ISGC 2017
May 16rd - 19th

N°455 / FC
TOPIC(s) : Renewable carbon / Catalytic systems

Hydrodeoxygenation of cresol isomers over nickel phosphide supported catalyst: toward the production of renewable chemicals and fuels

AUTHORS

Vinicius O.O. GONÇALVES / INSTITUT DE CHIMIE DES MILIEUX ET MATÉRIAUX DE POITIERS, UMR 7285 UNIVERSITÉ DE POITIERS - CNRS, 4 RUE MICHEL BRUNET, POITIERS
Fabio B. NORONHA / CATALYSIS DIVISION, NATIONAL INSTITUTE OF TECHNOLOGY, AV. VENEZUELA 82, RIO DE JANEIRO
Priscilla M. DE SOUZA / CATALYSIS DIVISION, NATIONAL INSTITUTE OF TECHNOLOGY, AV. VENEZUELA 82, RIO DE JANEIRO
Victor T. DA SILVA / UNIVERSIDADE FEDERAL DO RIO DE JANEIRO/COPPE/CHEMICAL ENGINEERING PROGRAM/ NUCAT, P.O. BOX 68502, RIO DE JANEIRO
Corresponding author : Frédéric RICHARD / frederic.richard@univ-poitiers.fr

PURPOSE OF THE ABSTRACT

Lignocellulosic biomass as a renewable and sustainable source of energy is of growing importance due to the increasing attention on environmental concerns. Such raw materials could be transformed into chemicals and fuels in a biorefinery [1]. The first step required is its depolymerization which can be carried out by several processes [2]. The bio-oil produced has to be upgraded by hydrodeoxygenation (HDO) in order to reduce its oxygen content, leading to a better physical and chemical properties such as higher heating values, lower viscosity, stability, pH values, and combustion properties compared to the crude bio-oil.

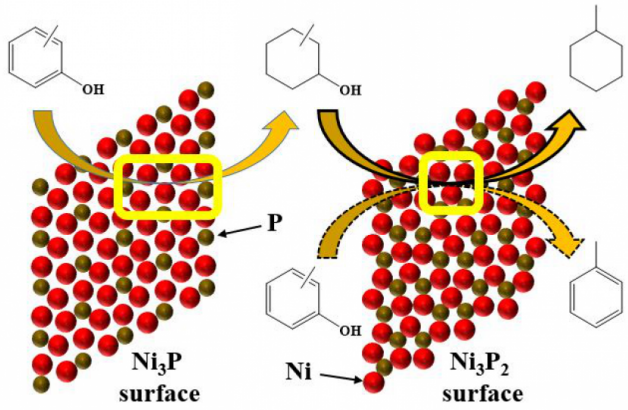
Transition metal phosphides have emerged as new class of catalysts featuring several advantages compared to other catalysts used in HDO, especially due to its low cost when compared with noble metal catalysts and the low selectivity for other reactions than deoxygenation with respect to non-noble metal catalysts [3]. In general, catalytic behavior of different transition metal phosphides are interpreted in terms of the electron property of metal site, Brønsted acidity or a combination of both [4].

In this work the catalytic properties of a Ni2P/SiO2 catalyst were evaluated for the hydrodeoxygenation of cresol isomers as model oxygenated compounds under high pressures of hydrogen (between 1.6 and 3.2 MPa) at temperatures between 250 and 340 °C. The different pathways involved during the transformations of such model molecules were carefully considered, in particular by using a kinetic model. The nature of active sites present on the nickel phosphide phase and the reaction mechanisms involved were also discussed.

The present word demonstrated that the HDO of cresols isomers over Ni2P/SiO2 catalyst involved two parallel deoxygenation routes. Different reactions such as hydrogenolysis, hydrogenation, dehydration and isomerization took place on this catalyst leading to several products. The main pathway (so-called HYD) led to oxygenated (ketones and alcohols) and deoxygenated products (cycloalkenes and cycloalkane), whereas the DDO route yielded only toluene by hydrogenolysis of the C-O bond. The use of a relative high pressure of hydrogen (3.2 MPa) allowed to ensure a remarkable stability of the nickel phosphide phase. An effect of the position of the methyl group was highlighted, depending on the pathway considered. The reactivity of cresols followed: m-cresol > p-cresol > o-cresol, the DDO route being more affected by the position of the methyl group than the HYD route. This result suggests that active sites involved in both deoxygenation routes could be different. The effect of temperature and hydrogen pressure was also dependent on the deoxygenation route: temperature favored more the DDO route whereas an increase of the hydrogen pressure was more beneficial for the HYD route. Nevertheless, it is important to underline that an increase of both experimental parameters allowed a higher deoxygenation degree of m-cresol (close to 100%), in spite of low conversion rates (lower than 20%).

Based on these experimental results, several kinds of active sites and adsorption modes were proposed to explain the formation of the products observed experimentally. The Ni(1) sites present on the Ni3P2 surface seem to be associated to hydrogenolysis reactions which take place in the transformation of cresols into toluene and methylcyclohexanols into methylcyclohexane. These reactions probably need an activation of the C-O bond through the adsorption by the oxygen atom. On the opposite, Ni(2) sites, presents on the Ni3P surface, are likely to be active for hydrogenation of aromatic ring, probably suggesting a flat adsorption of cresols. In addition, Brønsted acid sites (probably PO-H groups) were involved in dehydration and isomerization reactions.

FIGURES



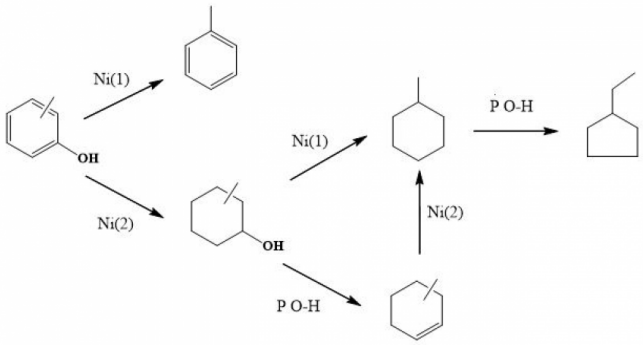


FIGURE 1

Several reactions taking place in the different terminations of a Ni2P crystal.

Proposals of the active sites involved during the transformation of cresols and their intermediates.

FIGURE 2

Proposals of the different active sites likely to be involved during the transformation of cresols over Ni2P phase.

Reaction scheme of the transformation of cresols at 4 MPa and 340 ºC, including the active sites responsible for the different reactions observed (hydrogenolysis, dehydration, hydrogenation and isomerisation).

KEYWORDS

hydrodeoxygenation | nickel phosphide | kinetics | phenolic compounds

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