquid products. In the case of co-feeding lignin with 50 wt% methanol, the yield of the organic liquid products (mainly aromatics) increased to 26.3%, which was significantly higher than the yield of 16.1% in the absence of methanol. Especially, adding methanol into lignin much improved the yield and selectivity of *p*-xylene in the aromatics. Without adding methanol, the yield of *p*-xylene obtained from the catalytic pyrolysis of lignin was only 4.0% with a selectivity of 24.8%. In the case of co-feeding lignin and 50 wt% methanol, however, the yield and selectivity of *p*-xylene increased significantly to 14.0% and 53.2%, respectively. For the co-catalytic pyrolysis of lignin and methanol, the yields of benzene and toluene were obviously decreased, indicating that partial benzene and toluene were converted into xylenes by the methylation reactions over the 20% $\text{La}_2\text{O}_3/\text{HZSM-5}$ catalyst. As can be seen from Figure 3, the catalytic pyrolysis of methanol also yielded aromatics by the aromatization of methanol. However, it was also found that the yield of *p*-xylene increased non-linearly with increasing the methanol content in the mixture, which may suggest there is a synergistic effect between two feeds during co-catalytic pyrolysis of lignin and methanol. Thus, the products distribution from the co-catalytic pyrolysis process mainly depended on the catalytic cracking of lignin/methanol, methylation of aromatics and other polymerization reactions.

The temperature programmed oxidation (TPO) analyses for determining the carbon content deposited on the used catalysts were also carried out by a thermogravimetric

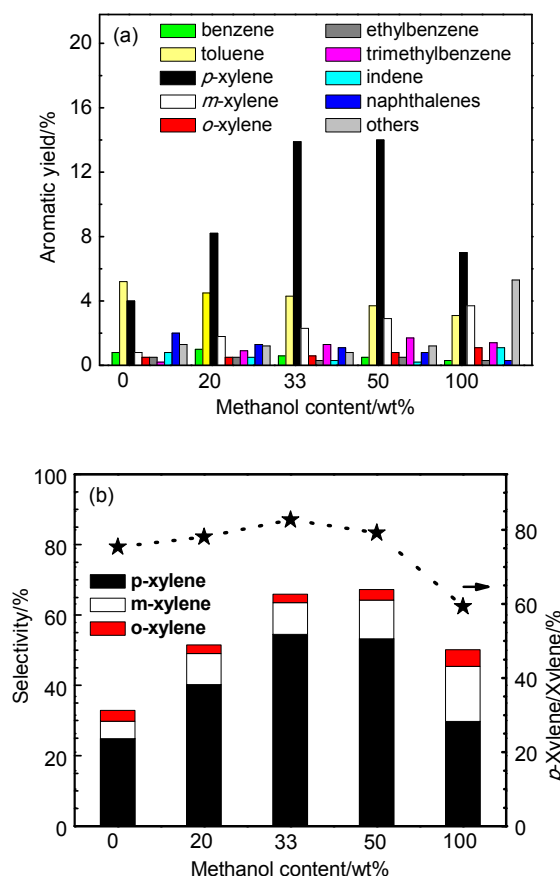


Figure 3 Influence of the methanol content on the production of *p*-xylene by the co-catalytic pyrolysis of lignin and methanol. Reaction condition: $T=450\text{ }^{\circ}\text{C}$ and $m(\text{catalyst}) : m(\text{lignin})=2 : 1$, 20% $\text{La}_2\text{O}_3/\text{HZSM-5}$ catalyst.

analyzer (TGA). In the case of adding methanol [$m(\text{lignin})/m(\text{methanol})=2 : 1$], the coke content on the used catalyst was about 3.9 wt%, which was lower than the value of 5.1 wt% in the absence of methanol. Thus, the addition of methanol into lignin inhibited the deposition of coke on the catalyst.

