

Hydrothermal conversion of lignin model compound eugenol

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Introduction

Eugenol can be used as a model compound for a lignin monomer because of its chemical structure close to sinapyl, coniferyl and coumaryl alcohols[1]. In this work, eugenol transformation is studied using various heterogeneous catalysts that have been synthesized and characterized; several metals (Pd, Ru or Pt) supported either on zirconia or on carbon and hydrotalcites. The reactions take place in an autoclave loaded with an ethanol/water mixture, eugenol and the catalyst, in the absence of gaseous H₂.

A kinetic study of the reaction is realized using the best catalyst. The influence of temperature, eugenol concentration and amount of catalyst has been studied and a plausible reaction mechanism will be presented.

Materials and Methods

The metal supported catalysts were prepared using an impregnation method. The experiments were run in a batch reactor autoclave under autogenous pressure. The kinetic studies were conducted between 250 and 300 °C, with a eugenol concentration between 0.25 vol.% and 5 vol.% and using a catalyst concentration varying from 0.66 wt.% to 1.33 wt.%. The autoclave containing water and catalyst was purged under nitrogen, heated to the desired temperature, then a solution of eugenol in ethanol was introduced using a high pressure pump. Liquid samples were periodically collected and were analyzed by GC/MS on a ZB-WAXplus column.

Results and Discussion

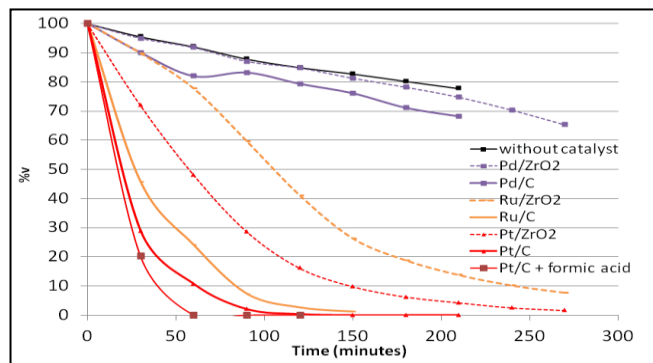


Figure 1. Eugenol conversion at 300 °C using different metal supported catalysts. (Conditions : 5 vol.% eugenol, 1 wt.% catalyst, P = 120 bar).

Pt/C is the most active catalyst. Carbon supported catalysts are more active than zirconia supported catalysts loaded with similar amounts of metal except for Pd-based catalysts which exhibit virtually no activity.

Figure 2 shows the typical transformation profile of eugenol under hydrothermal conditions.

Figure 3 shows the initial reaction rate using different eugenol concentration.

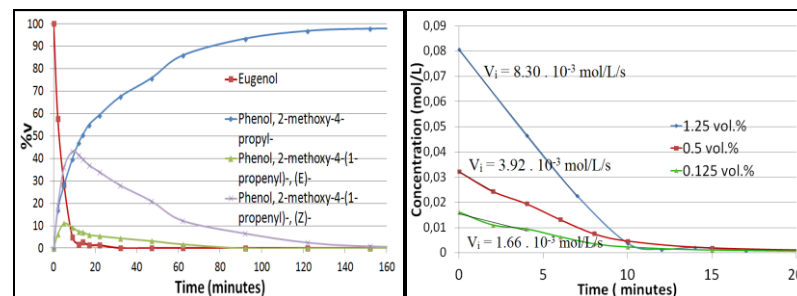


Figure 2. Transformation reaction profile of eugenol at 250 °C.

1 wt.% Pt/C, 1.25 vol.% eugenol, P=85bar.

Figure 3. Conversion of eugenol versus time at different eugenol concentrations.

1 wt.% Pt/C, T = 250 °C, P = 60 bar.

Significance

Eugenol conversion is rapid and reaches 98 % after 10 min of reaction. The product distribution profile is typical of consecutive reactions, in which the terminal double bond of the propylene fragment is rapidly isomerized into two isomers (E and Z forms).

The double bonds of the isomers are then hydrogenated more slowly and phenol-2-methoxy-4-propyl is formed, probably with ethanol as reducing agent. The dependence of the initial reaction rate on the eugenol concentration indicates that the reaction is controlled by the reaction of two adsorbed surface intermediates. An apparent activation energy for the conversion of eugenol of 52 kJ/mol was measured. The methoxy and hydroxyl groups on the aromatic ring, however, do not react under these conditions, evidencing the high stability of lignin-derived compounds.

References

- [1] O. Bobleter, "Hydrothermal degradation of polymers derived from plants," *Progress in polymer science*, vol. 19, no. 5, pp. 797–841.