

ARTICLE

Synthesis of Cumene from Lignin by Catalytic Transformation

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Cumene is an important intermediate and chemical in chemical industry. In this work, directional preparation of cumene using lignin was achieved by a three-step cascade process. The mixture aromatics were first produced by the catalytic pyrolysis of lignin at 450 °C over 1%Zn/HZSM-5 catalyst, monocyclic aromatics with the selectivity of 85.7 wt% were obtained. Then, the catalytic dealkylation of heavier aromatics resulted in benzene-rich aromatics with 93.6 wt% benzene at 600 °C over H β catalyst. Finally, the cumene synthesis was performed by the aromatic alkylation, giving cumene selectivity of 91.6 C-mol% using the [bmim]Cl-2AlCl₃ ionic liquid at room temperature for 15 min. Besides, adding a small amount of methanol to the feed can efficiently suppress the coke yield and enhance the aromatics yield. The proposed transformation potentially provides a useful route for production of cumene using renewable lignin.

Key words: Lignin, Cumene, Catalytic pyrolysis, Dealkylation, Alkylation

I. INTRODUCTION

Over the past decade, the development of alternative bio-fuels or bio-chemicals from renewable biomass has stimulated significant interest, mainly because of its potential environmental benefits and the continual decrease in fossil sources [1–3]. Lignin, a natural polymer consisting of phenylpropane type units bonded through several different C–O and C–C linkages, is a main constituent of lignocellulosic biomass. Considering its aromatic structure characteristics, lignin can be used potentially as a plentiful and renewable starting material for the production of green aromatics [1–6]. So far, there has been considerable work involved in the lignin chemistry as well as its utilization by means of lignin hydrogenation reduction, oxidation, pyrolysis, catalytic pyrolysis, aqueous phase reforming, or enzymatic conversion [2, 7–10]. Catalytic pyrolysis of lignin over zeolites, for instance, has been widely investigated, mainly producing a variety of the mixture aromatics such as benzene, alkylbenzenes, naphthalenes and indenes [5, 7, 10–13]. Another typical conversion route for lignin use is the hydrogenation of lignin, which involves lignin depolymerization followed by the removal of the functionality of the lignin subunits to form simpler monomeric compounds. The products, depending on catalysts and reaction conditions, generally con-

tain a wide range of compounds such as phenols, aromatics, alkanes, and low oligomers [8, 14–16]. And the directional transformation of lignin into the desired chemicals is still a challenging task.

Cumene is an important basic organic chemical raw material that is mainly used for the production of phenol and acetone, and more than 90% of the worldwide phenol production is based on the cumene process [17–19]. Besides, cumene is also in demand for the manufacture of bisphenol-A, α -methylstyrene, cymene, the synthesis of perfume and the additive for high octane number of fuel oil and so on [17]. Currently, the capacity of cumene production throughout the world, which is only 9.5 million mt/yr by the end of 1998 and up to 550.0 mt/yr in 2014, has increased significantly [20, 21]. Traditionally, cumene is prepared by the isopropylation of benzene with propylene or isopropanol (namely the Friedel-Craft alkylation reactions) [21–23]. For example, UOP's Cumox process and Monsanto-Lummus cumene process are the two typical technique widely used on industrial scale. Cumox process is conducted in the mixture reaction system of propylene with excess benzene using solid phosphoric acid catalyst, offering a high propylene conversion and high selectivity of cumene [22]. For the Monsanto-Lummus process, dry benzene and propylene are reacted through the alkylation reaction under low benzene recycle ratio using the AlCl₃-HCl catalyst, and this process produces the lowest cost [22]. However, the traditional technique of the cumene production may suffer from some problems such as equipment corrosion and pollutant discharge due to

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the use of strong acid catalysts. Alternatively, the use of zeolite catalysts offers an environmentally friendly route to produce cumene, which can achieve a high selectivity of the desired product through pore size and acidity control [17, 24–27]. The ZSM-5 catalyst is one of the most promising candidates for the selective conversion of benzene into cumene. Other zeolites with different structures and acidities have also been investigated in alkylation of benzene, such as beta, mordenite, TNU-9 and SSZ-33 [27]. The remaining challenges for the production of cumene by the benzene alkylation using zeolite catalysts include improving the selectivity and yield of the target product, especially enhancing the benzene conversion.

As far as we know, there is no report regarding directional production of cumene from lignin. In this work, we demonstrated that lignin was directionally converted into cumene by a three-step process. This process included the catalytic pyrolysis of lignin into the mixture aromatics, followed by the dealkylation of aromatics to benzene-rich aromatics and the alkylation of benzene-rich aromatics to cumene by room-temperature liquid phase reactions using the ionic liquid catalysts. Potentially, the proposed cumene synthesis route provides a useful way for the production of the basic petrochemical material and of the high-value chemical using the abundant natural aromatic resource of lignin.

II. EXPERIMENTS

A. Materials

The lignin was purchased from Lanxu Biotechnology Co. Ltd. (Hefei, China). It was a brown and sulfur-free lignin powder manufactured from wheat straw. And the 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). All analytical reagents used were purchased from Sinopharm Chemical Reagent Company Ltd. (Shanghai, China).

B. Catalysts preparation and characterization

The zeolite catalysts including HZSM-5, H β , and Re/HY were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China). Prior to use, the zeolite catalysts were calcined at 550 °C for 4 h at nitrogen atmosphere. The catalyst of 1%Zn/HZSM-5 was prepared by the impregnation method. The HZSM-5 zeolite was impregnated in the corresponding zinc nitrate solution over night, followed by rotary-evaporation at 60 °C, and drying at 110 °C for 6 h. Finally, the dried sample was calcined at 550 °C for 5 h, and crushed to 40–60 mesh. The [bmim]Cl- x AlCl₃ ($x=1-2$) (bmim refers to 1-butyl-3-methylimidazolium chloroaluminate) ionic liquid was prepared by the same method described in our previous

TABLE I Main properties of the catalysts. Si/Al is the ratio of silicon to aluminum in the zeolites, S_{BET} is Brunauer-Emmett-Teller surface area in m²/g and V_{p} is pore volume in cm³/g. The acid density was estimated by the Gaussian fitting of NH₃-TPD profiles. Total acidity is in $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$.

