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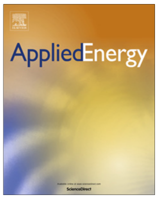

Efficient valorization of lignin depolymerization products in the present of $Ni_xMg_{1-x}O$

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HIGHLIGHTS

- Hydrogenation of lignin depolymerization product was catalyzed by $Ni_xMg_{1-x}O$.
- 98.91% phenol conversion and 100% cyclohexanol selectivity were obtained at 70 °C.
- The molecular weight and the oxygen content of the phenolic oligomer were decreased.
- C=O structure of oligomer was broken and aliphatic C—H and C—C bond was formed.
- No catalytic activity loss for phenol hydrogenation was shown after 5 runs.

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ABSTRACT

Efficient conversion of lignin depolymerization products to more stable chemicals has attracted increasing attention during last few years. Here, we reported a novel and efficient method for lignin depolymerization products valorization on the simple and economic catalyst $Ni_xMg_{1-x}O$. In which, the unsaturated ingredients were converted to thermal and chemical stable products, resulting in the obvious decreasing of the unsaturated degree of the products and the repolymerization of the phenolic oligomer. The results showed that more than 98% of phenol, a model chemical of lignin depolymerization products, could be converted to cyclohexanol with 100% selectivity. Further investigation demonstrated that it was also efficient for the real lignin depolymerization products, where a significant decrease on the oxygen content and the average molecular weight were shown. Moreover, the $Ni_xMg_{1-x}O$ catalyst was recyclable, and no significant loss of the catalytic activity was exhibited even after 5 runs.

1. Introduction

Lignin, the second abundant and the unique aromatic component of renewable biomass, is one of the most important and promising feedstock for the future energy, chemicals and biofuel producing with the consideration of the currently increasing depletion of fossil fuels and serious environmental problems [1]. However, this natural aromatic material is recalcitrant to be degraded than carbohydrate because of its complex structure and chemical bonding. Generally, thermal processes, such as pyrolysis, gasification and liquefaction, catalytic oxidization and catalytic hydrogenolysis were reported to be efficient approaches for lignin utilization [1–5]. However, gasification is a high temperature process; pyrolysis and liquefaction usually suffered obvious disadvantages of low aromatic products yield and selectivity, and the serious carbon formation because of the complex chemical bond and high carbon content in the lignin molecule [6,7]. Particularly, the severe carbon deposition on the catalyst, which is caused by the repolymerization of lignin depolymerization products (including unsaturated phenolic monomer and the oligomer) and the following dehydration, is a considerable challenge for the efficient utilization of this sustainable aromatic polymer [8,9]. Therefore, novel technologies with efficient char elimination are important and essential. Base catalytic depolymerization is a promising approach due to its gentle catalyst carbon deposition [10–12], but, the repolymerization of phenolic oligomer is inevitable [13]. The aromatic radicals capping reagents and H-donating solvents such as formic acid [10,14], boric acid [15] and phenol [16] were

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also used to reduce char formation. However, phenolic oligomer, the main cause for char formation, had not reduced. Furthermore, the addition of above reagents results in obvious difficulty in the products separation. Hence, the exploration of novel and efficient strategies for the reduction of the phenolic oligomer from lignin depolymerization is desired and necessary.

Ni-base catalyst has been considered as a powerful and popular catalyst for hydrogenation process due to its excellent hydrogen-added activity and cost-efficient property. $Ni_xMg_{1-x}O$ was widely used in stream reforming, hydrogenation of sorbitol and lignin gasification [17–19]. However, few investigations of this catalyst focused on the upgrading of the lignin depolymerization product. According to the reported literature [20], NiO has the sodium chloride structure, and the prepared NiO at lower temperature has two Ni vacancies on the Ni (0 1 1) face. When a Lewis base is presented on the surface of this *p*-conductor, the effect of the Ni vacancy would be compensated, giving two hydroxyls. Lewis base MgO has a stable structure. Furthermore, Mg^{2+} has the same valence as Ni^{2+}, and its ionic radius is comparable to that of Ni. Therefore, the composition of MgO and Ni would activate both of them.

In this study, we provided a novel and efficient strategy for the valorization of lignin depolymerization products in the presence of $Ni_xMg_{1-x}O$ catalyst. The catalytic activity of this catalyst for phenol, a typical model chemical of lignin depolymerization products, was investigated. Under the optimized conditions, the hydrogenation of real lignin depolymerization products including phenolic monomer and oligomer was also studied.

