MICROKINETIC AND FIRST-PRINCIPLES MECHANISTIC STUDY OF EUGENOL HYDROTREATMENT OVER Ru/C

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Abstract

Hydrotreatment of a lignin model compound eugenol has been studied experimentally in a three-phase slurry reactor and *in-silico* by the micro-kinetic modelling, supported by density functional theory (DFT) results. Commercial Ru/C material has been selected as a catalyst, which has been thoroughly characterized prior to its use. Microkinetic model has been developed that took into account mass transfer phenomena in a three-phase contactor, as well as adsorption and desorption kinetics and catalytic reaction kinetics on the catalyst surface. Competitive reaction kinetics of ring saturation and (hydro)deoxygenation has been quantitatively addressed and also supported by DFT results. Since activation energy of dehyroxylation or demethoxylation is significantly higher compared to ring (and especially allyl group) saturation, temperature increase shifts the selectivity towards deoxygenated products.

Keywords

Lignin Hydrogenolysis, Density Functional Theory (DFT), Micro-Kinetic Modelling, Slurry Reactor.

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Introduction

Lignin is an abundant natural polymer composed of aromatic monomeric units interconnected via C-C and ether bonds, being thus a very promising renewable source for the bio-based chemicals production. Catalytic hydrotreatment has been shown as a promising lignin valorization route. Due to the structural complexity, lignin valorization studies are often based on the model compounds. In this regard, lignin defunctionalization has been usually examined on the monomer model compounds. Various catalytic systems have been tested in this process based on the noble and non-noble transition metals supported on neutral and acidic supports. Noble metals have recently gained increasing attention due to the high hydrogenation activity and stability.

The present study represents an integrated theoretical and experimental assessment of the catalytic hydrotreatment of eugenol, a representative lignin monomer model compound, over the Ru/C catalyst. A micro-kinetic model has been developed to describe experimental observations at more fundamental level accompanied by DFT calculations.

Catalyst characterization

Fresh Ru/C (5 wt% Ru, Sigma Aldrich, St. Louis, MO, USA, reference number 206180) was used as a catalyst. Prior to use, the catalyst was thoroughly characterized for its morphological (SEM, TEM), textural (N_2-physisorption) and chemical (NH_3-TPD, CO-TPD, H_2-TPD, H_2-TPR) properties of the surface. Concentration of surface metal sites was determined to be 38 μmol g^{-1} according to the CO-TPD method, while concentration of acidic sites was negligible. Specific surface area or the catalyst was measured to be 650±30 m^2g^{-1} with an average pore width of 5 nm.

Catalytic hydrotreatment tests

Experiments have been performed in a cylindrical stainless steel slurry reactor (Autoclave Engineers) in a completely batch regime. A typical experiment was performed with 5 wt% (4.5 g) of eugenol, 0.2 wt% (0.2 g) of the Ru/C and 94.8 wt% (85.3 g) of the solvent (hexadecane) at 275 °Ca and 5 MPa of initial hydrogen pressure under vigorous mixing of 1000 min^{-1}. Reactions proceeded for 3 h at the final temperature (heating up period 30 – 45 min). During the experiment, sampling of the liquid and gas phase took place. Liquid samples were analyzed by using a gas chromatograph with flame ionization detector (GC–FID) coupled with a mass spectrometer detector (GC–MS), while gas samples were analyzed by using gas chromatography (GC) and Fourier Transform Infrared (FTIR) Spectroscopy. An influence of various operating conditions on the product distribution has been investigated. The influence of temperature has been examined in the range of 225 – 325 °C, of the pressure in the range 4 – 7 MPa, of the agitation speed in the range of 100 – 1000 min^{-1}, of the catalyst loading in the range 0 – 0.4 wt%. Blank and experiments with important intermediates have been also performed at typical operating conditions.

Micro-kinetic modelling

Based on a reaction pathway network, proposed according to the experimentally-determined intermediates and DFT study, a microkinetic model of hydrotreatment in a three-phase slurry reactor has been developed, that includes the influence of i) thermodynamics, ii) hydrodynamics, iii) mass transfer (gas – liquid, liquid – solid surface), iv) adsorption and desorption kinetics, v) surface reaction kinetics, vi) reaction kinetics in bulk phase on the global reaction rate [1-3]. Mass balances for each component in every phase (gas, liquid, catalyst surface) have been written as a set of ordinary differential equations (ODE) and were solved numerically. Kinetic, mass transfer and thermodynamic parameters were obtained either by empirical correlations, DFT calculations or regression analysis.

