Supporting Information

Selective and Controllable Purification of Monomeric Lignin Model Compounds via Aqueous Phase Reforming

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Contents

1 Determination of MeOH Amounts

$$m_{\mathrm{MeOH}} = \frac{n_{\mathrm{MeO}}}{3} \frac{\mathrm{M}_{\mathrm{MeOH}}}{\mathrm{M}_{\mathrm{Aromatic}}} m_{\mathrm{Aromatic}}$$

$$m_{\mathrm{MeOH}} = n_{\mathrm{MeOH}} \mathrm{M}_{\mathrm{MeOH}}$$
$$n_{\mathrm{MeOH}} = \frac{1}{3} n_{\mathrm{Guaiacol}}$$
$$n_{\mathrm{Guaiacol}} = \frac{m_{\mathrm{Guaiacol}}}{\mathrm{M}_{\mathrm{Guaiacol}}}$$

2 Reaction Network

2.1 Reaction Progressions

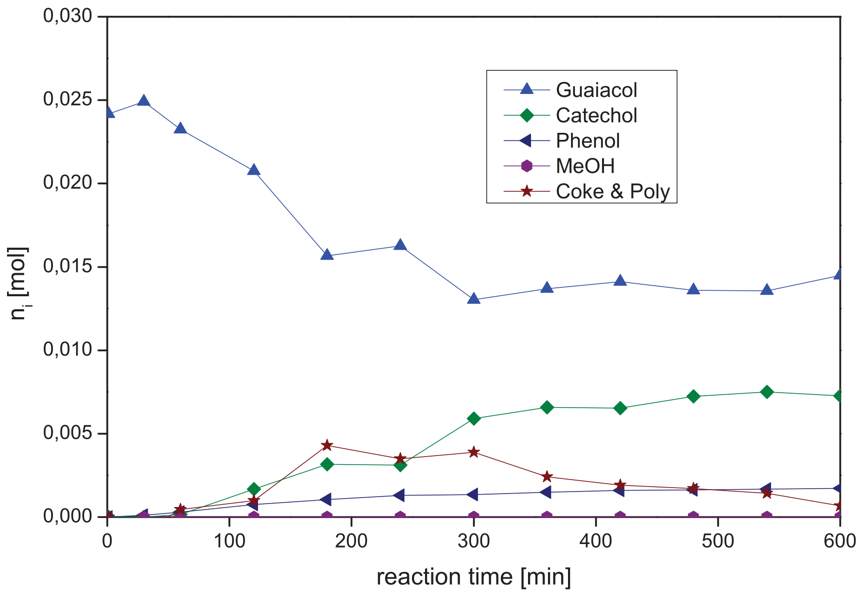

Figure S.1: Compounds' amounts of the reaction guaiacol in water at 245 °C with Pt/γ-Al_2O_3

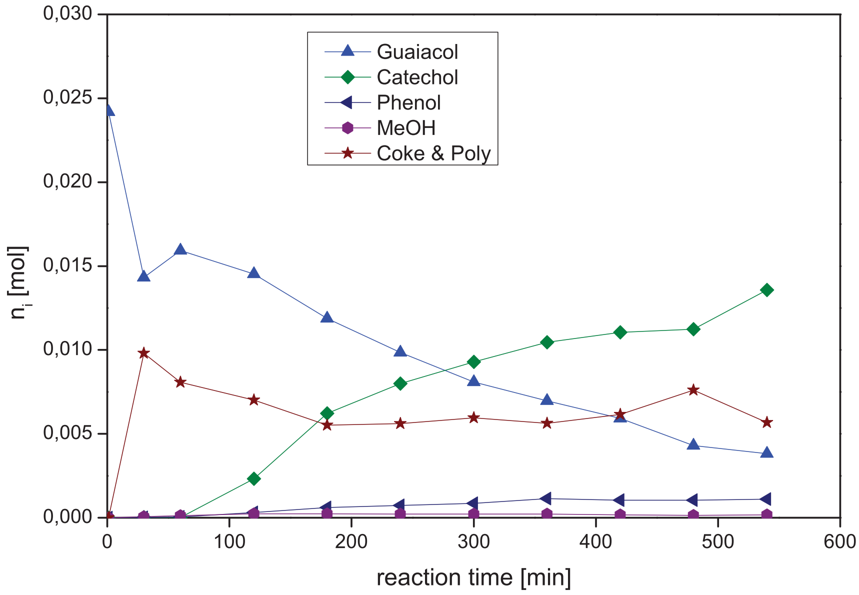

Figure S.2: Compounds' amounts of the reaction guaiacol in water at 245 °C with Pt/C

2.2 Monitored Compounds

1 Syringol

2 1,2-Benzenediol,3-Methoxy (1,2-BD,3-MeO) (+ isomers)

3 1,2,3-Trihydroxybenzene (1,2,3-THB) (+ isomers)

