Catalytic hydrogenation, hydrodeoxygenation and hydrocracking processes of lignin monomer model compound eugenol over magnetic Ru/C–Fe_2O_3 and mechanistic reaction microkinetics

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2. Model

2.1. Model development

Elementary steps taken into account are described by Eq. 1–7.

$$H_{(g)} \underset{k_{-l}}{\overset{k_l}{\rightleftarrows}} H_{(l)} \quad (1)$$

$$H_{(l)} \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} H_{(s)} \quad (2)$$

$$RC_{(l)} + H_{(l)} \xrightarrow{k_{RC-i}^{hom}} PR_{(l)} \quad (3)$$

$$H_{(s)} + 2* \underset{k_H^{des}}{\overset{k_H^{ads}}{\rightleftarrows}} 2H_{ads} \quad (4)$$

$$RC_{(l)} \underset{k_{-s}}{\overset{k_s}{\rightleftarrows}} RC_{(s)} \quad (5)$$

$$RC_{(s)} + \gamma* \underset{k_{RC}^{des}}{\overset{k_{RC}^{ads}}{\rightleftarrows}} RC_{ads} \quad (6)$$

$$RC_{ads} + nH_{ads} \xrightarrow{k_{RC-i}^{cat}} PR_{ads} + n* \quad (7)$$

Meanings of symbols in aforementioned equations are: * a vacant active site, γ the number of active catalytic sites covered by any component *RC*, *n* the number of hydrogen atoms consumed in the catalytic reaction, *g*, *l*, *s*, *ads* concentrations of components in the gas, liquid, film around catalyst particles, and adsorbed on the catalyst surface in the same order, *H* hydrogen, *RC* any reacting component and *PR* the product of non-catalytic (in the bulk liquid) or catalytic reaction, k_l gas–liquid mass transfer coefficient, k_s liquid–solid mass transfer coefficient, k_{RC-i}^{hom} homogeneous (non-catalytic) reaction rate constant, k_{RC-i}^{cat} catalytic reaction rate constant, k_H^{ads} hydrogen adsorption constant, k_H^{des} hydrogen desorption constant, k_{RC}^{ads} adsorption constant and k_{RC}^{des} desorption constant of *RC*.

Eugenol HDO reaction network (Fig. 8 main part), primarily determined for the Ru/C, has been shown valid for tested catalyst in this study considering product evolution over the reaction time. Taking into account proposed reaction network and elementary steps given by Eq. 1 – 7, differential molar balance equations for each component in liquid phase and on the catalyst surface were formulated as given by Eq. 8 – 11. Concentration of components in the thin film around catalyst particles was expressed algebraically as a result of negligible accumulation capacity in the liquid film, due to its negligible volume (Eq. 12).

$$\frac{dc_{\mathrm{H(l)}}}{dt} = r_{\mathrm{H}}^{\mathrm{g-l}} - r_{\mathrm{RC}}^{\mathrm{l-s}} - \sum r_{\mathrm{i}}^{\mathrm{hom}} \tag{8}$$

$$\frac{dc_{\mathrm{RC(l)}}}{dt} = r_{\mathrm{RC}}^{\mathrm{l-s}} \pm \sum r_{\mathrm{i}}^{\mathrm{hom}} \tag{9}$$

$$\frac{dc_{\mathrm{RC(ads)}}}{dt} = r_{\mathrm{RC}}^{\mathrm{ads}} - r_{\mathrm{RC}}^{\mathrm{des}} \pm \sum r_{\mathrm{i}}^{\mathrm{cat}} \tag{10}$$

$$\frac{dc_{\mathrm{AS}}}{dt} = \sum r_{\mathrm{i}}^{\mathrm{cat}} + \sum r_{\mathrm{RC}}^{\mathrm{des}} - \sum r_{\mathrm{RC}}^{\mathrm{ads}} \tag{11}$$

$$0 = r_{\mathrm{RC}}^{\mathrm{l-s}} - r_{\mathrm{RC}}^{\mathrm{ads}} + r_{\mathrm{RC}}^{\mathrm{des}} \tag{12}$$

