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Ethanolysis of Kraft lignin to platform chemicals on a MoC_{1-x}/Cu-$MgAlO_z$ catalyst

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ABSTRACT

The complete conversion of Kraft lignin is examined over a MoC_{1-x}/Cu-$MgAlO_z$ catalyst in pure ethanol to give value-added chemicals with small molecular weight, including C_6 alcohols, C_8—C_{10} esters, benzyl alcohols and arenes, without the formation of char or tar. MoC_{1-x}/Cu-$MgAlO_z$ exhibited much higher activity than the previously reported MoC_{1-x}/AC, $CuMgAlO_y$ and Cu-$MgAlO_z$ catalysts and achieved the highest yield of aromatic compounds, 575 mg/g lignin, at 330 °C. The complete cleavage of aryl-O bonds in phenols is observed at temperatures over 300 °C. Furthermore, the MoC_{1-x}/Cu-$MgAlO_z$ catalyst is reusable with a 22.4% loss in the yield of aromatic compounds after 5 cyclic runs.

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1. Introduction

Nowadays, with the depletion of the fossil fuels, biomass as a renewable resource of fuels and chemicals draws worldwide attention. Lignin accounts for 15–30 wt% of non-edible biomass, and is produced in a huge amount in the biosphere of the earth [1]. Lignin has a macromolecular structure composed of phenyl-propane units linked by C—O and C—C bonds, with β-O-4 as the most common linkage [2–4]. Hence, lignin has been shown promising to be used as a resource for the production of aromatic chemicals [5–7]. For centuries, Kraft lignin has been produced in a great amount as the byproduct of pulping process in which cellulosic fiber is separated and utilized to produce paper, while lignin is left in the black liquor as a pollution waste [8,9]. In recent decades, lignin has been isolated from the black liquor due to the environmental concerns, however, still mostly used as a low heating value boiler fuel up to date [10].

Many strategies including hydrolysis [11–15], oxidation [16–21] and reduction [22] have been explored in lignin depolymerization. Among them, reduction is the most exhaustively investigated approach with the existence of hydrogen or a hydrogen donner, e.g. methanol [23–25], ethanol [26] and i-propanol [27], suppressing the condensation of the phenolic intermediates [18,28,29]. Ford and his coworkers decomposed organosolv lignin to cyclohexyl derivatives with a Cu-doped porous metal oxide catalyst in methanol at 300 °C without external hydrogen [23]. However, this approach caused the hydrogenation of aromatic rings. Afterwards, they reported that the same catalyst catalyzes the conversion of eucalyptus wood to a liquid fuel with a 77% conversion and a 71% selectivity to higher alcohols and ethers (HAE), especially the substituted cyclohexyl alcohols and ethers (CAE) in methanol [24]. Song et al. [26] reported the depolymerization of birch wood lignin over a nickel-based catalyst in alcohols, including methanol, ethanol and ethylene glycol under an auto-generated pressure at 200 °C for 6 h. A selectivity to propylguaiacol and propylsyringol as high as 90% was achieved with a lignin conversion of about 50%. Ferrini and Rinaldi [27] reported the catalytic extraction of lignin from poplar wood in 2-Propanol/H_2O (7:3, v/v) with Raney Ni as the catalyst with a 15–26% yield of non-pyrolytic lignin bio-oil containing diols, cyclohexanols, phenols, guaiacols and syringols etc. Volatile components accounted for 55% of the oil sample at 300 °C. Huang et al. [30] investigated the depolymerization of alkali lignin in supercritical ethanol at 300 °C with $CuMgAlO_y$ as the catalyst. A 23 wt% yield of aromatics was achieved without char formation. Earlier to Huang's work, our group reported the catalytic

