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Lignin fragmentation over magnetically recyclable composite $Co@Nb_2O_5@Fe_3O_4$ catalysts

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ABSTRACT

Recoverable catalysts for lignin fragmentation were prepared as Xwt%$Co@Nb_2O_5@Fe_3O_4$ composites having magnetite as an inner core. A shell of niobia covering the magnetic nanoparticles (leading to intermediate $Nb_2O_5@Fe_3O_4$ composite) was deposed from a solution of ammonium niobate (V) oxalate complex by precipitation with NH_3. Finally, the deposition of cobalt following the deposition–precipitation method generated the Xwt%$Co_3O_4@Nb_2O_5@Fe_3O_4$ composites that were reduced with hydrogen to Xwt %$Co@Nb_2O_5@Fe_3O_4$. Catalysts with loading of cobalt in the range $X = 1–20$ were prepared using this procedure. The different steps of the preparation were followed using various techniques such as surface area measurements, XRD, Raman and NH_3-DRIFT spectroscopy, XPS, Mössbauer and TEM. On this basis it was concluded that the synthesized composites exhibit both Lewis and Brønsted acid sites associated with the niobia shell and contain finely dispersed cobalt nanoparticles. The fragmentation of lignin occurred on the constituent parts of this composite, i.e. Fe_3O_4, Nb_2O_5, $Nb_2O_5@Fe_3O_4$ but with lower performances. The addition of cobalt ($Co@Nb_2O_5@Fe_3O_4$ catalysts) led to a complete fragmentation of lignin where the dominant fragments were those containing C20–C28 molecules. This catalytic behavior is explained on the capability of niobia to catalyze the acidic hydrolysis of the β-O-4′ bounds and of Co to break the C–C bonds *via* hydrogenolysis. The optimization of the catalyst composition indicated a loading of 4 wt% as optimal. Working at 180 °C and 10 atm H_2 this catalyst allowed a conversion of 53% leading to a mixture containing over 96% in C20–C28 and C29–C37 fragments. The investigated catalysts were completely recyclable as it was showed in six successive cycles. No leaching of the elements included in the composition was determined by ICP-OES.

1. Introduction

Biomass is used since ancient times as a raw material in construction and transportation, and also as a source of energy. The development of the society led to more sophisticated materials and systems replacing these sources with non-renewable resources. Consequently, after more than two centuries of intensive development we are faced with the decrease of the fossil fuel reserves, an increased impact of the greenhouse gases on the environment, and economic effects caused by the fluctuations in oil and mineral resource prices. From the perspective of the reduction of the emissions of carbon dioxide, the replacement of fossil oil with biomass is expected to bring important advantages. However, this is conditioned by the use of genetic modified fast growing trees or wastes, as source of biomass [1]. In this context the abundance and complex structure of lignin may offer various possibilities of exploitation. It is exceeded only by cellulose and hemicellulose, and comprises 15–25% of the dry weight of woody plants [2]. However, its transformation in fuels or chemicals supposes a complex chemistry involving the cleavage of C–O and C–C bonds and altering of the functional groups.

From the chemical point of view, lignin is an irregular phenolic copolymer whose monomers, 4-hydroxycinnamyl alcohol, coniferyl alcohol, and sinapyl alcohol, are linked by C–O and C–C bonds, of which the most abundant is the β-O-4 ether linkage [3]. Based on this structure, the valorization of the lignin requires an efficient disruption of both the etheric and C–C bonds meaning the presence of catalysts exhibiting acid/base functions and of a metal.

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Early works proposed reductive depolymerization and hydrolysis as potential routes. Reductive depolymerization is one of the oldest strategies and used a copper–chromium oxide catalyst, which works at high pressure and temperature [4]. Initial work on the hydrolysis of lignin to smaller entities was suggested to be catalyzed by mineral acids [5]. Other proposed alternatives are as follows: (i) lignin pyrolysis to veratryl-glycol-β-guaiacyl and guaiacyl-glycol-β-guaiacyl-ethers, followed by the supported metal-catalyzed hydrogenation to guaiacol and derivative by-products [6]; (ii) conversion to *syn*-gas with further production of hydrocarbons [7,8]; In terms of energetics of the reaction, both routes require more energy than catalytic hydrolysis and C–C bond disruption routes; (iii) steam explosion [9]; (iv) enzymatic hydrolysis [10,11]; (v) anaerobic microbial consortia [12] and (vi) catalytic and non-catalytic oxidation [13,14].

Catalytic hydrolysis is a rather complex procedure and strongly depends on reaction conditions and the initial lignin structure.

Despite the intense work and the insight that both the acid- and base-catalyzed hydrolysis involve the disruption of the aryl–ether bonds, experiments carried out with either lignin or lignin-compounds stimulants led to different mechanistic conclusions [15–21]. Accordingly, the mechanism by which an acid cleaves the β-O-4 linkages is yet not fully elucidated and it was also suggested that part of hydrolysis takes place randomly [22]. Obviously it is accepted that β-O-4 linkages are cleaved from the phenolic ends and the presence of methoxy groups affects the identity of the condensation products and protects reaction intermediates from rapid self-condensation [23]. It also depends on the internal hydroxyl groups of lignin [24]. Both acid- [9] and base-catalyzed systems are solvent dependent [21]. Organic solvents [25], hot-water [14], and supercritical solvent (methanol/ethanol) [26,27] yield highly differing results.