Symbols in the previous equations represent: c component concentration, t reaction time, $r_{\mathrm{H}}^{\mathrm{g-l}}$ hydrogen transport rate through the gas–liquid interface, $r_{\mathrm{RC}}^{\mathrm{l-s}}$ transport of any component *RC* through the film around the catalyst particles, $r_{\mathrm{RC}}^{\mathrm{ads}}$ and $r_{\mathrm{RC}}^{\mathrm{des}}$ the rate of component *RC* adsorption and desorption respectively, $r_{\mathrm{i}}^{\mathrm{cat}}$ the rate of reaction *i* on the catalyst surface and *AS* index refers to active sites.
Mass transport, adsorption, desorption and reaction rates are calculated as follows:

$$r_{\mathrm{H}}^{\mathrm{g-l}} = \frac{k_{\mathrm{l}} A_{\mathrm{g}} \left(\frac{p_{\mathrm{H}}}{He} - c_{\mathrm{H(l)}}\right)}{V_{\mathrm{l}}} \tag{13}$$

$$r_{\mathrm{RC}}^{\mathrm{l-s}} = \frac{k_{\mathrm{s}} A_{\mathrm{s}} \left(c_{\mathrm{RC(l)}} - c_{\mathrm{H(l)}}\right)}{V_{\mathrm{l}}} \tag{14}$$

$$r_{\mathrm{RC}}^{\mathrm{ads}} = k_{\mathrm{RC}}^{\mathrm{ads}} c_{\mathrm{RC(s)}} c_{\mathrm{AS}} \tag{15}$$

$$r_{\mathrm{RC}}^{\mathrm{des}} = k_{\mathrm{RC}}^{\mathrm{des}} c_{\mathrm{RC(ads)}} \tag{16}$$

$$r_{\mathrm{i}}^{\mathrm{hom}} = k_{\mathrm{RC-i}}^{\mathrm{hom}} c_{\mathrm{RC(l)}} c_{\mathrm{H(l)}} \tag{17}$$

$$r_{\mathrm{i}}^{\mathrm{cat}} = k_{\mathrm{RC-i}}^{\mathrm{cat}} c_{\mathrm{RC(ads)}} c_{\mathrm{H(ads)}} \tag{18}$$

$$K_{\mathrm{H}} = \frac{k_{\mathrm{H}}^{\mathrm{ads}}}{k_{\mathrm{H}}^{\mathrm{des}}} \tag{19}$$

$$K_{\mathrm{RC}} = \frac{k_{\mathrm{RC}}^{\mathrm{ads}}}{k_{\mathrm{RC}}^{\mathrm{des}}} \tag{20}$$

K_{H} (Eq. 19) and K_{RC} (Eq. 20) are related to the adsorption–desorption equilibrium constants for hydrogen and component *RC*. Estimations of Henry's constant (*He*) and mass transport coefficients as well as interfacial areas, A_{g} (gas–liquid) and A_{s} (liquid–solid) are available in our previous work [1]. All abbreviation, symbols and labels are also provided in Table S1-S3. The temperature dependence of the constants is assumed to follow Arrhenius law given by Eq. 21. Homogeneous reaction rate constants have been also assumed to follow Arrhenius law, their kinetic parameters were determined in our previous work [1].

$$k_{\mathrm{RC-i}}^{\mathrm{cat}}(T_2) = k_{\mathrm{RC-i}}^{\mathrm{cat}}(T_1) \times \exp\left(\frac{Ea_{\mathrm{RC-i}}^{\mathrm{cat}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{21}$$

Relevant criteria for evaluating mass (Thiele modulus) and heat (Prater number) transfer limitations have been calculated for similar system in our previous study [1]. It has been confirmed that external or intra-particle mass transfer limitations (as well as temperature gradients) do not affect the global reaction rate. Taking into account similarity of particle sizes and catalyst material (Ru/C from previous work and synthesized magnetic Ru) it can be concluded that reactions over magnetic Ru are also carried out in a kinetically controlled regime.

