

Hydrodeoxygenation of benzofuran and its oxygenated derivatives (2,3-dihydrobenzofuran and 2-ethylphenol) over NiMoP/Al₂O₃ catalyst. Effect of H₂S in the feed.

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Introduction

With the decline of available petroleum resources, it is very important to develop new liquid fuels which could proceed from biomass. For this purpose, the aim of the European Union is to introduce 5.75% of biofuels in conventional fuels by 31 December 2010 [1]. Solid biomass such as waste materials and forest products, which contain cellulose, hemicellulose and lignin, can be used as source of bio-fuel [2]. For example, pyrolysis oils can contain about 40-55 wt% of oxygen [3]. A lot of oxygenated functions are observed in these oils such as acid, aldehyde, alcohol, phenolic and furanic functions. Bio-oil upgrading to liquid fuel requires oxygen removal by a hydrodeoxygenation process (HDO) [3] in which oxygen is removed as water and/or carbon oxides under high pressure (4-10 MPa) of hydrogen at moderate temperature (300-500°C). Conventional hydrotreating catalysts such as sulfided CoMo/Al₂O₃ or NiMo/Al₂O₃ can be used. Benzofuran (BF) is a common probe molecule to evaluate the sulfided catalyst performances in HDO reactions [3]. In the present paper, the transformation of benzofuran and its oxygenated derivatives were studied under conditions close to hydrotreatment. The effect of hydrogen sulfide (H₂S) was also investigated.

Materials and Methods

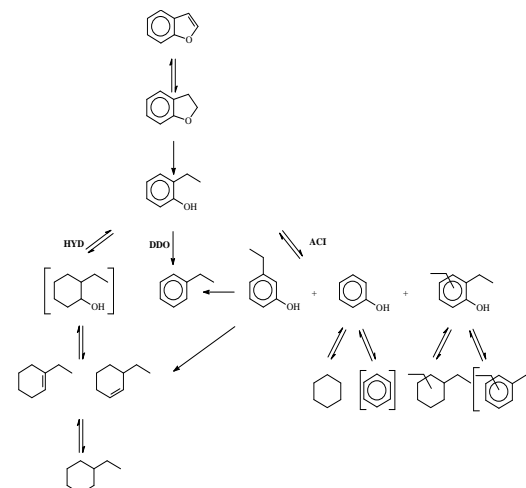
The transformation of benzofuran (BF), 2,3-dihydrobenzofuran (2,3-DHBF) and 2-ethylphenol (2-EtPh), as well as the competitive effect between furanic compounds (benzofuran and 2,3-dihydrobenzofuran) and a phenolic compound (2-propylphenol) over a sulfided NiMoP/Al₂O₃ catalyst were studied under a total pressure of 7 MPa at 340°C in a fixed bed reactor. The transformation of each oxygenated compounds was carried out with or without H₂S (from dimethyldisulfide). The NiMoP/Al₂O₃ catalyst used contains 3 wt.% NiO, 2.4 wt.% phosphorous and 16 wt.% MoO₃.

Results and Discussion

The global reaction scheme of BF has been established (Scheme 1) [4]. Over the sulfided NiMoP/Al₂O₃ catalyst, the first step involved for the transformation of BF was an hydrogenation of the C=C bond leading to 2,3-DHBF. By a C_(sp3)-O bond cleavage, 2,3-DHBF led to 2-EtPh which was always the main product of BF and 2,3-DHBF transformations. The mechanism involved in the 2,3-DHBF transformation into 2-EtPh could be a nucleophilic substitution reaction (S_N2) using a SH⁻ group as nucleophilic. The promoting effect of H₂S on the transformation of 2,3-DHBF into 2-EtPh can be explained by this mechanism.

The low rate of deoxygenation observed from BF and 2,3-DHBF was due to competitive adsorption between oxygenated compounds on the active sites of the catalyst.

Indeed, the transformation of BF and 2,3-DHBF led mainly to 2-ethylphenol (2-EtPh) which transformation was inhibited by the presence of BF and/or 2,3-DHBF. 2-EtPh was converted into deoxygenated products by two parallel pathways. The main one proceeded by hydrogenation and dehydration reactions (HYD pathway) leading to ethylcyclohexane as the main deoxygenated product. The other was a direct deoxygenation route (DDO pathway) leading to ethylbenzene which formation involves a basic site such as a sulfur anion and vacancies present on the surface of the catalyst. H₂S promoted the HYD pathway whereas it inhibited the DDO pathway. This observation could be interpreted, in part, on the basis of an interconversion of DDO and HYD active sites. In addition, 2-EtPh was also converted in oxygenated products by isomerization and disproportionation reactions (acidic route: ACI) leading to phenol, 3-ethylphenol and diethylphenol isomers which could also be deoxygenated.



Scheme 1. Transformation of benzofuran over NiMoP/Al₂O₃ catalyst. HYD: hydrogenation route; DDO: direct deoxygenation route; ACI: acidic route

Significance

In conclusion, benzofuran is a good model molecule since its transformation requires all the various reactions involved in hydrodeoxygenation process and could also underline the inhibiting effects that will be present during the transformation of a real feed stock. Finally, this probe molecule could be used to design new catalysts in HDO.

References

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