2. Materials and methods

2.1. Materials

All chemicals were analytic grade and used without further purification. $MgCl_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $NH_3{\cdot}H_2O$, $AgNO_3$ and CH_3OH were purchased from Tianjin Chemical reagents Co., Ltd. (Tianjin, China). Phenol and naphthane were supplied by Aladdin (Shanghai, China). Tetrahydrofuran (THF, HPLC grade) was provided by Aldrich (Milwaukee, WI, USA). The alkali lignin was purchased from Sigma Aldrich China (Shanghai, China). The carrier MgO was prepared by homogenous precipitation and calcined at 850 °C for 4 h. The $Ni_xMg_{1-x}O$ catalysts were prepared by an incipient-wetness impregnation method and characterized by Brunauer–Emmett–Teller (BET), X-ray diffractometer (XRD) and energy spectrum analysis (EDS). Detail catalyst preparation and characterization can be found in the Supplementary data.

2.2. Hydrogenation of phenol

In a typical process, 0.2 g phenol, 0.08 g $Ni_xMg_{1-x}O$ and 20 mL naphthane was loaded into a 50 mL stainless autoclave equipped with an electromagnetic-driven stirrer (Dalian Tongda Co., Ltd., China). After the displacing of air, the reactor was pressured with 3.0 MPa H_2 and heated up to 70 °C for 60 min under strong stirring of 600 r min^{-1}. When the hydrogenation process was finished, the reactor was cooled to room temperature using cool water during 30 min.

The mixtures of catalyst, reactant and products were first separated by filtration, and the solid catalyst was washed by naphthane until no obvious products were detected in the solvent. After further washing by hexane and ethanol three times (3 × 10 mL) and drying at 50 °C under vacuum, the residual solid (used catalyst) was used for the next run to examine the recyclability of the catalyst. The filtrate (including free feedstock, reaction medium and products) and naphthane from catalyst washing was then collected together for conversion and yield determination.

2.3. Hydrogenation of lignin depolymerization products

Lignin depolymerization products were obtained according to the previous study in CH_3OH with $CrCl_3$ catalyst [13]. Typically, 1.0 g lignin, 5 mmol $CrCl_3$ and 40 mL CH_3OH were charged into a 100 mL stainless autoclave (316L stainless, made by Weihai Chemical Machinery Co., Ltd.) equipped with a mechanical agitation in sequence. After the air displacement by N_2 for three times, the reactor was heated to 260 °C for 30 min. When the reaction was finished, the reactor was cooled to room temperature during 30 min using cool water.

After careful isolation of the solid, a transparent liquid was achieved including solvent (CH_3OH), phenolic monomer and its oligomer. When CH_3OH was quickly removed at 30 °C under reduced pressure, a mixture of volatile phenolic monomer and the nonvolatile oligomer was then diluted by 20 mL naphthane to give the feedstock for hydrogenation process as above phenol hydrogenation.

2.4. Product analysis

The quality analysis of volatile products was conducted on an Agilent 7890 gas chromatography (GC) with an Agilent 5975 inevt mass-selective detector and identified according to the NIST MS library. The products were separated by a HP-INNOWAX capillary column (30 m × 0.25 mm × 0.25 μm) where 99.999% helium was used as carrier gas. The oven temperature was programmed as following: the initial temperature was 60 °C (hold for 2 min), and then it was ramped up to 260 °C with 10 °C min^{-1} and hold for another 10 min. The injector was kept at 280 °C in spit mode with spit ratio of 5:1. The quantitative analysis was performed on an Agilent 7890 GC with a flame ionization detector (FID) using acetophenone as internal standard compound at the same capillary column and temperature program as the GC–MS analysis.

The weight of the nonvolatile products were measured after careful removal of the solvent at 80 °C under vacuum until no obvious weight loss was detected. The gel permeation chromatography (GPC) analyses of the nonvolatile raw phenolic oligomer and the hydrogenation products were carried out on an Agilent 1260 high performance liquid chromatography (HPLC) with a differential refraction detector (RID detector). THF was used as elution with a flow rate of 1.0 mL min^{-1}. The oven temperature was 30 °C. The average molecular weight was measured using external standard method with polystyrene as standard compound. The main composed elements of the phenolic oligomer and its hydrogenation products were obtained on a vario EL III element analyzer. And the oxygen content was estimated by the conservation of mass based on the assumption that the sample only contains C, H, N, S and O. Fourier Transform Infrared (FT-IR) analysis was performed on a Nicolet is50 FT-IR spectrometer by KBr peleting method. ^1H Nuclear Magnetic Resonance (^1H NMR) and ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) results were recorded on a Bruker Advance 400 III spectrometer, where d_6-DMSO was used as solvent.

3. Results and discussion

3.1. Catalytic hydrogenation of phenol

Phenol, the simplest phenolic monomer from lignin depolymerization, was selected as the model chemical for the catalytic activity test of $Ni_xMg_{1-x}O$ with various Ni loaded amounts. The results

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