2.2. Parameters estimation

Measured concentrations ($c_{\mathrm{RC}}^{\mathrm{exp}}$) were fitted to modelled values ($c_{\mathrm{RC}}^{\mathrm{calc}}$), in order to obtain the kinetic parameters for the eugenol hydrotreatment for every catalyst used. A determination of initial parameter assumptions was carried out through the Box–Behnken experimental design (BB-DOE) method, to systematically test different combinations of model parameters and to take the best one in terms of error defined by Eq. 22 as the initial value for subsequent regression analysis. Optimized reaction rate constants obtained in the previous study [1] were used as input data for BB-DOE method carried out in this work. New value for a reaction constant has been obtained in a way: $k_{\mathrm{RC-i}}^{\mathrm{cat}} = k_{\mathrm{RC-i}}^{\mathrm{Ru/C}} \times 10^{\mathrm{b}\times\mathrm{BB}}$, where $k_{\mathrm{RC-i}}^{\mathrm{Ru/C}}$ represents optimized reaction rate constant for Ru/C catalyst, *b* represents a coefficient which had values 1, 2, 3, 4 or 5 in separated five loops, while BB represents Box–Behnken matrix (combinations of numbers –1, 0 and 1 with dimensions 125 × 9 ((number of combinations) × (number of variables)). Accordingly $k_{\mathrm{RC-i}}^{\mathrm{Ru/C}}$ reaction constant will be reduced, unchanged or increased for the factor of 10^{b}. The constants from the best combination (minimal error defined by Eq. 22) of these five loops were subsequently undergone to the iterative procedure of four cycles where each cycle included five loops (b values 1, 2, 3, 4, 5). Input data for the subsequent cycle was the best combination from the previous one. Testing of 125 × 5 × 5 = 3125 (combinations × loops × cycles) combinations in total finally provided the best combination of reaction rate constants subsequently undergone regression analysis optimization procedure. Nelder–Mead simplex and Levenberg–Marquardt algorithms were applied in order to minimize the objective function given by Eq. 22 and thus to optimize the kinetic parameters $k_{\mathrm{RC}}^{\mathrm{ads}}$, $k_{\mathrm{RC}}^{\mathrm{des}}$, $k_{\mathrm{H}}^{\mathrm{ads}}$, $k_{\mathrm{H}}^{\mathrm{des}}$, $k_{\mathrm{RC-i}}^{\mathrm{cat}}$, $E\mathrm{a}_{\mathrm{RC-i}}^{\mathrm{cat}}$ (representing adsorption and desorption constants of components, adsorption and desorption constants of hydrogen, reaction rate constants and their corresponding activation energies in the same order). Optimized activation energies for the Ru/C catalyst were varied in a similar way: $E\mathrm{a}_{\mathrm{RC-i}}^{\mathrm{cat}} = E\mathrm{a}_{\mathrm{RC-i}}^{\mathrm{Ru/C}} \pm e$ where *e* had values 50, 25, 12.5 or6.25 kJ mol^{-1} in four separated loops. Analogously to the rate constants, the best combination from the previous was taken as an initial in the subsequent loop. The best combination from these 500 tested was undergone to the regression analysis.

$$f(k_{\mathrm{RC}}^{\mathrm{ads}}, k_{\mathrm{RC}}^{\mathrm{des}}, k_{\mathrm{H}}^{\mathrm{ads}}, k_{\mathrm{H}}^{\mathrm{des}}, k_{\mathrm{RC-i}}^{\mathrm{cat}}, E\mathrm{a}_{\mathrm{RC-i}}^{\mathrm{cat}} = \sum_{\mathrm{j}=1}^{\mathrm{J}} \left(c_{\mathrm{RC}}^{\mathrm{exp}} - c_{\mathrm{RC}}^{\mathrm{calc}}\right)^2 \quad (22)$$