There are several previous studies reported on co-feeding of biomass or its derivatives (bio-oil) with methanol over HZSM-5 catalysts.^[19,30] In all these investigations, it has been shown that the yields of aromatics were improved and the coke yield was reduced when methanol was co-fed with the biomass or its derivatives. Similar im-

provement was also observed in the present work. The hydrogen to carbon effective ratio (H/C_{eff}) of the feed can be improved by co-feeding of biomass with methanol, and a higher H/C_{eff} favors to produce more petrochemicals.^[18] Regarding the production of *p*-xylene, Cheng *et al.*^[23] reported that ZSM-5 impregnation with 3.8 wt% Ga increased *p*-xylene selectivity from 32% for ZSM-5 to 58% for 3.8 wt% Ga/ZSM-5 in co-catalytic fast pyrolysis of 2-methylfuran with propylene. Similar improvement was also observed for co-CFP of pine wood and LDPE (low-density polyethylene) with Ga/ZSM-5.^[20] They suggested that this improvement was mainly attributed to the partial blockage of pore openings of Ga/ZSM-5 zeolites by Ga-oxides.^[23] On the other hand, it has proved that the alkylation of toluene or benzene with methanol can produce xylenes including *p*-xylene when using zeolite as a catalyst.^[2] It was found that more desired *p*-xylene was formed in the co-catalytic pyrolysis of lignin and methanol. The improvement of the xylenes yields and *p*-xylene selectivity in the co-feed process can be explained by the fact that methanol produces methyl radicals, and then benzene and toluene formed from catalytic pyrolysis of lignin are alkylated to xylenes. Meanwhile, the metal oxides-modified HZSM-5 catalysts (like 20%La₂O₃/HZSM-5) enhanced the isomerization of *m*/*o*-xylenes to *p*-xylene due to the modulation of the acidity and strong acid sites, along with the partial blockage of pore openings for the modified zeolites.

2.3 Influence of temperature on production of lignin-derived *p*-xylene

Figure 4 shows the influence of temperature on the production of *p*-xylene by the co-catalytic pyrolysis of lignin and methanol over the selected 20%La₂O₃/HZSM-5 catalyst. For carbon yields, increasing reaction temperature reduced the yields of organic liquid products. Increasing temperature also significantly affected the yields and selectivity of the individual aromatic product in organic liquid products. The major aromatic product observed in the temperature range of 450~550 °C was *p*-xylene, together with smaller amounts of other aromatics including benzene, toluene, ethylbenzene and the heavier C₈⁺ aromatics (e.g., trimethylbenzene, naphthalene, *m*-naphthalene and indene). The yields of benzene and toluene increased with increasing temperature, along with a decrease in the yields of xylenes and other heavier C₈⁺ aromatics. This may be attributed to the second catalytic pyrolysis of heavier aromatics to form light aromatics through the removal of the alkyl groups in the heavier aromatics, which generally occurred at higher temperatures. In addition, increasing the temperature tends to decrease both the *p*-xylene and overall xylenes yields due to the catalytic cracking of xylenes. When increasing temperature from 450 to 600 °C, the selectivity of *p*-xylene decreased from 54.5% to 19.9%. The selectivity of *m*/*o*-xylenes slightly increased at high temperatures, which caused that the ratio of *p*-xylene to xylenes was reduced from 82.7% to 60.7%. It has been

shown that the alkylation of benzene/toluene to xylenes and the isomerization of *m*-xylene/*o*-xylene to *p*-xylene generally occur at lower temperatures (e.g., $T < 450$ °C) when using zeolite as a catalyst.^[2~4] Accordingly, it seems to be unfavorable for the alkylation and isomerization reactions at high temperatures, leading to the decrease in the *p*-xylene selectivity in the co-catalytic pyrolysis of lignin and methanol.

