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Investigation of deactivation mechanisms of a solid acid catalyst during esterification of the bio-oils from mallee biomass

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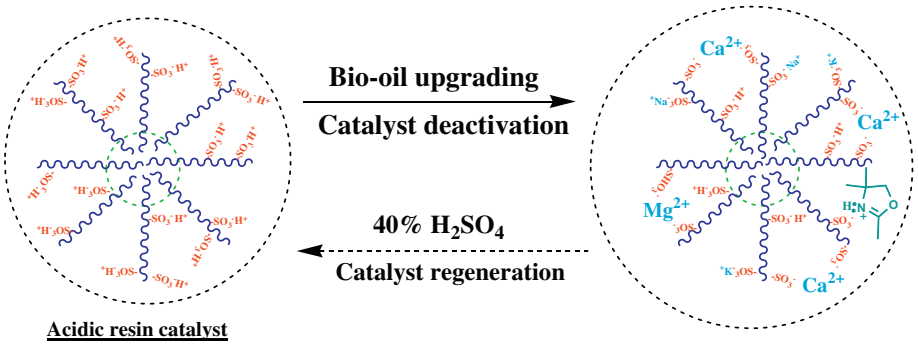
HIGHLIGHTS

- Deactivation of a solid acid catalyst in bio-oil esterification was investigated.
- The bio-oils from wood, bark, and leaves contain quite different catalyst poisons.
- Metal ions, N-containing organics and polymer in bio-oil poison catalyst.
- Ion exchange can substantially but not completely regenerate the catalyst.
- Metal ions and N-containing organics are reversible poisons while polymer is not.

GRAPHICAL ABSTRACT

The oligomers, N-containing organics and metal ions in bio-oil poison the solid acid catalyst via different ways. Processing with a concentrated sulfuric acid significantly improved the catalytic activity via removal of the poisons.



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ABSTRACT

This study reports the deactivation mechanisms of the solid acid catalyst Amberlyst 70 during the esterification of bio-oils from mallee biomass and the methods for catalyst regeneration. The metal ions in bio-oil deactivated Amberlyst 70 via ion exchange with the hydrogen ions on/in catalyst, which changed structure of catalysts and reduced availability of acidic sites. N-containing organics reacted with the hydrogen ions on/in catalyst, forming neutral salts and resulting in complete catalyst deactivation. Polymers formed during the esterification of bio-oils deposited on/in catalyst, reducing the accessibility of catalytic sites. Washing with solvents could remove some adsorbed organics and restore some catalytic activity but not much. In comparison, ion exchange in a concentrated sulfuric acid removes most of metal ions and the N-containing organics and significantly improves the catalytic activity.

1. Introduction

Production of bio-oil from renewable and abundantly available biomass is a potential solution to mitigate the reliance on the limited fossil fuel reserves and the increasing CO_2 emissions [1–3]. However, the raw bio-oil cannot be directly used as fuels for vehicles due to the deleterious properties such as instability, corrosiveness, and high oxygen content [4–7]. Upgrading of raw bio-oil has been performed via various ways such as stabilization [8], esterification [9,10], extraction followed by acid-treatment [11], hydrogenation [12] and cracking [13]. Catalysts were generally employed to facilitate the upgrading [14–20]. However, many catalysts

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developed so far are designed for simple reaction systems or for fossil fuel refineries, and most of them are sensitive to various poisons in reactants.

Bio-oil is a very complex mixture of organic and inorganic species, deriving from the complexity of biomass. Cellulose, hemicellulose and lignin are the basic components of biomass. During pyrolysis, the macro structures of biomass are destructed and decomposed to volatile compounds, oligomers, and bio-char, depending on the extent of pyrolysis [21]. Some oligomers may have high affinity to the catalyst, occupying the active sites and leading to catalyst deactivation. Moreover, some organics in bio-oil may be detrimental to catalyst. For example, N-containing organics were present in the bio-oil from the pyrolysis of mallee leaves, which have detrimental effects on acid catalysts [22].

In addition to the organics, inorganic metals were also found in bio-oil [23]. The catalysts such as zeolites are very sensitive to alkali metals such as sodium [24]. Thus, understanding potential effects of these species such as oligomers, organics and metals in bio-oil on catalyst performance can provide valuable information for us to develop effective catalysts to upgrade bio-oil. Thus, this study is devoted to the investigation of the potential effects of the organic and inorganic species in bio-oil on the catalytic activity of Amberlyst 70, a commercial solid acid resin catalyst. The bio-oils from the wood, bark, and leaves of mallee trees were prepared and used to represent the bio-oil from whole mallee tree. The deactivation mechanisms of Amberlyst 70 in the three different bio-oils were distinct, and the methods for regeneration of deactivated catalysts were explored as well.