Catalysts	Si/Al	S_{BET}	V_{p}	Total acidity
HZSM-5	25	413.2	0.27	580.6
1%Zn/HZSM-5	25	396.1	0.25	549.5
3%Re/HY	5	532.6	0.37	982.8
H β	26	745.0	0.47	750.0

work [28]. Briefly, [bmim]Cl was first prepared by the reactions of N-methylimidazolium with 1-chlorobutane at the temperature of 80–85 °C for 24 h. Then the mixture was cooled to room temperature, and the unreacted reactants were removed using a rotary evaporator. The resulting imidazolium salt was washed using acetonitrile as solvent, and dried in a vacuum drying box to remove the residual solvent and water. Finally, the ionic liquid of [bmim]Cl- x AlCl₃ ($x=1-2$) was prepared by slowly adding the dried aluminum chloride to the imidazolium salt with a given molar ratio of 1.0–2.0 between AlCl₃ and [bmim]Cl and stirring overnight. The ionic liquid, once prepared, was stored in a dry nitrogen atmosphere.

The metallic element contents in the catalysts were determined by inductively coupled plasma and atomic emission spectroscopy (ICP/AES, Atomscan Advantage, Thermo Jarrell Ash Corporation, USA). The zeolite catalysts were also characterized by N₂ adsorption/desorption and ammonia temperature-programmed desorption (NH₃-TPD) analyses [29]. Typically, the N₂ adsorption/desorption isotherms of the catalysts were performed at 77 K using the Micromeritics ASAP 2020 V3.00 analyzer. The acidity of the catalysts was measured by NH₃-TPD from 100 °C to 800 °C with a heating rate of 10 °C/min. Main properties of the catalysts were summarized in Table I. Moreover, Acidity characterizations of the ionic liquid were carried out by infrared spectroscopy (Bruker Tensor 27 FT-IR spectrometer) using pyridine as the probe molecule of Lewis and Bronsted acid at room temperature. The samples were prepared by mixing pyridine and the ionic liquid in a volume ratio of 5:1, and then smeared into liquid films on KBr windows. All spectra were acquired at a 1 cm⁻¹ resolution with a total of 16 scans. The ¹H NMR and ²⁷Al NMR measurements were carried on a high-resolution liquid nuclear magnetic resonance spectrometer (Bruker Avance 300 MHz).

C. Procedures for production of cumene using lignin

The lignin was directionally converted into cumene by a three-step process under atmospheric pressure, including the catalytic pyrolysis of lignin into the mixed

aromatics (first step), the dealkylation of the alkylaromatic compounds to benzene (second step), and the alkylation of the benzene-rich aromatics to cumene by the low-temperature liquid phase reactions (third step).

In the first step, the production of aromatics by the catalytic pyrolysis of lignin was performed in the continuous flow pyrolysis reactor using the 1%Zn/HZSM-5 catalyst [30, 31]. The system was mainly composed of a tube reactor, a feeder for solid reactants, two condensers and a gas analyzer. Before each run, the reactor was flushed with nitrogen (300 mL/min) for 2 h, and was externally heated to a given temperature by the carborundum heater. To reduce the coke deposition and the deactivation of the catalysts, co-feeding lignin with methanol was conducted in this step. Generally, the catalytic pyrolysis experiments were carried out under the following reaction conditions: 400–550 °C, N₂ gas flow rate of 200 mL/min, and the methanol content of 0–50 wt% in the lignin/methanol mixture. The organic liquid products (named as catalytic pyrolysis oil, CPO) were collected by two condensers, weighed and analyzed by a GC-MS mass spectrometer.

In the second step, the catalytic dealkylation of alkylaromatic compounds (namely CPO) to benzene was conducted over the zeolite catalysts (HZSM-5, H β , and Re/HY). The dealkylation reactions were run in a fixed-bed reactor, similar to the procedures described in the first step. Typical reaction condition for the catalytic dealkylation process was as follows: temperature of 560 °C, space velocity of 0.5 h⁻¹, and the methanol content of 30 wt% in the CPO/methanol mixture. The resulting organic liquid products (named as catalytic dealkylation aromatics, CDA) were collected by two condensers, weighed, and analyzed by a GC-MS mass spectrometer.

In the third step, the alkylation of rich-benzene aromatics of CDA to cumene was conducted by the low-temperature liquid phase reactions using the catalysts of ionic liquid, in which propylene was used as an alkylating agent. The alkylation reactions were run in batch mode in a 20-mL reactor equipped with a gas-inlet, a reflux cooler, sampling exit and a magnetic stirrer under the following reaction conditions: mass ratio of CDA/catalyst of 4:1, propylene flow rate (f) of 30 mL/min, temperature of 20–80 °C and time of 5–90 min. At the end of the reactions, the products on the upper layer were separated from the ionic liquid catalyst at the bottom of the flask by decantation, weighed and analyzed.

D. Products analysis and evaluation

The gas products obtained in each run were analyzed using a gas chromatograph (GC-SP6890, Shandong Lunan Co., Ltd., China). The gas chromatograph equipped with two detectors: a TCD for analysis of H₂, CO, CH₄, and CO₂ separated on TDX-01 column and a FID for gas hydrocarbons separated on Porapak Q column. The moles of the gas products were determined

by the normalization method with standard gases. 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 organic liquid products were determined by the normalization method with standard samples and a known concentration. The conversion, yield, selectivity and distribution of the products were calculated as described in our previous work [30, 31].

$$Y_i = \frac{\text{Mass in gas, liquid or solid products}}{\text{Mass fed in}} \times 100\% \quad (1)$$

$$Y_j = \frac{\text{Mass of a liquid product}}{\text{Mass of all liquid products}} \times 100\% \quad (2)$$

$$Y_k = \frac{\text{Volume of a gas product}}{\text{Volume of all gas products}} \times 100\% \quad (3)$$

$$Y_l = 1 - \frac{\text{Mole of a remaining reactant}}{\text{Mole of the reactant fed in}} \times 100\% \quad (4)$$

$$S_i = \frac{\text{Carbon moles in a product}}{\text{Carbon moles in all products}} \times 100\% \quad (5)$$

where Y_i , Y_j , Y_k , Y_l , and S_i are overall weight yields, liquid products distribution, distribution of gas products, conversion, and selectivity of products. All the tests were repeated three times and the reported data are the mean values of three trials.

