ISGC 2022

N°805 / OC
TOPIC(s) : Mechanism investigations / Homogenous, heterogenous and biocatalysis

Investigation of demethoxylation mechanism of anisole over Raney-Ni catalyst

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PURPOSE OF THE ABSTRACT

Lignocellulosic biomass can be converted into useful precursors of fine chemicals and fuels by pyrolysis or hydrothermal upgrading followed by hydrogenation (HYD) of products at severe reaction conditions. Compared to the classic hydrodeoxygenation (HDO) of the biomass to chemicals intermediates (e.g., pyrolysis oil) over supported catalysts using gaseous hydrogen, HDO/HYD over a Raney-Ni® catalyst in presence of an H-donor solvent (e.g., 2-propanol) can be achieved at mild reaction conditions (<100 °C, 1 bar).

Experimentally was confirmed that Raney-Ni catalyst had high selectivity towards demethoxylation of methoxyphenols under mild reaction conditions (70 °, 1 bar, 2-propanol), however, no HDO of phenols was observed and only HYD of aromatic ring occurred.[1] The cleavage of the alkoxy (Ar?O?R) ether bond present in anisole is an interesting HDO reaction, due to the presence of two different C?O bonds, Caryl?O or Calkyl?O, which could be potentially cleaved. Understanding the key factors of the mechanism of anisole demethoxylation (and of other methoxyphenols) would help to tune the catalysts to enhance their activity towards direct aromatics production.

Detailed characterization of the Raney-Ni catalyst (ICP-OES, XRD, XPS, BET) together with computational calculation (DFT, VASP PBE-D3) of the anisole HDO over Raney-Ni was applied. Characterization of the Raney-Ni catalyst is challenging since its bulk composition differs substantially from its surface composition (e.g. residual Al is concentrated on the surface).

Here, calculation of anisole HDO over NixAly (111, 110, 211, 533) surfaces demonstrated that direct Caryl-O cleavage is less favourable on the Ni-rich surfaces, where dehydrogenation of CH3- group is dominant first step followed by phenol formation, which is contradict with the experimental data. Thus, we focused on the investigation of different NixAly surfaces (flat, stepwise) to determine one with the lowest energy barriers towards benzene formation. Additionally, possible direct hydrodeoxygenation and H-transfer from 2-propanol to Ar-O-R were investigated.

FIGURES

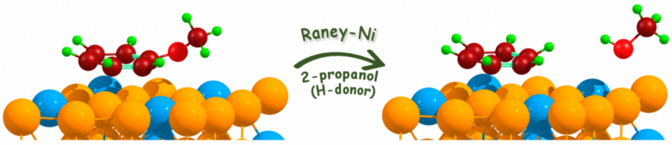

FIGURE 1

Graphical abstract

Deoxygenation of anisole to benzene

FIGURE 2

KEYWORDS

Biomass | Aromatics | hydrogenation | DFT

BIBLIOGRAPHY