Most of the acid–base hydrolysis experiments are carried out using homogeneous catalysts [20,28–34]. Beckham and co-workers used sulfuric acid to catalyze the lignin depolymerization [23]. They indicated that the reaction proceeds *via* an ionic, unzipping mechanism wherein β-O-4 linkages are cleaved from the phenolic ends and the presence of methoxy groups affects the identity of the condensation products and protects reaction intermediates from rapid self-condensation. The presence of coal may favor the acid depolymerization at low temperature with protection of the disrupted entities [35]. Miller et co-workers studied liquid hydroxides (soluble KOH, NaOH, CsOH, LiOH, Na_2CO_3 and less soluble $Ca(OH)_2$) for the same scope [36]. In the presence of KOH, under supercritical ethanol at 290 °C both Kraft- and Organosolv-derived lignins were depolymerized with high yields. Strong bases gave superior conversion, and that combinations of bases led to both positive and negative synergistic effects. For the same case of the base-catalyzed hydrolysis, Lercher and co-workers [21] suggested that boric acid forms esters with phenolic hydroxyl groups and thus reduces concurrent oligomerization and polymerization. The capping capability is strongly pH dependent [37].

The reductive depolymerization of lignin to chemical products was also considered at industrial scale. It followed two main routes. One was the catalytic hydrogenolysis proposed in 1952 by the Noguchi Institute of Japan to produce mono phenols. However, the Noguchi process developed on this basis (1966) has been abandoned due to the low yield to mono phenols [38]. The other is the catalytic hydroconversion of the liquid fraction collected from lignin hydroliquefaction, the HRI or Lignol process developed by Hydrocarbon Research Inc., which is a continuous process involving a heterogeneous catalyst and a solvent [39].

However, despite these achievements, the oldest reductive depolymerization remains a promising lignin depolymerizing route [4]. This concept has been reconsidered where besides the initial Cu–Cr catalysts many active metals and sulfides, including nanoparticles have been tested [40–50]. One advantage of this procedure is that the conversion may be enhanced by transfer hydrogenation either from donor solvents or from internal hydroxyl groups of lignin [24].

Homogeneous metal catalysts for aryl–ether bond cleavage in model molecules were reported using both noble [41,47,48,51] and non-noble [42,52,53] metal complexes. However, some of these complexes are either very expensive or decompose to nanoparticles during the reactions. The use of nanocatalysts ensures the bridges between homogeneous and heterogeneous catalysis [54]. Palladium nanoparticles on carbon coupled with Zn(II) Lewis acids are also reported to selectively cleave C–O bonds in a variety of monomeric, dimeric, and polymeric lignin molecules under relatively mild conditions [55].

Classic Ni–Mo/Cr_2O_3 catalysts showed a high lignin depolymerization activity but at a very high pressure of hydrogen (140 atm) [56]. High pressures (100 atm) and temperatures (260 °C) were also required for the catalytic hydrocracking of pyrolytic lignin in supercritical ethanol using Ru/ZrO_2/SBA-15 or Ru/SO_4^{2-}/ZrO_2/SBA-15 catalysts [57]. Working with nickel-Raney led to better results, >99% conversion in the cleavage of diphenyl ether in aprotic non-polar solvents at 90 °C and 50 atm [58] or to a non-pyrolytic lignin bio-oil in (2-PrOH)/H_2O [59]. Even better results were reported using bimetallic Zn/Pd/C catalysts for aryl–ether bond cleavage of a model compound, guaiacyl-glycerol-β-guaiacyl ether, working in methanol at 20 atm of hydrogen [55].

However, even in the nano-state such catalysts may have more limited applicability relative to truly heterogeneous catalysts for lignin depolymerization in an applicable biorefinery system. A common inconvenience of most of the catalysts investigated to date, and especially of the nanocatalysts, is their separation from insoluble non-reacted solid substrates, as it is the case of lignin. To avoid this, a solution might be the use of core–shell nano-catalysts containing a magnetic core [60–62]. These nanomaterials should exhibit superparamagnetic characteristics to allow both an efficient separation and a redispersion in the reaction medium [63,64]. Supplementary to the separation advantage, the use of the typical heterogeneous catalysts is associated with mass transfer limitations that generate additional inconveniences. The use of the magnetic core–shell nano-catalysts minimizes such effects and limits the possibility of nanocatalyst aggregation during recovery, thus improving the durability of the catalysts [65].

To the best of our knowledge, to date, the use of magnetic recoverable nanoparticles in direct connection to lignin was reported only with the scope of adsorbents for its removal from aqueous solutions [66]. The aim of this study was to investigate the synthesis of superparamagnetic core shell catalysts for the fragmentation of lignin in the liquid phase. To accomplish this aim, magnetic nanoparticles were covered with a niobia shell with a double role to protect the magnetic nanoparticles and to generate the acidic function and, on this composite, cobalt nanoparticles were deposed in order to catalyze the C–C bond splitting. Cobalt was reported for its activity in hydrogenolysis of both the C–C and C–O bonds [67–70]. Niobia typically exhibits the required acidity, activity, stability and insolubility to catalyze reactions in aqueous media [71]. This oxide contains strong Lewis and Brönsted acid sites. As a support, niobium oxide may lead to strong interactions between metal and support (SMSI) that may provide active centers for catalytic hydrogenations [72].

2. Experimental

2.1. Materials

The reagents used in this study were of analytic purity, and were used without any further purification: Ammonium niobate