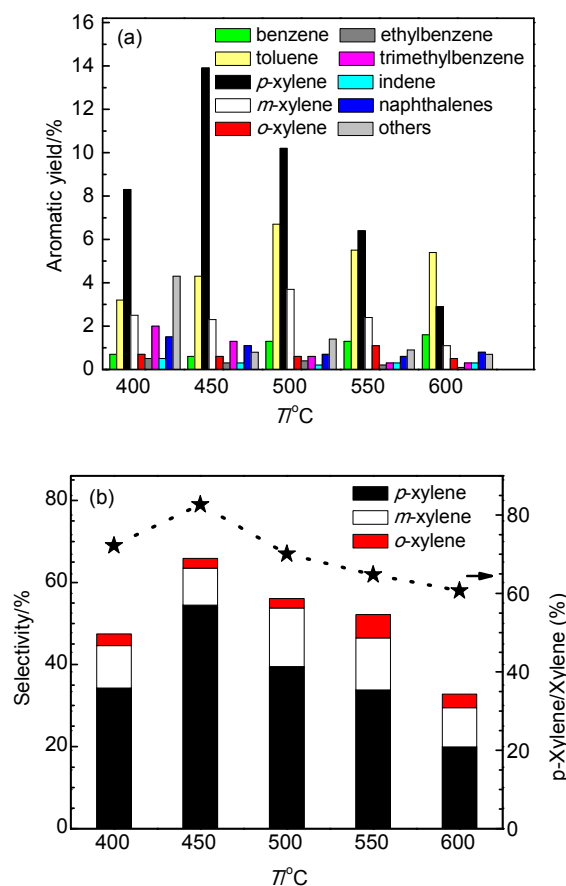


Figure 4 Influence of temperature on the production of *p*-xylene by the co-catalytic pyrolysis of lignin and methanol
Reaction condition: $m(\text{lignin}) : m(\text{methanol}) = 2 : 1$ and $m(\text{catalyst}) : m(\text{lignin}) = 2 : 1$, 20% La₂O₃/HZSM-5.

2.4 Reactions pathways

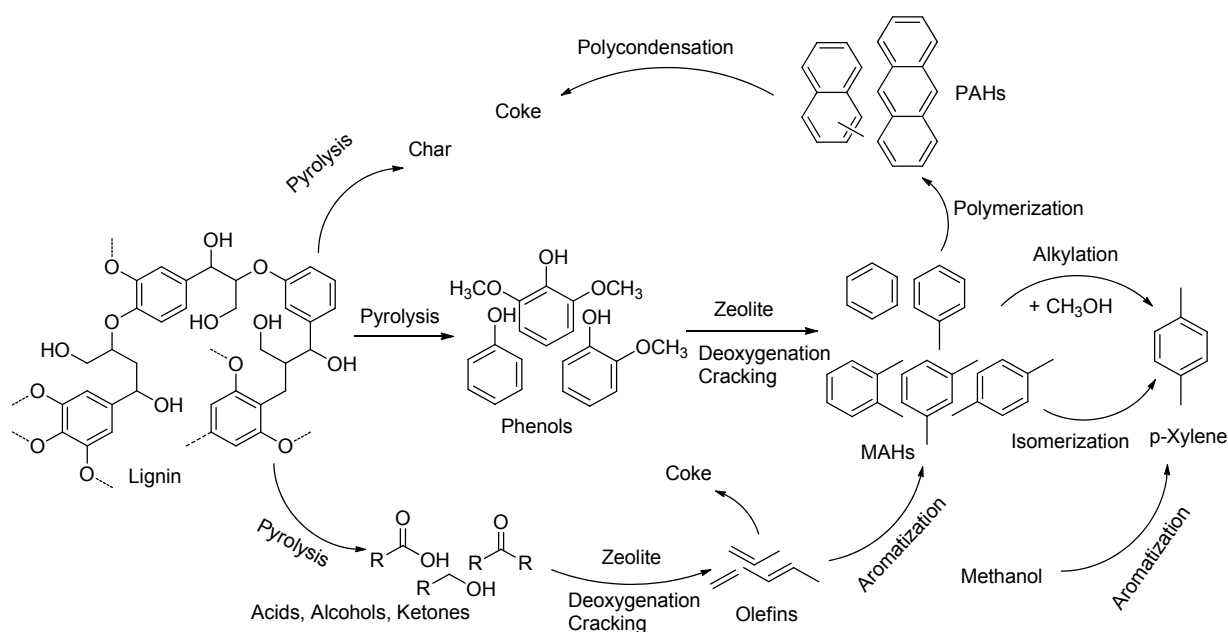
Considerable work has been reported with regard to fast pyrolysis and catalytic fast pyrolysis of lignin.^[5~17] The chemical compositions of oxygenates derived from the pyrolysis of lignin mainly consists of phenolic compounds including guaiacol-type phenols with a methoxy group on the aromatic rings, syringol-type phenols with dimethoxy group on the aromatic rings, phenol-type derivatives (phenol, catechol, and alkyl phenol), and lower molecular weight derivatives (like acetic acid, acetaldehyde, formic acid and acetone).^[14] On the other hand, the catalytic pyrolysis of lignin can promote the formation of aromatic hydrocarbons through cracking, deoxygenation, oligomerization and aromatization, especially using various zeolites as catalysts.^[15]