2. Experimental

2.1. Materials

The chemicals used were analytic grade and the details can obtained from Supporting information of the literature: [25]. The commercially available solid acid catalyst Amberlyst 70 (Rohm and Haas) was used directly without any further pre-treatment. The bio-oils used were produced from the fast pyrolysis of the wood, bark, and leaves of mallee eucalypts (*E. loxophleba* ssp. gratiae) in a fluidised-bed reactor at 500 °C. The composition of the bio-oil from wood, bark, and leaves can be found in the literatures [26–28].

2.2. Experimental procedure

Esterification of bio-oils was performed in a 130 mL Hastalloy batch autoclave reactor. Specific composition of reaction mixtures and detailed reaction conditions were specified in the table and figure captions. The autoclave was purged with nitrogen three times and heated to the desired reaction temperature with a stirring rate of 700 rpm under an autonomous pressure in ca. 20 min. After cooling down of the reactor, the catalyst was separated from the bio-oil via filtration.

Catalytic activities of the catalysts were also evaluated in a model compound experiment (esterification of acetic acid with methanol in water). Typically, the experiments were performed at 60 °C for 30 min in a conical beaker with a magneton equipped with a drain sleeve. Concentrations of acidic sites on/in catalyst were determined by a titration method following the literature [29].

Regeneration of the catalyst was performed via washing with organic solvents and ion exchange in a concentrated sulfuric acid (40 wt.%). The deactivated catalyst was washed with acetone and then with chloroform/methanol (v/v: 4/1) to remove the organics adsorbed on catalyst surface. The washed catalysts were then immersed in a 50 ml sulfuric acid for 24 h and stirred for another 4 h at room temperature. After that, the metal ions released into the solution were determined by ICP/OES, and the catalysts were separated and washed with the deionized water until residual solution was neutral for further measurement.

2.3. Analytical methods

Products were analyzed with Agilent GC–MS (6890 series GC with a 5973 MS detector) equipped a capillary column (HP-INNO-Wax) (film thickness: 0.25 μm of crosslinked polyethylene glycol; length: 30 m; internal diameter: 0.25 mm.). Details of the procedure for GC–MS analysis can be found in the literature [14].

Mineral contents of bio-oils were determined with a Perkin Elmer OPTIMA 7600 DV ICP/OES. For each sample an average of 5 replicates was determined. Methanol solutions are introduced into the ICP/OES via an isomist system, lowering the injection temperature to −5 °C.

The FT-IR spectra were recorded using a Perkin–Elmer Spectrum GX FT-IR/Raman spectrometer in the 4000–500 cm^{-1} range with a spectral resolution of 4 cm^{-1} at room temperature. Each spectrum represents the average of at least six scans. The fresh and processed Amberlyst 70 were dried at 105 °C, grinded to powder and mixed with KBr (ca. 1 wt.% to KBr) and pressed into a pellet for the characterizations.

Surface morphologies of the catalysts were observed with a Zeiss EVO SEM microscope, operated in secondary electron mode after being coated with a 5 nm platinum coating. The beam current, working distance, and spot size of the instrument were modified to obtain the best possible images without producing significant charging on surface of samples. Briefly, beam current was varied between 10 and 15 keV, working distance ranged from 3.5 to 5 mm.

3. Results and discussion

3.1. Activities of the fresh catalyst in esterification of the different bio-oils

There are various carboxylic acids existing in bio-oil, depending on the origin of biomass. In the bio-oils from mallee biomass, acetic acid is most abundant one while others such as propanoic acid are present in trace concentration. Thus, the conversion of acetic acid during esterification was focused on. Acetic acid conversions in esterification of the different bio-oils were summarized in Fig. 1. Acetic acid concentrations in bark bio-oil (4.84 wt.%) and the wood bio-oil (5.92 wt.%) were not varied much. However, with the catalyst loading of 1 wt.% (Fig. 1a), the catalyst was completely inert in esterification of bark bio-oil but was active in that of wood bio-oil. Although the water content in bark bio-oil (ca. 40 wt.%) was higher than that in wood bio-oil (ca. 20 wt.%), the water contents only affected reaction equilibrium. Thus, the 1 wt.% catalyst during esterification of bark bio-oil did not exert any of its potential activity for esterification (Fig. 1a). Further increasing the catalyst loading to 3 and 5 wt.% (Fig. 1b and c), the esterification of acetic acid proceeded to some extent. However, the catalyst still performed somewhat poorer than that in wood bio-oil. Apparently, some difference in the wood bio-oil and the bark bio-oil resulted in the different catalytic behaviors of the catalysts. The catalyst in the esterification of the leaves bio-oil even performed worse than that in bark bio-oil esterification (Fig. 1c). The increase of reaction temperature to even 170 °C did not remarkably improve the catalytic activity in leaves bio-oil esterification (Fig. 1d). These results indicated that the catalyst must be deactivated by something at least in the bark bio-oil and the leaves bio-oil.