3. Results and discussion

3.1. Catalyst characterization

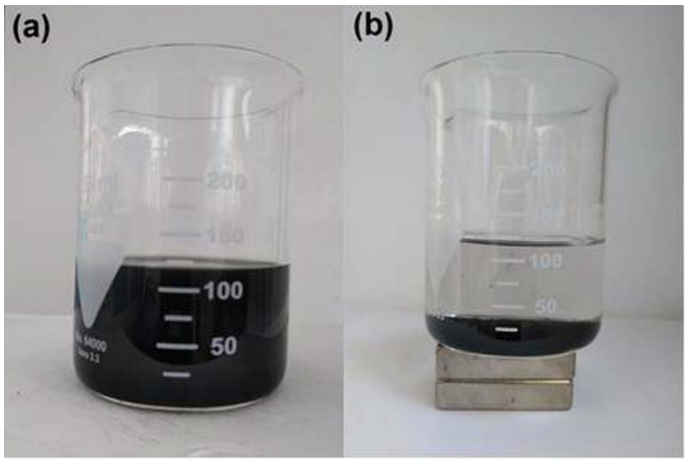

Figure S1. Catalyst separation by laboratory permanent magnet a) before separation b) after separation

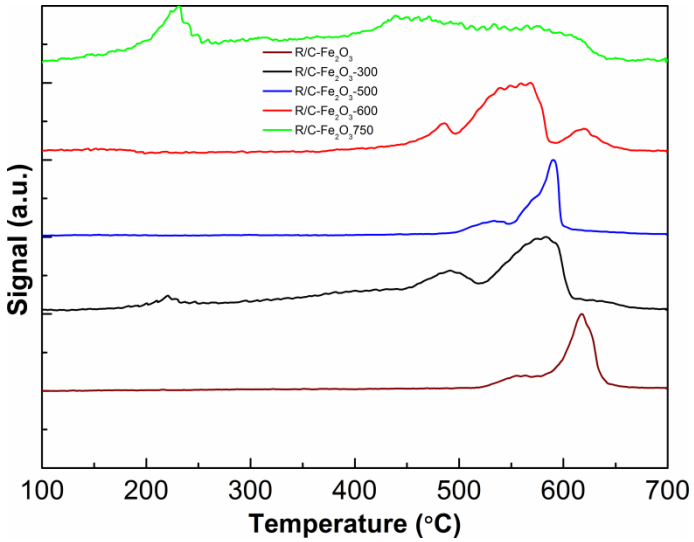

Figure S2. NH_3-TPD results for Ru/C-Fe_2O_3, Ru/C-Fe_2O_3-300, Ru/C-Fe_2O_3-500, Ru/C-Fe_2O_3-600, Ru/C-Fe_2O_3-750

3.2. Hydrotreatment results

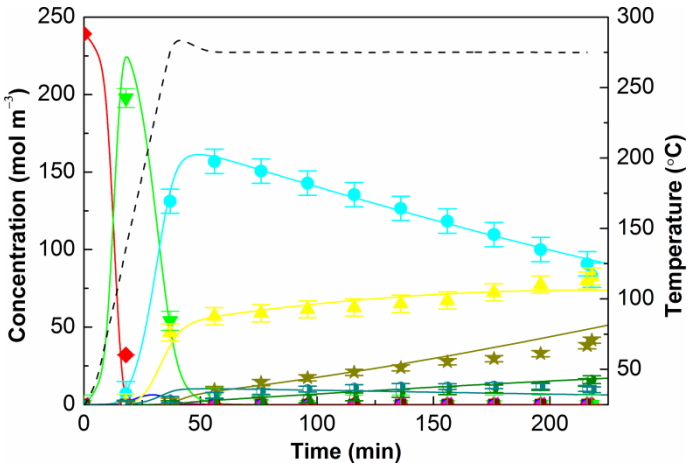

Figure S3. Experimental and model results over commercially available Ru/C at 275 ºC and 5 MPa. Meaning of symbols is as follows: ◆HMAB, ▼HMPB, ■HPB, ●HMPC, ◀PB, ▲HPC, ★PC, ◨IHMAB, ◑PCP, ◑HHPC, --- temperature