III. RESULTS AND DISCUSSION

A. Transformation of lignin into aromatics

To produce cumene from the lignin, first of all, the transformation of lignin into aromatics is required. This conversion was conducted through the catalytic depolymerization and deoxygenation of lignin over the selected 1%Zn/HZSM-5 catalyst. As shown in FIG. 1(a), co-feeding lignin with methanol significantly decreased the formation of coke and tar, as a result, enhanced the yield of the resulting organic liquid products (namely CPO) as well as the gas products. For example, the yield of coke and tar derived from the catalytic pyrolysis of lignin was 40.2 wt%, and reduced to 27.2 wt% when co-feeding lignin and methanol with the mass ratio of 1:1. Adding methanol into lignin also changed the aromatic distribution in the aromatics (FIG. 1(b)). Without adding methanol, the composition of CPO obtained from the lignin essentially consisted of 17.3 wt% benzene, 27.9 wt% toluene, 26.2 wt% xylenes and 15.5 wt% naphthalenes. For co-feeding lignin with methanol, however, the content of benzene was obviously decreased accompanied by the increase in contents of toluene and xylenes, indicating that part of benzene was converted into toluene and xylenes by the methylation process. Besides, adding methanol into the lignin also suppressed the formation of polycyclic aromatics caused by the polymerization of aromatics. Considering that methanol itself also formed aromatics by the aromatization of methanol, as a result, the CPO

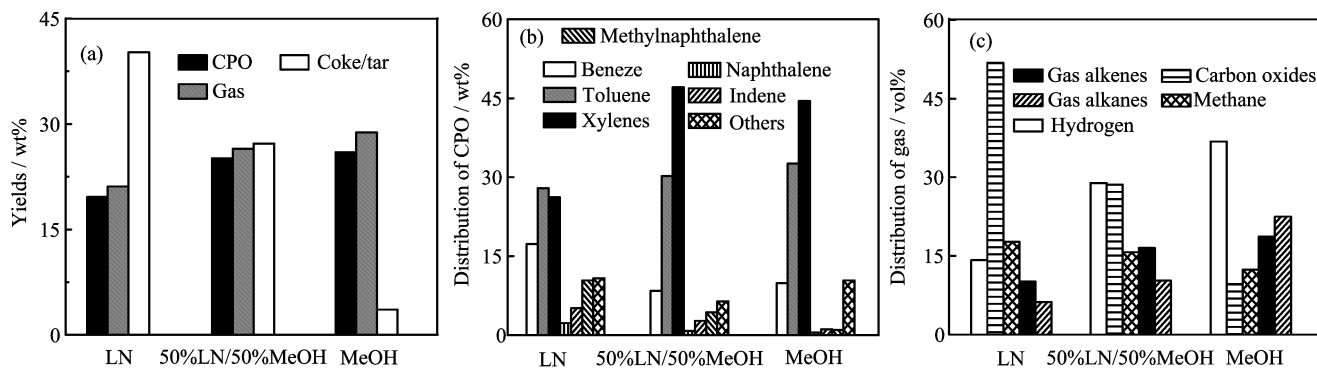


FIG. 1 The effect of co-feeding methanol (MeOH) on the production of aromatics by the catalytic pyrolysis of lignin (LN) over 1%Zn/HZSM-5. Reaction conditions: the weight ratio of catalyst to lignin of 2 at 450 °C. CPO: catalytic pyrolysis oil.

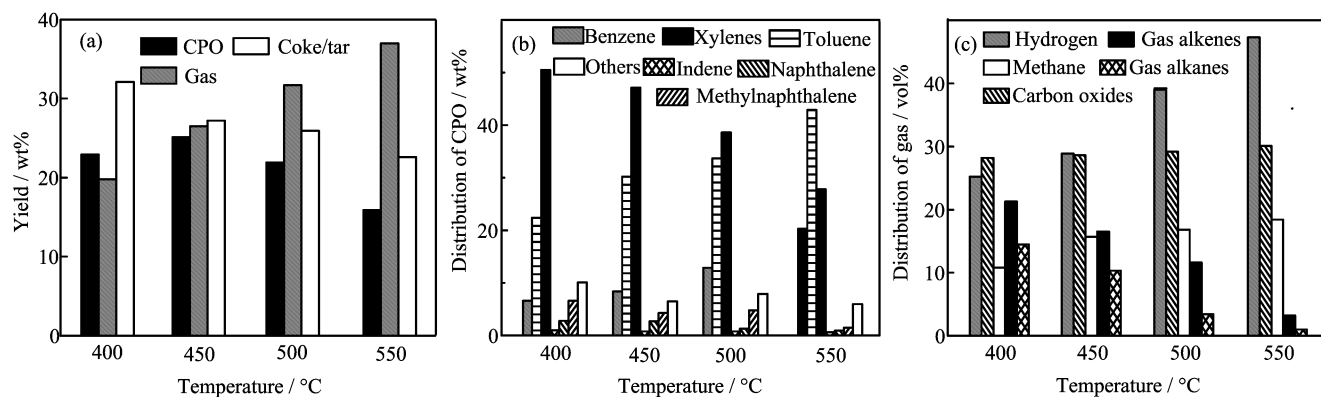


FIG. 2 Effect of temperature on the production of aromatics by the catalytic pyrolysis of lignin/methanol mixture over 1%Zn/HZSM-5. Reaction conditions: the weight ratio of catalyst to lignin=2, lignin/methanol=1:1, $T=400-550$ °C.

distribution for co-feeding methanol with lignin was determined by the competitive reaction pathways, mainly including the catalytic pyrolysis of lignin, aromatization of methanol, methylation of aromatics and polymerization of aromatics [13, 32, 33]. In addition, adding methanol increased the gas products of H_2 , alkenes and alkanes, along with the decline of carbon oxides and methane. So methanol also influenced the distribution of gas.