The purpose of this work is to directionally produce aromatic chemical (*p*-xylene) using renewable lignin. It was demonstrated that one-step transformation of lignin into *p*-xylene via the catalytic pyrolysis of lignin over the metal oxides-modified HZSM-5 catalysts. The main reaction pathways for the selective conversion of biomass into *p*-xylene in this work are summarized in Scheme 1, in view of the products identified, the characterizations of catalyst and previous work on pyrolysis and catalytic pyrolysis of lignin.^[14,15,16] The transformation mainly included four cascade reactions: (1) the pyrolysis of lignin into oxygenated organic compounds, (2) the catalytic pyrolysis of oxygenated organic compounds into the low-carbon aromatic monomers, (3) the alkylation of light aromatics to xylenes, and (4) the isomerization of *m*-xylene and *o*-xylene to *p*-xylene. In the initial step, the oxygenated organic compounds like phenols and other oxygenates were formed by the thermal decomposition of lignin through the disruption of the C—C bonds and C—O bonds in the lignin polymer.^[5] In the second reaction step, the catalytic pyrolysis of oxygenates into aromatic monomers mainly involved the deoxygenation of oxygenates, catalytic cracking and aromatization of low-molecular-weight organics (like acetic acid, formic acid and methanol) and oligomerization reactions over the acidic sites of the zeolite.^[16] Present work shows that the acid modulated zeolite catalyst by the incorporation of La, Mg, Ce, or Zn species effectively reduces the formation of coke, and thereby increases the yield of monocyclic aromatics. The third reaction step involves the improvement of xylenes yield by the alkylation reactions of low carbon aromatics such as benzene and toluene using methanol as alkylating agent. The metal oxides-modified HZSM-5 catalysts (especially La₂O₃-modi-

fied HZSM-5), which were tuned the acidity and the ratios of strong acid sites to the weak acid sites in the zeolite catalysts, were proved to be good active for the alkylation of benzene and toluene into xylenes. Finally, the subsequent isomerization resulted in the transformation of *m/o*-xylenes to *p*-xylene over the same metal oxides-modified HZSM-5 catalysts. La₂O₃-modified HZSM-5 catalyst had good active for isomerization of *m*- or *o*-xylene into *p*-xylene. The conversion of *m*-xylene was 19.8% with a *p*-xylene selective of 46.3%. Under the same conditions, The conversion of *o*-xylene was 17.6% with a *p*-xylene selective of 35.7%. On the other hand, several previous works suggested that the aromatic formation reactions proceed through “hydrocarbon pool” as the common intermediates using the zeolite catalyst.^[14,16] Co-feeding methanol with lignin may alter the “hydrocarbon pool” and improve the yield and selectivity of *p*-xylene.

2 Conclusions

One-step process that lignin was directionally converted into *p*-xylene by the co-catalytic pyrolysis of lignin and methanol over metal oxides-modified HZSM-5 catalysts was developed. The transformation mainly involved four cascade reaction steps: pyrolysis of lignin into oxygenates, catalytic pyrolysis of oxygenates into aromatic monomers, alkylation of light aromatics into xylenes and isomerization of *m/o*-xylenes into *p*-xylene. The acid modulated zeolites by the metal oxides (La₂O₃, MgO, CeO₂ or ZnO) effectively increased the *p*-xylene yield. The 20% La₂O₃/HZSM-5 catalyst shows high active for alkylation of light aromatics and isomerization of *m/o*-xylenes to *p*-xylene. The highest *p*-xylene selectivity of 54.5% with a *p*-xylene/



Scheme 1 Reaction pathways for the co-catalytic pyrolysis of lignin and methanol into *p*-xylene over the metal oxides-modified HZSM-5 catalysts

xylenes ratio of 82.7% was obtained by the co-catalytic pyrolysis of lignin with 33 wt% methanol over the 20% La₂O₃/HZSM-5 catalyst. Present process potentially provides a useful way for the production of bio-based *p*-xylene using renewable lignin resource.