4. Materials and Methods

4.1. Materials

Used chemicals and gases in this work are: Ru/C (5 wt% Ru, Sigma Aldrich, St. Louis, MO, USA, reference number 206180), hexadecane (95 wt%, Alfa Asar, Karlsruhe, Germany, reference number 43283), eugenol (>99 wt%, Sigma Aldrich, St. Louis, MO, USA, reference number E51791), propylbenzene (98 wt%, Sigma Aldrich, St. Louis, MO, USA, reference number P52407), 4-propylanisole (>98 wt%, Sigma Aldrich, St. Louis, MO, USA, reference number W293008), 2-methoxy-4-propylphenol (>99 wt%, Sigma Aldrich, St. Louis, MO, USA, reference number W359807), 4-propylphenol (>97 wt%, Sigma Aldrich, St. Louis, MO, USA, reference number W364908), 4-propylcyclohexanol (>98 wt%, Tokyo Chemical Industry co. LTD, Tokyo, Japan, reference number P1874), 2-methoxy-4-propylcyclohexanol (>90 wt%, BOC Sciences, NY, USA, reference number 23950-98-3), 4-propylcyclohexanone (>99 wt% , Sigma Aldrich, St. Louis, MO, USA, reference number 82160), propylcyclohexane (>98 wt%, Tokyo Chemical Industry co. LTD, Tokyo, Japan, reference number P0681), hydrogen (5.0, Messer, Bad Soden am Taunus, Germany), NH_3 (5 vol% in He, Linde, Pullach, Germany), helium (5.0, Messer, Bad Soden am Taunus, Germany), nitrogen (5.0, Messer, Bad Soden am Taunus, Germany), oxygen (5 vol% in He, Linde, Pullach, Germany), and carbon monoxide (5 vol% CO in He, Linde, Pullach, Germany. Iron (III) sulphate hydrate (puriss., Sigma-Aldrich, St. Louis, MO, USA, reference number 12357), iron (II) sulfate heptahydrate (98%, Alfa-Aesar, Karlsruhe, Germany, reference number A15178), ammonium hydroxide (25% solution J.T. Baker, Avantor, Corporate Parkway Center Valley, PA, USA, reference number 10700312), citric acid monohydrate (99-102%, Alfa-Aesar, Karlsruhe, Germany, reference number 36665), acetone (HPLC, J.T. Baker, Avantor, Corporate Parkway Center Valley, PA, USA, reference number 9002-02), D-(+)-glucose (99%, Alfa-Aesar, Karlsruhe, Germany, reference number A16828), ruthenium (III) 2,4-pentadionate (97%, Sigma-Aldrich, St. Louis, MO, USA, reference number 282766), 2-propanol (HPLC, J.T. Baker, Avantor, Corporate Parkway Center Valley, PA, USA, reference number 9095-02) were used as received.

4.2. Catalysts characterization

Size distribution functions for Ru nanoparticles were obtained by measuring Ru nanoparticles on the TEM image using Gatan Digital Micrograph. Prior to the nitrogen adsorption/desorption measurements, samples were degassed over night at 120 °C in vacuum. 100-points isotherms were

recorded with the equilibration time of 60 s. The surface area was calculated with the Brunauer–Emmett–Teller (BET) equation using the nitrogen adsorption data in the p/p_0 range between 0.05 and 0.3 (7-point analysis) and the pore volume was extracted from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method. Previously reduced samples in the flow of 5 vol% H_2 in Ar at 600 °C (the temperature ramp 5 K min^{-1}) were purged by 5 vol% CO in He (50 mL min^{-1}) with simultaneous heating up to 150 °C by the rate of 10 K min^{-1}. After 30 min at 150 °C, the samples were cooled down to 40 °C and subsequently flushed with pure He (50 mL min^{-1}) until the baseline was stable. Thereafter the samples were heated up (with the rate of 10 K min^{-1}) to 900 °C, kept at this temperature for 10 min and subsequently cooled-down to the room temperature. In the case of NH_3-TPD, the reduced samples were flushed by 10 vol% of NH_3 in He for 1 h. Then the gas flow was switched to pure He in which the samples were heated up to 700 °C with the temperature ramp of 5 K min^{-1} and kept for 10 min at this temperature. The samples were cooled to the room temperature afterwards.

References

[1] A. Bjelić, M. Grilc, B. Likozar, Chemical Engineering Journal 333 (2018) 240-259.