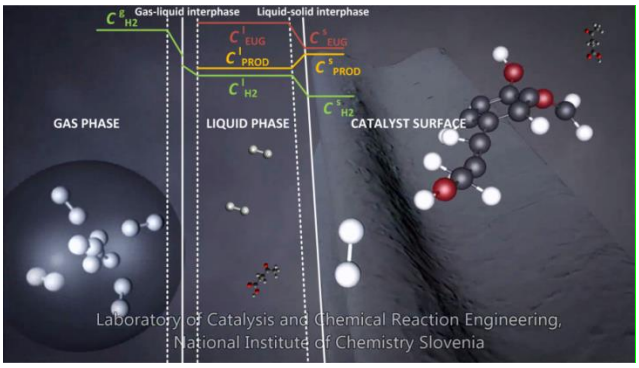

Figure 1. Scheme of potential mass-transfer limitations in a three-phase slurry reactor.

DFT calculations

Density functional theory calculations have been performed in a Quantum Espresso open-source software using computationally-cheap approaches, specifically; Plane-Wave DFT with Perdew–Burke–Ernzerhof functional (PBE) and Grimme-D2 for van der Waals interactions. Unit cell consisted of 96 Ru atoms (4x6x4). Approximately 500.000 core-hours were spent for 500 stable and transition-state structures search and optimization [2].

Results and discussion

Ru/C catalyzed hydrotreatment of eugenol yielded 2-methoxy-4-propylphenol (HMPB), 4-propylphenol (HPB), 2-methoxy-4-propylcyclohexanol (HMPC), 4-

propylcyclohexanol (HPC), propylbenzene (PB), propylcyclopentane (PCP), propylcyclohexane (PC), 4-propylcyclohexanone (KPC), 4-propyl-1,2-cyclohexanediol (HHPC), trans-isoeugenol (IHMAB), 2-metyl-1-propylcyclopentate (MePCP) and 2-methoxy-4-propylcylohexanone (KMPC). Blank experiment reviled that allyl double bond isomerization and hydrogenation proceed also without the catalyst, what has been supported by DFT calculations. Reaction network of eugenol hydrotreatment over the Ru/C has been established based on the product evolution over the reaction time and experiments performed with intermediates [1]. The proposed reaction network has been confirmed by the DFT calculations.

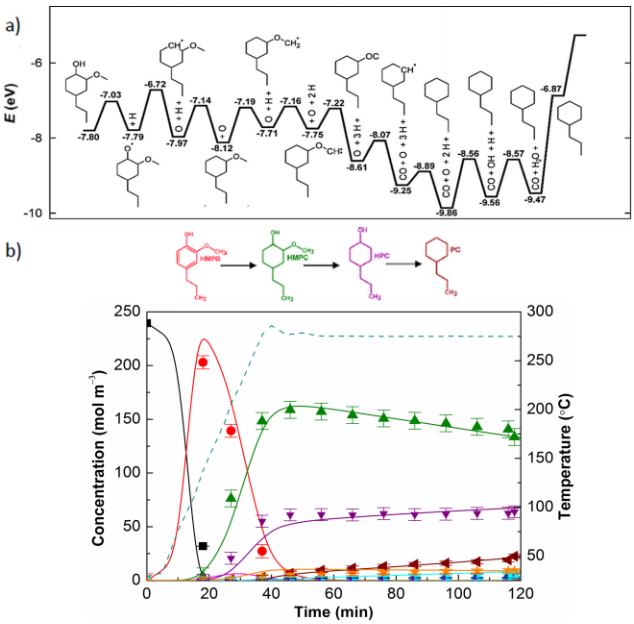

Figure 2. a) Potential energy surface for the minimum energy pathway of the HMPC deoxygenation obtained by the DFT b) eugenol hydrotreatment over the Ru/C at 275 °C (other operating conditions: 5 wt% of eugenol, 0.2 wt of the Ru/C, 94.8 wt% of hexadecane, 5 MPa, 1000 min^{-1}).

Temperature variation influenced the product distribution the most significantly. Hydrogenation reactions took place predominantly at lower temperatures as a consequence of low activation energies (approx. 50 kJ mol^{-1}) estimated by the model. On the other side, deoxygenation reactions were significantly promoted at higher temperatures due to greater activation energies (approx. 100 kJ mol^{-1}). Pressure change affected primarily the yield of hydrogenated products. Agitation speed variation indicated absence of the external mass transfer limitations in the tested range. The catalyst loading promoted all reactions, as expected. Demethoxylation and dehydroxylation rate constants have been estimated 36- and 42-fold higher for aromatics relative to oxygen-containing cycloalkanes. Energy diagram, determined for HMPC deoxygenation by the DFT, has been provided in Fig 2a, while Fig. 2b demonstrats integrated experimental and micro-kinetic model results obtained for the experiment performed at 275 °C.

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