Tungsten Carbide: A Remarkably Efficient Catalyst for the Selective Cleavage of Lignin C-O Bonds

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PURPOSE OF THE ABSTRACT
A remarkably effective method for the chemoselective cleavage of the C-O bonds of typical b-O-4 model compounds and the deconstruction of lignin feedstock was developed by using tungsten carbide as the catalyst. High yields of C-O cleavage products (up to 96.8%) from model compounds and liquid oils (up to 70.7%) from lignin feedstock were obtained under low hydrogen pressure (0.69 MPa) in methanol. The conversion efficiency was determined to a large extent by solvent effects and was also affected by both the electronic and steric effects of the lignin model compounds. In situ W2C/activated carbon (AC)-catalyzed hydrogen transfer from methanol to the substrate was proposed to be responsible for the high performance in methanol solvent. The conversion of 2-(2-methoxyphenoxy)-1-phenylethanol showed that the catalyst could be reused five times without a significant loss in activity for C-O bond cleavage, whereas the selectivity to value-added styrene increased markedly owing to partial oxidation of the W2C phase according to X-ray diffraction, Raman spectroscopy, and transmission electron microscopy characterization. 2D-HSQC NMR spectroscopy analysis showed that W2C/AC exhibited high activity not only for b-O-4 cleavage but also for the deconstruction of more resistant a-O-4 and b-b linkages, so that a high yield of liquid oil was obtained from lignin. Corn stalk lignin was more liable to be depolymerized than birch lignin owing to its loosened structure (scanning electron microscopy results), larger surface area (BET results), and lower molecular weight (gel-permeation chromatography results), whereas its liquid oil composition was more complicated than that of birch wood lignin in that the former lignin contained more p-hydroxyphenyl units and the former contained noncanonical units.
Hydrogenolysis of 2-(2-methoxyphenoxy)-1-phenylethanol catalyzed by W2C/AC under different reaction conditions.

[a] Reactions conditions: unless otherwise specified, a stainless-steel autoclave was charged with the substrate (100 mg), 30 wt% W2C/AC (100 mg), and methanol (30 mL), and the vessel was pressurized with H2 (0.69 MPa); the reactions were performed at different temperatures for 2 h.

Recycling results for the W2C/AC-catalyzed C-O bond cleavage of 2-(2-methoxyphenoxy)-1-phenylethanol. E + S is the abbreviation of the total yield of ethylbenzene plus styrene.

FIGURE 1

FIGURE 2

KEYWORDS
Aromatics | Biomass | Lignin | Methanol

BIBLIOGRAPHY