FIG. 2 shows the effect of temperature on the production of aromatics by the catalytic pyrolysis of lignin/methanol mixture over 1%Zn/HZSM-5 catalyst. Increasing the reaction temperatures resulted in the decrease in the yields of CPO and coke/tar, accompanied by the increase in the gas yield (FIG. 2(a)). This indicates that high temperatures enhance the catalytic depolymerization and gasification of lignin, and reduce the polymerization of aromatics. For the distribution of organic liquid products (FIG. 2(b)), the CPO consisted primarily of C_6-C_8 monocyclic aromatics and a small amount of polycyclic aromatics. For example, the typical CPO obtained at 450 °C contained 8.4 wt% benzene, 30.2 wt% toluene and 47.1 wt% xylenes. These mixed aromatics mainly originated from the C–C and C–O bonds cleavage of lignin together with the decarboxyla-

tion, decarbonylation, dehydration, aromatization and polymerization over the zeolite catalyst [34–36]. Notably, the formation of benzene and toluene increased with increasing temperature along with a decrease in the heavier aromatics (like xylenes and other C_8^+ aromatics), attributed to the removal of the alkyl groups in the heavier aromatics at higher temperatures. In addition, oxygen in the lignin was removed mainly by the decarbonylation, decarboxylation, and dehydration, considering that CO, CO_2 and H_2O were the dominant oxygen-containing products observed. Gaseous olefins and alkanes that come from the catalytic pyrolysis of the lignin/methanol mixture exhibited a descending trend with increasing the temperature (FIG. 2(c)), because of the enhanced decomposition and/or aromatization of light olefins and alkanes at higher temperatures [34–36].

B. Reforming of aromatics mixture into benzene

Since CPO derived from the direct catalytic pyrolysis of lignin was complex aromatic compounds, the transformation of these aromatics into the key intermediate of benzene was further conducted by the catalytic dealkylation process. As can be seen from FIG. 3(a), within the tested catalysts, the HZSM-5 catalyst pro-

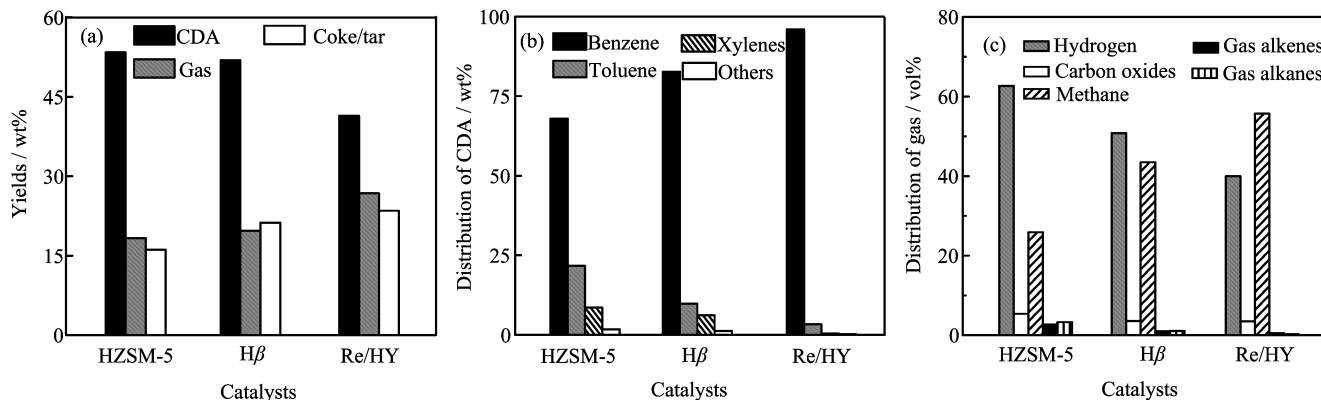


FIG. 3 Transformation of CPO into benzene over the different catalysts. Reaction conditions: $T=560$ °C, CPO:MeOH=0.7:0.3. CPO was obtained by the catalytic pyrolysis of lignin at $T=450$ °C, lignin/methanol=1:1, and the weight ratio of catalyst to lignin=2. CDA: catalytic dealkylation aromatics.

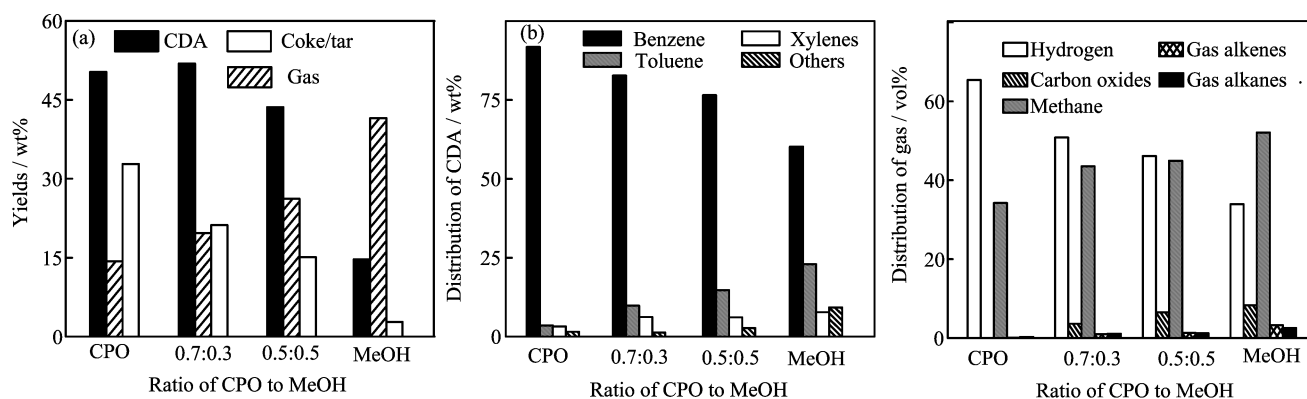


FIG. 4 Influence of methanol on the production of benzene by the catalytic dealkylation of CPO over H β . Reaction conditions: $T=560$ °C. CPO was the same sample as described in FIG. 3.

