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Catalytic pyrolysis of corn straw fermentation residue for producing alkyl phenols

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ABSTRACT

Phenolic-oil can be upgraded by etherification with methanol to decrease the polarity and acidity of the product oil. However, alkoxy phenols have an inhibiting effect to the etherification of alkyl phenols in the phenolic mixture. So, it is very important to produce alkyl phenols with high selectivity and extremely low content of alkoxy phenols, through a catalytic pyrolytic process. Herein, the effects of HZSM-5, NaY, and KH_2PO_4/AA (KH_2PO_4 loaded on activated Al_2O_3) on the pyrolysis of corn straw fermentation residue are investigated, for producing alkyl phenols high efficiently. KH_2PO_4/AA is found to be the best catalyst in promoting the formation of alkyl phenols and in inhibiting alkoxy phenols. Under the catalysis of KH_2PO_4/AA, the tar yield increases with rising temperature, and reaches to the maximum tar yield of 13.7% at 500 °C, and then declines with further increasing temperature. The tar obtained under optimized reaction conditions, nearly consists of 50% of alkyl phenols and over 23% of aliphatic hydrocarbons with zero content of alkoxy phenols. $K_3Al_2(PO_4)_3$ is generated from the solid phase reaction between KH_2PO_4 and Al_2O_3, through which alkoxy phenols can be high selectively adsorbed and activated, and thus leads to the formation of alkyl phenols.

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1. Introduction

Phenolic-oil is a major fraction in biomass pyrolytic liquid [1–5]. So, the development on value added application of the phenolic-oil is of great importance. The phenolic-oil can neither be directly used as a liquid fuel due to its strong acidity and corrosivity, nor be used as a blended fuel with gasoline or diesel restricted by its high polarity [5–9]. Therefore, an idea of etherification of phenolic-oil with methanol was put forward [10], through which the polar phenolic hydroxyl group could be converted to an ether group in weak polarity and acidity. However, our previous investigation showed that alkoxy phenols had an inhibiting effect on the etherification of alkyl phenols in the phenolic mixture, due to an adsorption competition between the two types of phenols on the surface of catalyst [10].

There may be two approaches to solve this problem. The first one is to develop a more advanced catalyst with a higher activity to the both type of phenolic compounds. In fact, this is a part of work that we are doing, but the present results seem still rather pessimistic, since the performance of a catalyst commonly relates to a specific structure of the object for conversion. The second method is to make a separation between the alkyl phenols and the alkoxy phenols. However, the homologue separation is very hard, because of the close properties of the two types of phenols. Column chromatographic separation method can be an effective choice [11], but the low time efficiency and the high energy consumption in distillation of eluting solvent are unavoidable shortcomings.

So, a third approach is put forward herein. The idea is to make a pyrolysis control to produce alkyl phenols high selectively, with extremely low content of alkoxy phenols in the pyrolytic liquid. To achieve this goal, a catalytic conversion of alkoxy phenols to alkyl phenols may be an effective approach.

Most of the researches on catalytic pyrolysis of biomass have been aiming to upgrade the bio-oil by deoxygenation to yield more aliphatic and/or aromatic hydrocarbons, instead of alkyl phenols. Zeolites, particularly the one of ZSM-5, were studied earliest and most extensively for biomass pyrolysis. In Kalogiannis et al.'s work [12], a bio-oil with oxygen content less than 7% was

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obtained under catalysis of ZSM-5. The ZSM-5 catalyst was also found effective in decreasing the N mass fraction of the bio-oil and increasing the amount of aromatic compounds. The mesoporous Al-MCM-41 and the FCC catalyst produced more aliphatic hydrocarbons but had significant losses of C towards coke production. Engtrakul et al. [13] studied the impact of acidity of ZSM-5 on bio-oil composition, with varied SiO_2 to Al_2O_3 ratio (SAR) from 23 to 280. The results showed that the bio-oil was highly deoxygenated to aromatics over all tested ZSM-5 catalysts. As the acidity increased, the selectivity to alkyl aromatics decreased, while the selectivity to unsubstituted aromatics and polycyclic aromatics increased. Considering the both of quality and quantity of the upgraded bio-oil, Stefanidis et al. [14] compared the catalytic effects of FCC catalyst, ZSM-5, MgO, alumina, NiO, zirconia/titania, tetragonal zirconia, and titania. It was found that high surface area alumina displayed the highest selectivity to hydrocarbons, but in lowest oil yield. MgO deoxygenated the bio-oil high efficiently too, but yielded a rather low oil product as well. Zirconia/titania and ZSM-5 yielded a high oil product with higher aromatics content. The FCC, ZSM-5 and NiO all yielded about a same amount of oil product but the FCC's organic fraction was much more oxygenated. Stefanidis et al. [15] further investigated the effect of MgO. Despite negligible acidity of MgO, the MgO catalysts effectively reduced the oxygen content of the bio-oil and exhibited similar or even better performance compared to that of an industrial ZSM-5. The basic sites of the MgO catalysts favored the deoxygenation via ketonization and aldol condensation reactions. Oxygen was removed mainly via the preferred pathway of CO_2 formation, compared to CO and water as in the case of ZSM-5 zeolite. Kim et al. [16] found that the production of phenolics and monoaromatics were promoted in the pyrolysis of lignin over H-V-MCM-41. Perego and Bianchi [17] summarized that the shape selectivity and the acid property of zeolites were crucial parameters; the aromatic fraction in bio-oil was increased from 7 to 74% over HZSM5 in different reaction conditions; mesoporous catalysts such as Al-MCM-41 significantly increased the yields of phenols, hydrocarbons and polycyclic aromatics; the catalysts modified by transition metals (Fe–Al-MCM-41 and Cu–Al-MCM-41) provided the best results in terms of phenols production.