Table S1. Nomenclature: Latin letters

Notation	Expression	Unit
A_g	Gas–liquid interfacial surface	m^2
A_s	Solid–liquid interfacial area	m^2
c_{AS}	Concentration of active sites	mol m^{-3}
c_H	Concentration of hydrogen	mol m^{-3}
c_{RC}	Concentration of any component *RC*	mol m^{-3}
c_{RC}^{calc}	Calculated concentrations of component *RC* in the m^{th} experiment	mol m^{-3}
c_{RC}^{exp}	Experimental concentrations of component *RC* in the m^{th} experiment	mol m^{-3}
$Ea_{RC\text{-}i}^{cat}$	Activation energies of catalysed reaction	J mol^{-1}
He	Henry's constant	Pa m^3mol^{-1}
k_{RC}^{ads}	Adsorption rate constant of component *RC*	m^3mol^{-1} min^{-1}
k_H^{ads}	Adsorption rate constant of hydrogen	m^3mol^{-1} min^{-1}
k_{RC}^{des}	Desorption rate constant of component *RC*	min^{-1}
k_H^{des}	Desorption rate constant of hydrogen	min^{-1}
k_{RC-i}^{cat}	Catalysed reaction rate constant	m^3mol^{-1} min^{-1}
$k_{RC\text{-}i}^{hom}$	Homogeneous reaction rate constant	m^3mol^{-1} min^{-1}
k_l	Gas–liquid mass transfer constant	m min^{-1}
k_s	Liquid–solid mass transfer constant	m min^{-1}
m_{cat}	Mass of the catalyst	Kg
m_r	Mass of the reactant	Kg
m_s	Mass of the solvent	Kg
N	The number of hydrogen atoms consumed in the catalytic reaction	/
p_H	Hydrogen pressure	Pa
PR	Final product	/
R	Universal gas constant	J mol^{-1} K
$r_H^{g\text{-}l}$	Mass transfer rate for hydrogen through the film around the bubbles	mol min^{-1}
$r_{RC}^{l\text{-}s}$	Mass transfer rate for component *RC* through the film around the catalyst particles	mol min^{-1}
r_i^{cat}	Rate of catalytic reaction	mol m^{-3} min^{-1}
r_i^{hom}	Rate of homogeneous reaction	mol m^{-3} min^{-1}
r_{RC}^{ads}	Rate of component *RC* adsorption	mol m^{-3} min^{-1}
r_{RC}^{des}	Rate of component *RC* desorption	mol m^{-3} min^{-1}
T	Time	Min
T	Temperature	K
V_l	Volume of the liquid phase	m^3

Table S2. Nomenclature: Sub/superscripts

Notation	Expression
Ads	Adsorption/adsorbed
AS	Active sites
Calc	Calculated
Cat	Catalytic (reaction)
Des	Desorption/desorbed
Exp	Experimental
G	Gas phase
H	Hydrogen
Hom	Homogeneous (reaction)
I	Reaction
J	The total number of components
L	Liquid phase
RC	Reacting component
S	Solid phase (on the catalyst surface but still not adsorbed)

Table S3. Nomenclature: Abbreviations

1. Abbreviations of components (principle of giving abbreviated names)	
A	Ally group
B	Benzene
C	Cyclohexane
CP	Cyclopentane
H	Hydroxyl group
I	Iso (for isoeugenol)
K	Keto group
M	Methoxy group
Me	Methyl group
P	Propyl group
An example	HMPC (1-hydroxy-2-methoxy-4-propylcyclohexane (2-methoxy-4-propylcyclohexaonol))
2. Principle of reaction rate constants and activation energies labelling	
$k_{\mathrm{RC-i}}^{\mathrm{cat}}$	– *RC* represents a reacting component (for labelling see section 2 of the Table 8)
$E\mathrm{a}_{\mathrm{RC\text{-}i}}^{\mathrm{cat}}$	–i represents a reaction
I	
–A	Allyl group hydrogenation
–B	Benzene ring hydrogenation
–C	Ring opening-closing (ring contraction)
–H	Hydroxyl group removal
–HMe	Removal of $–CH_2OH$ group
–IA	Allyl group isomerization
–M	Methoxy group removal
–MH	Substitution of methoxy by hydroxyl group
An example	$k_{\mathrm{HMPC\text{-}M}}^{\mathrm{cat}}$ – rate constant of methoxy group removal from HMPC component