duced more organic liquid products (CDA) along with lower yields of coke/tar and gas. The CDA, after the catalytic dealkylation reactions at 560 °C over HZSM-5, consisted of 67.9 wt% benzene together with toluene (21.7 wt%), xylenes (8.6 wt%) and other heavier aromatics (1.8 wt%). The Re/HY catalyst that had a strong acidity (Table I), present the highest dealkylation efficiency for the C_6^+ aromatics, leading to the highest content of benzene (95.9 wt%) in the liquid products (FIG. 3(b)). However, the catalytic dealkylation using this catalyst produced more coke/tar by the oligomerizations of aromatics and more gas products by gasification of aromatics (FIG. 3(a) and (c)). Another catalyst H β with a medium acidity exhibited the high activity for the transformation of the mixture aromatics into benzene with a high liquid yield (FIG. 3(a) and (b)), which was selected in the catalytic dealkylation process.

FIG. 4 shows the influence of methanol on the catalytic dealkylation of alkylaromatic compounds over the H β catalyst. Adding methanol into CPO was able to effectively inhibit the formation of coke/tar. For example, the yield of coke/tar without adding methanol

was 32.8 wt%, but in the cases of 30 wt% and 50 wt% methanol added, was significantly reduced to 21.2 wt% and 15.1 wt% respectively. What's more, co-feeding methanol also apparently changed the aromatic distribution in the CDA. When 30 wt% methanol was co-fed with CPO, the content of benzene slightly decreased to 82.7 wt% along with the increase in the contents of toluene and xylenes. In view of that methanol also formed aromatics by the aromatization of methanol (FIG. 4(b)), the content of benzene in CDA should be affected by the dealkylation of aromatics, the oligomerizations of aromatics and the aromatization of methanol in the presence of methanol. Besides, the temperature also influenced the transformation of alkylaromatic compounds into benzene during the dealkylation of aromatics (FIG. 5). Increasing the reaction temperature decreased the CDA yield mainly due to the increase in the gas yield by the decomposition of aromatics. Notably, the content of benzene increased from 41.8 wt% to 93.6 wt% with increasing the temperature from 520 °C to 600 °C (FIG. 5(b)), accompanied by the decrease in toluene, xylenes and other C_8^+ heavier aromatics. This suggested that high temperatures

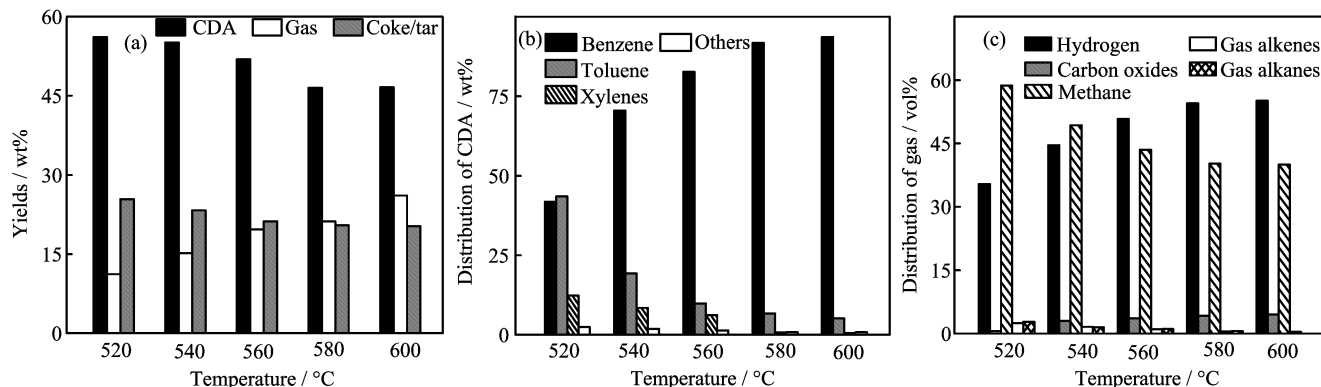


FIG. 5 Effect of temperature on the production of benzene by the catalytic dealkylation of CPO over $H\beta$. Reaction conditions: $T=520-600$ °C, CPO:MeOH=0.7:0.3. CPO was the same sample described in FIG. 3.

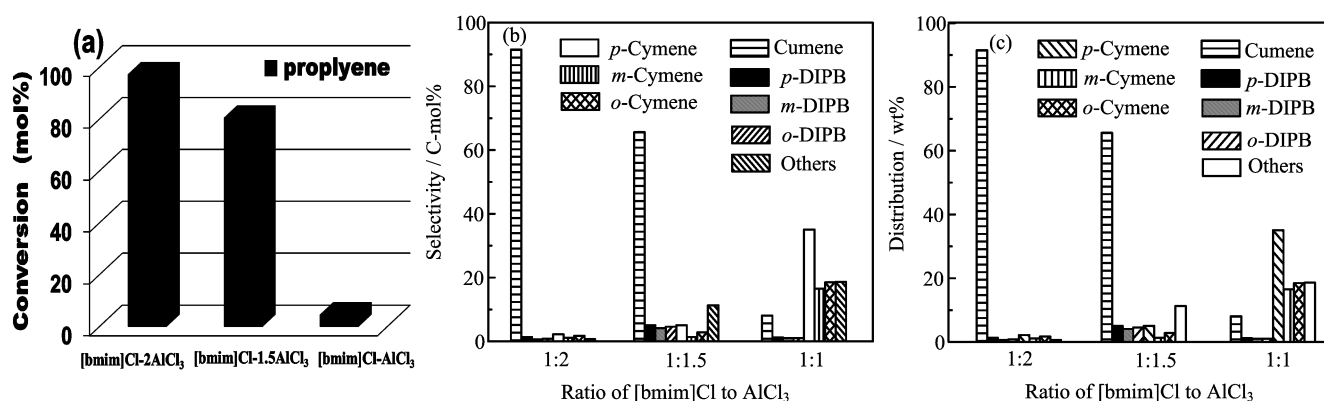


FIG. 6 Production of cumene by the alkylation of CDA over different ionic liquid catalysts. Reaction conditions: mass ratio of CDA/catalyst=4:1, $f(\text{propylene})=30$ mL/min, $T=20$ °C, $t=15$ min. CDA contained 93.6 wt% benzene, 5.1 wt% toluene, 0.5 wt% xylenes and other aromatics of 0.8 wt%.

enhanced the removal of the alkyl groups in the alkyaromatic compounds such as toluene and xylenes. In addition, the gas products mainly consisted of H_2 , and CH_4 (FIG. 5(c)), which come from the catalytic cracking of aromatics and methanol.