3 Experimental section

3.1 Materials

Lignin is a brown and sulfur-free powder manufactured from wheat straw, purchased from Lanxu Biotechnology Co. Ltd. (Hefei, China).^[25] The dried lignin contained carbon of 63.18 wt%, hydrogen of 5.72 wt%, oxygen of 29.45 wt% and nitrogen of 1.65 wt%, which was carried out by the elemental analysis with an elemental analyzer (Vario EL-III, Elementar, Germany). The oxygen content was calculated based on the difference using C, H, N content. All analytical reagents used were purchased from Sinopharm Chemical Reagent Company Limited (Shanghai, China).

3.2 Catalysts

The HZSM-5 (Si/Al of 50) zeolite was made to order by Nankai University Catalyst Co., Ltd. (Tianjin, China). The metal oxides-modified HZSM-5 catalysts, including La₂O₃/HZSM-5, MgO/HZSM-5, CeO₂/HZSM-5 and ZnO/HZSM-5, were prepared by the impregnation method.^[28] Briefly, the zeolite was impregnated in the corresponding metal nitrate solution for a night, followed by the rotary-evaporation at 80 °C for 6 h. Then, the dried sample was calcined at 550 °C for 5 h and crushed to 40~60 mesh before use. For the characterization of the catalysts, the X-ray diffraction (XRD) was performed on an X'pert Pro Philips diffractometer (Philips, Netherlands). The elemental analysis was carried out by inductively coupled plasma and atomic emission spectroscopy (Thermo Jarrell Ash Corporation, USA). The BET surface area and pore volume of the catalysts were determined by the N₂ physisorption method using a COULTER SA 3100 analyzer. The TPO analyses were conducted with a Q5000IR thermogravimetric analyzer (USA). The acidity of the catalysts was measured by NH₃-TPD from 100 to 800 °C with a heating rate of 10 °C·min⁻¹. Main properties of the catalysts are present in Table 1.

3.3 Experimental procedures for production of xylenes using lignin

Lignin was directionally converted into *p*-xylene by one-pot catalytic pyrolysis process under atmospheric pressure. The catalytic pyrolysis of lignin for the production of aromatics was carried out in a fixed-bed reactor using metal oxides-modified HZSM-5 catalysts, as the same procedures described in our previous work.^[27] The system was mainly composed of a tube reactor, a feeder for solid reactants, two condensers and a gas analyzer. Before each run, the catalysts were loaded into the reactor with the weight ratio of 2 : 1 between catalyst and biomass, and flushed with nitrogen (300 mL·min⁻¹) for 2 h. Then, the

catalyst bed was externally heated to a given temperature by a heater. To promote the alkylation of lignin-derived benzene and toluene into xylenes, co-feeding lignin with methanol was also conducted. In the case of co-catalytic pyrolysis of lignin and methanol, the methanol was synchronously fed by a multi-syringe pump (TS2-60, Baoding Longer Precision Pump) with a given feeding rate. Generally, the catalytic pyrolysis experiments were carried out under the following reaction conditions: 400~600 °C, N₂ gas flow rate of 200 mL·min⁻¹, and the methanol content of 0~100 wt% in the lignin/methanol mixture.

For the products analysis and evaluation, the gas products obtained in each run were analyzed using the gas chromatograph (GC-SP6890, Shandong Lunan Co., Ltd., China), equipped with TCD and FID detectors. The compositions of the liquid products were analyzed by GC-MS (Thermo Trace GC/ISQ MS, USA; FID detector with a TR-5 capillary column). The moles of main products were determined by the normalization method with standard samples and a known concentration. The yield, selectivity and distribution of the products were calculated as described in our previous work.^[26] All the tests were repeated three times and the reported data were the mean values of three trials. Carbon yield (*Y_i*%), the product selectivity (*S_i*%) and conversion (*C_{conv.}*%) of a specific organic compound were calculated based on the following Eqs. 1~3.

$$Y_i(\%) = \frac{\text{Carbon moles in a product}}{\text{Carbon moles fed in}} \times 100\% \quad (1)$$

$$S_i(\%) = \frac{\text{Carbon moles in a product}}{\text{Carbon moles in all products}} \times 100\% \quad (2)$$

$$C_{\text{conv.}}(\%) = \frac{\text{Carbon moles in an organic compound reacted}}{\text{Carbon moles in an organic compound fed in}} \times 100\% \quad (3)$$

Supporting Information TGA profiles of catalysts. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn>.

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