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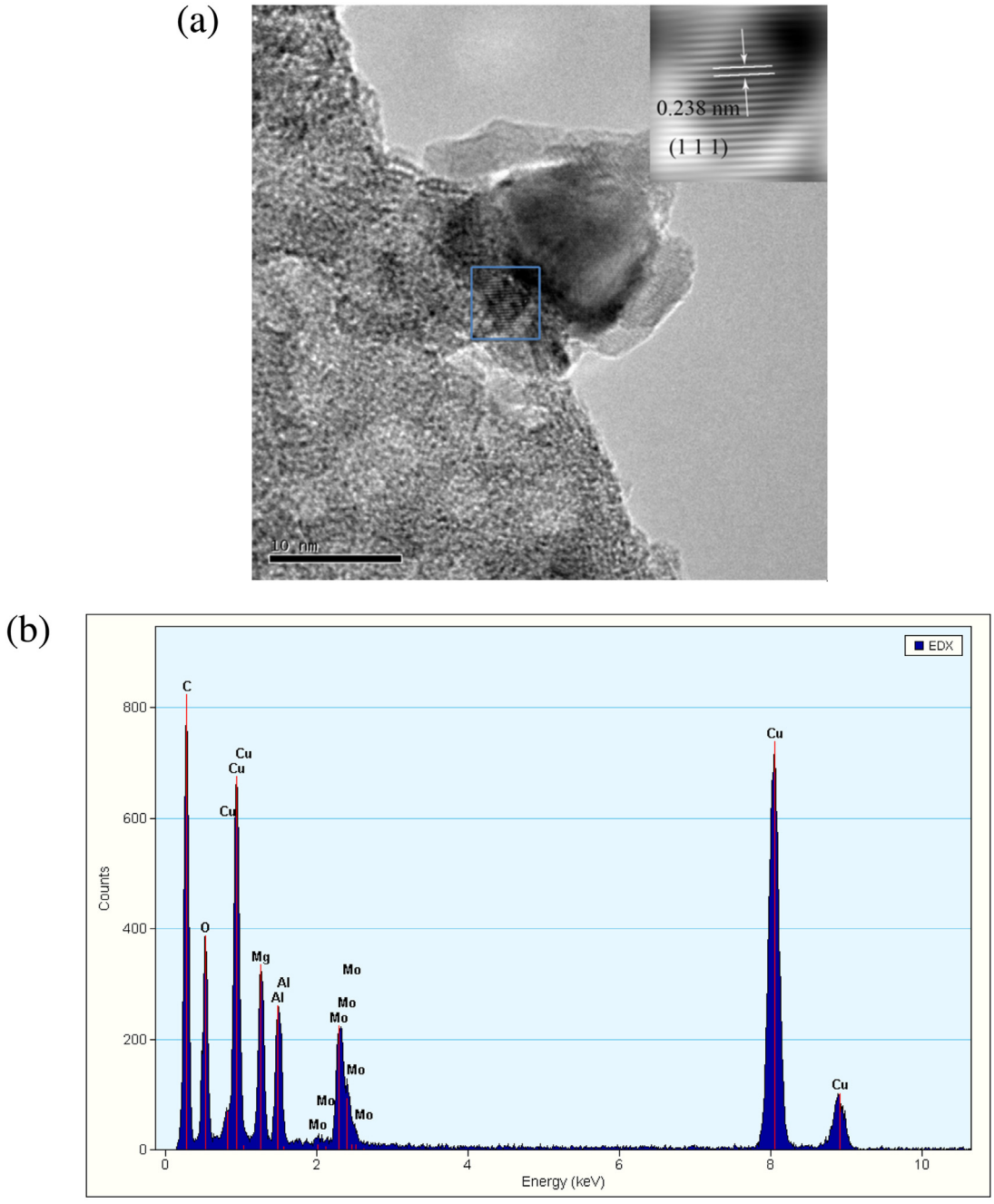

Fig. 1. (a) TEM image of MoC_{1-x}/Cu-$MgAlO_z$, the inset is the framed area after amplification. (b) Energy Dispersive Spectrum (EDS) of MoC_{1-x}/Cu-$MgAlO_z$.

ethanolysis of Kraft lignin with MoC_{1-x}/AC as a catalyst to produce value-added chemicals [31]. Five sorts of products including esters, alcohols, arenes, phenols and benzyl alcohols were obtained with a high overall yield. The selective production of five mono-phenols from Kraft lignin over a tungsten phosphide catalyst in hot compressed water–ethanol mixed solvent was also reported [32]. An activated carbon supported WP gave the highest overall phenols yield, 67.0 mg/g lignin.

In this work, we report the depolymerization of Kraft lignin in supercritical ethanol on a MoC_{1-x}/Cu-$MgAlO_z$ composite catalyst, which is virtually a combination of the reported catalysts of Huang et al. and Ma et al. [30,31] This catalyst gives a much higher yield of products than both the MoC_{1-x}/AC and $CuMgAlO_y$ catalyst, respectively, without any tar or char formation.

2. Experimental

2.1. Materials

The Kraft lignin was purchased from Sigma–Aldrich (product number 471003). The Kraft lignin contains Klason lignin, polysaccharides, extractives (fatty, resin acids and terpenoids), other orgainics and inorganics, with contents of 45.7, 10.1, 4.0, 27.1 and 13.1 wt%, respectively [31]. The elemental contents of the Kraft lignin are 49.5 wt% C, 4.71 wt% H, 0.15 wt% N and 2.80 wt% S, while the ash content is 19.4 wt%. Analytical reagents (AR), including ethanol, o-cresol, ammonium paramolybdate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, and Na_2CO_3 were purchased from Tianjin Guangfu Technology Development Co. Ltd. and used as received.

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