C. Synthesis of cumene by the alkylation of lignin derived aromatics

In the following step, we demonstrated that directional production of cumene was able to be realized by the room-temperature liquid-phase alkylation of the benzene-rich aromatics (CDA) using the ionic liquids. Three ionic liquid catalysts, [bmim]Cl-2AlCl₃, [bmim]Cl-1.5AlCl₃, [bmim]Cl-AlCl₃, have been tested for the alkylation of CDA to cumene via propylene as an alkylating agent (FIG. 6). The [bmim]Cl-2AlCl₃ ionic liquid, even at the room temperature (20 °C), showed excellent catalytic activity for the CDA alkylation with a propylene conversion of 97.3 mol% (FIG. 6(a)). Especially, the products obtained using [bmim]Cl-2AlCl₃ were dominated by the desired cumene with a selectivity of 91.6 C-mol% (FIG. 6(b)), together with small

amount of *p*, *m*, *o*-diisopropylbenzene (*p*, *m*, *o*-DIPB) and *p*, *m*, *o*-isopropyltoluene (*p*, *m*, *o*-cymene).

It was found that the molar ratio between the 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and aluminum chloride (AlCl₃) in the ionic liquids greatly affected the alkylation activity of CDA and the product selectivity. When the [bmim]Cl-AlCl₃ catalyst was used, for example, the conversion of propylene was only 4.6 mol% (FIG. 6(a)) and the main products became *p*, *m*, *o*-cymene (FIG. 6(b)), which was clearly different from the behavior of the [bmim]Cl-2AlCl₃ ionic liquid. Chemically, the [bmim]Cl-2AlCl₃ ionic liquid consists of the cations of 1,3-two alkyl substituted imidazolium together with the anions of Al₂Cl₇⁻, as demonstrated by the ²⁷Al NMR analysis (FIG. S1 in the supplementary materials) and ¹H NMR analysis (FIG. S2 in the supplementary materials). In addition, the acidic characteristics of the ionic liquid were also conducted by infrared spectroscopy using pyridine as a probe molecule of Lewis and Bronsted acid (FIG. S3 in the supplementary materials). The bands at 1454 and 1540 cm⁻¹ for pyridine/[bmim]Cl-2AlCl₃ ionic liquid were observed, corresponding to the characteristic peaks of Lewis acid

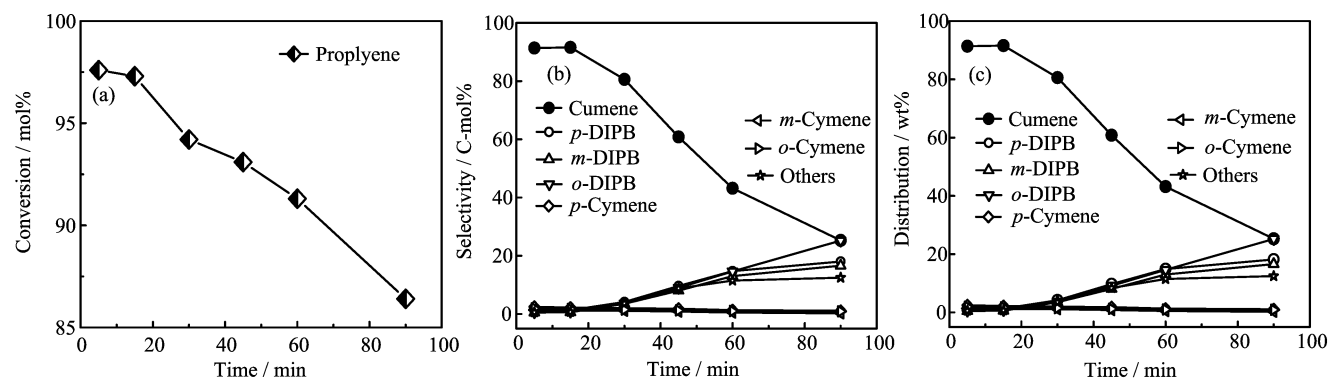


FIG. 7 Influence of the reaction time on the production of cumene by the alkylation of CDA using [bmim]Cl-2AlCl₃ ionic liquid catalyst. Reaction conditions: mass ratio of CDA/catalyst=4:1, $f(\text{propylene})=30$ mL/min, $T=20$ °C. CDA was the same sample as described in FIG. 6.

(pyridine bonded at a Lewis acid site) and Bronsted acid (pyridine bonded at a Bronsted acid site), respectively (Table S1 in the supplementary materials). In addition, the increase in the molar ratio of AlCl₃ to [bmim]Cl obviously increased the Lewis acid of the ionic liquids (FIG. S4 in the supplementary materials). The above characterization results supported that the ionic liquid [bmim]Cl-2AlCl₃ had the properties of both Lewis acid and Bronsted acid. The ionic liquid could enhance the olefinic protonation and the formation of active electrophilic species (positive ions of olefins or carbenium ions), leading to the enhancement of the alkylation reactions of aromatics [37].