Though some catalysts have been found promotive to the formation of phenols, special investigation on producing of alkyl phenols has never been reported. In this paper, the pyrolysis of corn straw fermentation residue (CSFR) over the three catalysts of HZSM-5, NaY, and KH_2PO_4/AA (KH_2PO_4 loaded on activated Al_2O_3) were investigated, in the aim of producing alkyl phenols with high selectivity. The material of CSFR is selected, because of its huge resource with low price and in rich of lignin, which is the origin of most phenolic compounds in bio-oil. The zeolite of HZSM-5 is selected because of its known deoxygenating effect [12–14], and the conversion from alkoxy phenols to alkyl phenols is just a deoxygenating process as well. The zeolite of NaY is selected because of its promotive effect to the formation of phenols [18]. The catalyst of KH_2PO_4/AA is selected because of its proved activity in activation of phenolic compounds when reacts with methanol [10].

2. Materials

The corn straw fermentation residue was offered by Henan Tianguan Group. Approximate and ultimate analysis of the sample was showed in Table 1. It can be seen that the ash content in CSFR is rather high, even higher than most of conventional biomass materials [19,20]. The sample of CSFR was first smashed to powders in the size of below 5 mm and then dried at 105 °C for 4 h before use.

Table 1
Approximate and ultimate analysis of CSFR (%).

A_d	V_d	FC_d[a]	C_d	H_d	N_d	S_d	O_d[a]
32.34	45.39	22.27	41.07	3.97	2.13	0.21	20.28

d-dried basis; A-ash; V- volatile matter; FC- fixed carbon.
[a] Obtained by difference.

3. Experimental

3.1. Catalyst preparation

The zeolites of HZSM-5 and NaY were purchased from Nanjing XFNANO Materials Technique Cooperation. The powder of HZSM-5 (mean particle size of 4.9 μm) has a specific surface area of 385 m^2/g with SiO_2 to Al_2O_3 ratio of 350–400. The specific surface area of NaY (mean particle size of 2.0 μm) is above 600 m^2/g with SiO_2 to Al_2O_3 ratio of 5.3. Prior to usage, the two zeolites were calcined in a muffle furnace at 715 °C for 8 h.

The catalyst of KH_2PO_4/AA was prepared by loading a potassium salt on the support of activated alumina (AA, γ-Al_2O_3) granules (diameter of 2 mm, produced by China Research Institute of Daily Chemical Industry). The support of γ-Al_2O_3 granules was first washed by distilled water and dried at 120 °C for 12 h, and then cooled to room temperature for use; thereafter the KH_2PO_4 solution was slowly added to γ-Al_2O_3 granules according to the isopyknic impregnation rules (theoretical loading amount of potassium is 10 wt% for all supported catalysts); the impregnated γ-Al_2O_3 granules were then placed in the open air at room temperature for 24 h, and finally calcined in a muffle furnace at 715 °C for 8 h.

3.2. Catalyst characterization

The chemical phase of the catalyst was analyzed by X-ray diffraction method (XRD, Rigaku Smartlab, Japan) with D/teX-Ultra detector and CuK_α radiation. The catalyst acidity was characterized by NH3-TPD (Temperature-Programmed Desorption) method. Ceramic ball was used as a reference for comparison with catalysts. The chemical composition of the ceramic ball was characterized by XRF (X-Ray Fluorescence) analysis, as showed in Table 2. It can be seen that the ceramic ball is in rich of SiO_2, and the two components of Al_2O_3 and K_2O are relatively abundant, while all other components are just in trace amounts.

3.3. Apparatus and procedure for pyrolytic experiments

The experiments on pyrolysis of CSFR were conducted in a lab-scale fixed bed reactor in atmospheric pressure. The diagram of the experimental setup is showed in Fig. 1. The sample of CSFR (15 g) and the catalyst (15 g) were loaded in a quartz basket (height of 90 mm, inner diameter of 31 mm, external diameter of 35 mm) sequentially, forming an up-layer of catalyst and a bottom-layer of CSFR sample. The quartz basket was then placed inside a quartz pipe (height of 620 mm, inner diameter of 41 mm, external diameter of 46 mm), which was heated by an electric furnace. Nitrogen (80 ml/min) used as carrier gas was introduced to purge air for 20 min. The reactor was then heated to a setting temperature in 40 min and held at the setting temperature for 20 min. Initial

Table 2
Chemical composition of the ceramic ball.

Composition	SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	Na_2O	CaO	MnO
Content (wt%)	68.32	24.24	4.01	1.25	0.66	0.64	0.30	0.16

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