FIG. 7 presents the influence of the reaction time on the alkylation of CDA at room temperature (20 °C). As increasing reaction time from 5 min to 90 min, the propylene conversion slightly reduced from 97.6% to 86.4%. Notably, the selectivity and distribution of the products were shifted towards the heavier aromatics by prolonging reaction time. The cumene selectivity decreased from 91.6 C-mol% to 25.3 C-mol% with increasing reaction time from 5 min to 90 min, accompanied with an increase of *p*, *m*, *o*-DIPB from 2.2 C-mol% to 59.3 C-mol%. The alkylation of aromatics in CDA is a consecutive reaction process, and the primary products (like the benzene alkylation to cumene) can generally undergo the second alkylation reactions (like the alkylation of cumene to *p*, *m*, *o*-DIPB). As a result, increasing the reaction time enhanced the cascade reaction, leading to the rise in the by-products for longer reaction time.

Moreover, the influences of temperature on the alkylation of CDA using the [bmim]Cl-2AlCl₃ ionic liquid was investigated (Table II). The conversions of propylene were slightly increased with the increasing temperature in the range of 20–50 °C, and then, showed a reduction trend over 50 °C. Considering that the aromatic alkylation is an exothermic reaction [38], increasing temperature results in the decrease of equilibrium constants and is not beneficial to the aromatic alkyla-

tion. But increasing temperature is conducive to overcome the activation energy required to the alkylation reactions. Meanwhile, the collision probability between ionic liquid and reactants could be enhanced at higher temperatures, leading to the increase in the reaction rates of the aromatic alkylation. Accordingly, the directional products of cumene were able to be expediently tuned via the reaction time and/or the the temperature during the alkylation of lignin derived aromatics using the [bmim]Cl-2AlCl₃ ionic liquid catalyst.

IV. CONCLUSION

This work demonstrated that lignin can be directionally converted into cumene by the catalytic pyrolysis of lignin into the mixture aromatics, followed by the dealkylation of alkylaromatic compounds to benzene-rich aromatics and the alkylation of benzene-rich aromatics to cumene under the moderate reactions. The liquid products consisted primarily of C₆–C₈ monocyclic aromatics and a small amount of polycyclic aromatics for the catalytic depolymerization and deoxygenation of lignin over the 1%Zn/HZSM-5 catalyst. Then, the key intermediate of benzene was produced with a high content of 93.6 wt% by dealkylation process at 600 °C over the H β catalyst. The [bmim]Cl-2AlCl₃ ionic liquid, even at the room temperature (20 °C), showed excellent catalytic activity for the aromatic alkylation in the third step. The desired production of cumene was obtained through the alkylation of the benzene-rich aromatics with a selectivity of 91.6 C-mol% at 20 °C, and can be tunable via the reaction time and/or the the temperature. Moreover, a small amount of methanol into the feed is beneficial for suppressing the coke yield and enhancing the yield of aromatics. Potentially, the proposed cumene synthesis route provides a useful way for the production of the basic petrochemical material using the abundant natural aromatic resource of lignin.

TABLE II Effect of temperature on the production of cumene by the alkylation of lignin-derived CDA using [bmim]Cl-2AlCl₃ ionic liquid catalyst^a.

<i>T</i> /°C	Conversion ^b	Selectivity of products/C-mol%							
		Cumene	<i>p</i> -DIPB	<i>m</i> -DIPB	<i>o</i> -DIPB	<i>p</i> -Cymene	<i>m</i> -Cymene	<i>o</i> -Cymene	Others
20	97.3	91.6	1.3	0.6	0.8	2.2	1.1	1.6	0.8
30	97.5	91.8	1.1	0.6	0.8	2.4	1.2	1.5	0.6
40	98.1	92.0	1.1	0.5	0.7	2.3	1.2	1.6	0.6
50	98.6	92.2	1.0	0.5	0.6	2.5	1.3	1.5	0.4
60	96.2	92.2	0.8	0.4	0.6	2.5	1.4	1.8	0.3
80	93.8	92.3	0.7	0.3	0.5	2.7	1.4	1.9	0.2

	Liquid products distribution/wt%							
	Cumene	<i>p</i> -DIPB	<i>m</i> -DIPB	<i>o</i> -DIPB	<i>p</i> -Cymene	<i>m</i> -Cymene	<i>o</i> -Cymene	Others
20	91.5	1.3	0.6	0.8	2.2	1.1	1.7	0.8
30	91.7	1.1	0.6	0.8	2.4	1.2	1.6	0.6
40	91.9	1.1	0.5	0.7	2.3	1.2	1.7	0.6
50	92.1	1.0	0.5	0.6	2.5	1.3	1.6	0.4
60	92.1	0.8	0.4	0.6	2.5	1.4	1.9	0.3
80	92.2	0.7	0.3	0.5	2.7	1.4	2.0	0.2

^a Reaction conditions: mass ratio of CDA/catalyst=4:1, *f*(propylene)=30 mL/min, *t*=15 min. CDA (catalytic dealkylation aromatics) contained 93.6 wt% benzene, 5.1 wt% toluene, 0.5 wt% xylenes and other aromatics of 0.8 wt%. The values reported are averages of three trials and standard deviations were ≤9.2% for all reported values.

^b Conversion to propylene.

Supplementary materials: The results of the ionic liquid characterization are shown. The [bmim]Cl-2AlCl₃ ionic liquid consists of the cations of 1,3-two alkyl substituted imidazolium together with the anions of Al₂Cl₇⁻, as demonstrated by the ²⁷Al NMR analysis with the peak around 103 ppm (see FIG. S1). Based on the comparison of ¹H NMR spectra before and after being titrated with KOH solution (FIG. S2), the absence of H in the star site after titrated with KOH solution suggests that the ionic liquid can provide protons from the ionic liquid. Furthermore, the acidic characteristics of the ionic liquid were conducted by infrared spectroscopy using pyridine as a probe molecule of Lewis and Brønsted acid. The bands at 1454 and 1540 cm⁻¹ for pyridine/[bmim]Cl-2AlCl₃ ionic liquid were observed (FIG. S3). These bands were attributed to the characteristic peaks of Lewis acid (pyridine bonded at a Lewis acid site) and Brønsted acid (pyridine bonded at a Brønsted acid site) respectively (see Table S1 in the Supporting Information). With increasing the content of AlCl₃ in the ionic liquid, the peak intensity at 1454 cm⁻¹ increased (FIG. S4), indicating Brønsted acid was enhanced at higher content of AlCl₃. In conclusion, the above observations supported that the ionic liquid had the properties of both Brønsted acid and Lewis acid.

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- [1] C. Xu, R. A. D. Arancon, J. Labidi, and R. Luque, *Chem. Soc. Rev.* **43**, 7485 (2014).
- [2] Q. Yao, Z. Tang, J. H. Guo, Y. Zhang, and Q. X. Guo, *Chin. J. Chem. Phys.* **28**, 209 (2015).
- [3] L. Zhang, R. Liu, R. Yin, and Y. Mei, *Renew. Sustain. Energy Rev.* **24**, 66 (2013).
- [4] Q. Y. Wu, L. L. Ma, J. X. Long, R. Y. Shu, Q. Zhang, T. J. Wang, and Y. Xu, *Chin. J. Chem. Phys.* **29**, 474 (2016).
- [5] P. Huang and L. F. Yan, *Chin. J. Chem. Phys.* **29**, 742 (2016).
- [6] Y. Zhao, L. Deng, B. Liao, Y. Fu, and Q. X. Guo, *Energy Fuels* **24**, 5735 (2010).
- [7] J. Chen, C. Liu, and S. B. Wu, *BioResources* **11**, 663 (2015).
- [8] W. Wei, S. Wu, and S. Xu, *J. Chem. Technol. Biotechnol.* **92**, 580 (2017).
- [9] L. P. Xiao, Z. J. Shi, F. Xu, and R. C. Sun, *Bioresour. Technol.* **118**, 619 (2012).
- [10] L. Xu, Y. Zhang, and Y. Fu, *Energy Technol.* **4**, 1 (2016).
- [11] B. Zhang, Z. P. Zhong, X. B. Wang, K. Ding, and Z. W. Song, *Fuel Process Technol.* **138**, 430 (2015).
- [12] C. Li, X. Zhao, A. Wang, G. W. Huber, and T. Zhang, *Chem. Rev.* **115**, 11559 (2015).

- [13] S. Adhikari, V. Srinivasan, and O. Fasina, *Energy Fuels* **28**, 4532 (2014).
- [14] S. Kang, X. Li, J. Fan, and J. Chang, *Renew. Sus. Energy Rev.* **27**, 546 (2013).
- [15] W. Y. Xu, S. J. Miller, P. K. Agrawal, and C. W. Jones, *ChemSusChem* **5**, 667 (2012).
- [16] C. Rutten, A. Ramírez, and J. Posada Duque, *J. Chem. Technol. Biotechnol.* **92**, 257 (2016).
- [17] Y. Zou, H. Jiang, Y. Liu, H. Gao, W. Xing, and R. Chen, *Sep. Purif. Technol.* **170**, 49 (2016).
- [18] J. Zhai, Y. Liu, L. Li, Y. Zhu, W. Zhong, and L. Sun, *Chem. Eng. Res. Des.* **102**, 138 (2015).
- [19] R. Navarro, S. Lopez-Pedrajas, D. Luna, J. M. Marinas, and F. M. Bautista, *Appl. Catal. A* **474**, 272 (2014).
- [20] T. F. Degnan, C. M. Smith, and C. R. Venkat, *Appl. Catal. A* **221**, 283 (2001).
- [21] M. P. Bailey, *Chem. Eng.* **121**, 79 (2014).
- [22] V. V. Bokade and U. K. Kharul, *Chem. Eng. J.* **147**, 97 (2009).
- [23] O. V. Shutkina, O. A. Ponomareva, and II. Ivanova, *Catal. Ind.* **7**, 282 (2015).
- [24] H. R. Norouzi, M. A. Hasani, B. Haddadi-Sisakht, and N. Mostoufi, *Chem. Eng. Commun.* **201**, 1270 (2014).
- [25] C. Perego and P. Ingallina, *Catal. Today* **73**, 3 (2002).
- [26] C. Dai, Z. Lei, J. Zhang, Y. Li, and B. Chen, *Chem. Eng. Sci.* **100**, 342 (2013).
- [27] T. Odedairo and S. Al-Khattaf, *Catal. Today* **204**, 73 (2013).
- [28] P. W. Jiang, X. P. Wu, L. J. Zhu, F. Jin, J. X. Liu, T. Y. Xia, T. J. Wang, and Q. X. Li, *Energ. Convers. Manage.* **120**, 338 (2016).
- [29] F. Gong, Z. Yang, C. Hong, W. Huang, S. Ning, Z. Zhang, and Q. Li, *Bioresour. Technol.* **102**, 9247 (2011).
- [30] M. H. Fan, S. M. Deng, T. J. Wang, and Q. X. Li, *Chin. J. Chem. Phys.* **27**, 221 (2014).
- [31] J. C. Wang, P. Y. Bi, Y. J. Zhang, H. Xue, P. W. Jiang, X. P. Wu, J. X. Liu, T. J. Wang, and Q. X. Li, *Energy* **86**, 488 (2015).
- [32] P. S. Rezaei, H. Shafaghat, and W. M. A. W. Daud, *Appl. Catal. A* **469**, 490 (2014).
- [33] G. Q. Zhang, T. Bai, T. F. Chen, W. T. Fan, and X. Zhang, *Ind. Eng. Chem. Res.* **53**, 14932 (2014).
- [34] G. Caeiro, R. H. Carvalho, X. Wang, M. A. N. D. A. Lemos, F. Lemos, M. Guisnet, and F. R. Ribeiro, *J. Mol. Catal. A* **255**, 131 (2006).
- [35] Y. Ono, *Catal. Rev.* **34**, 179 (1992).
- [36] N. Rahimi and R. Karimzadeh, *J. Anal. Appl. Pyrolysis* **115**, 242 (2015).
- [37] Z. Zhao, W. Qiao, X. Wang, G. Wang, Z. Li, and L. Cheng, *Appl. Catal. A* **290**, 133 (2005).
- [38] T. F. Degnan, C. M. Smith, and C. R. Venkat, *Appl. Catal. A* **221**, 283 (2001).