4 Guaiacol

5 Catechol

6 Phenol

7 H_2

8 CH_4

9 CO_2

10 Coke & Poly

11 Methanol

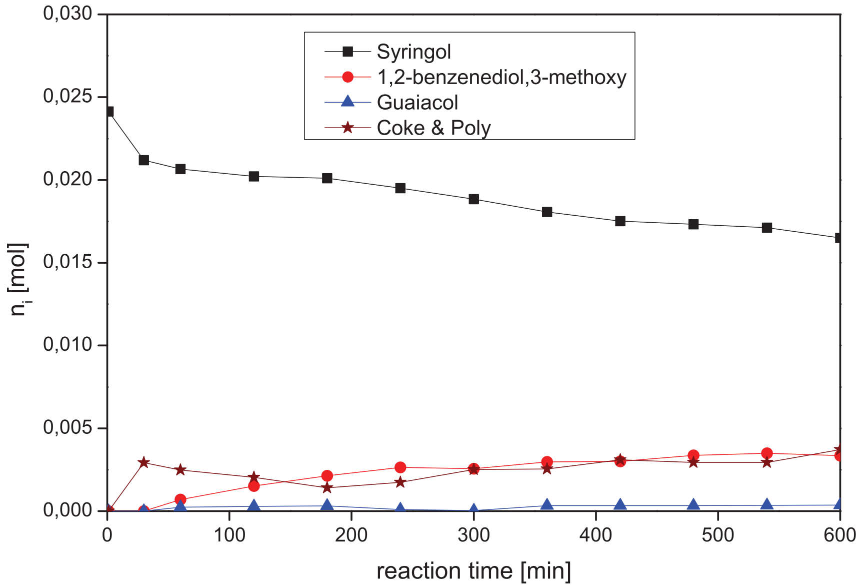

Figure S.3: Compounds' amounts of the reaction syringol in water at 245 °C with Pt/ZrO_2

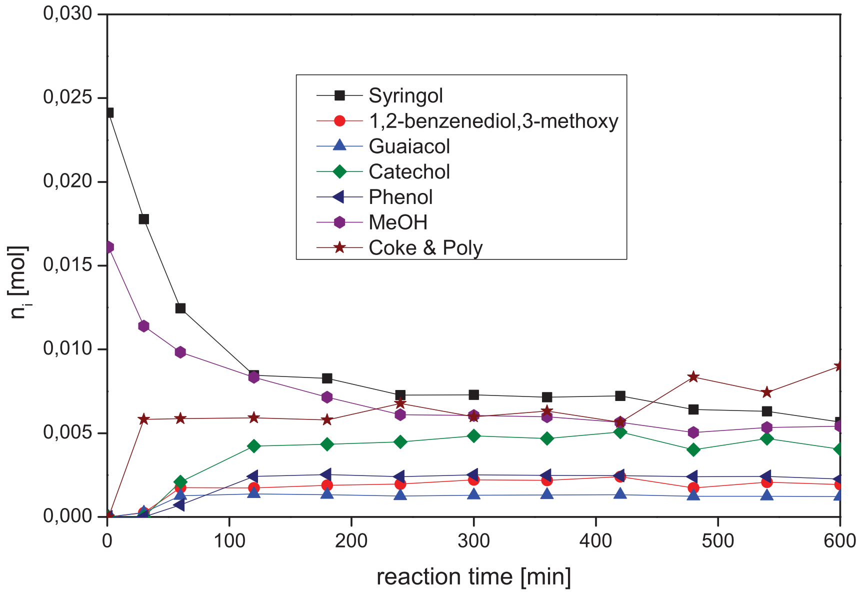

Figure S.4: Compounds' amounts of the reaction syringol and MeOH in water at 245 °C with Pt/ZrO_2

2.3 Reaction Network

2.3.1 Specific Reactions

$$\text{Syringol} + H_2O \xrightarrow{r_1} \text{1,2-BD,3-MeO} + \text{MeOH} \tag{1}$$

$$\text{Syringol} + H_2 \xrightarrow{r_2} \text{1,2-BD,3-MeO} + CH_4 \tag{2}$$

$$\text{Syringol} + H_2 \xrightarrow{r_3} \text{Guaiacol} + \text{MeOH} \tag{3}$$

$$\text{1,2-BD,3-MeO} + H_2O \xrightarrow{r_4} \text{1,2,3-THB} + \text{MeOH} \tag{4}$$

$$\text{1,2-BD,3-MeO} + H_2 \xrightarrow{r_5} \text{Guaiacol} + H_2O \tag{5}$$

$$\text{1,2-BD,3-MeO} + H_2 \xrightarrow{r_6} \text{Catechol} + \text{MeOH} \tag{6}$$

$$\text{1,2,3-THB} + H_2 \xrightarrow{r_7} \text{Catechol} + H_2O \tag{7}$$

$$\text{Guaiacol} + H_2O \xrightarrow{r_8} \text{Catechol} + \text{MeOH} \tag{8}$$

$$\text{Guaiacol} + H_2 \xrightarrow{r_9} \text{Catechol} + CH_4 \tag{9}$$

$$\text{Guaiacol} + H_2 \xrightarrow{r_{10}} \text{Phenol} + \text{MeOH} \tag{10}$$

$$\text{Guaiacol} \xrightarrow{r_{11}} \text{Coke \& Poly} + CO_2 \tag{11}$$

$$\text{MeOH} + H_2O \xrightarrow{r_{12}} 3H_2 + CO_2 \tag{12}$$

$$\text{Catechol} + H_2 \xrightarrow{r_{13}} \text{Phenol} + H_2O \tag{13}$$

$$\text{Catechol} \xrightarrow{r_{14}} \text{Coke \& Poly} \tag{14}$$

$$\text{Phenol} \xrightarrow{r_{15}} \text{Coke \& Poly} \tag{15}$$

2.4 Coking Parameters

$$\boldsymbol{k}_{\text{eff.}} = \boldsymbol{k}a \tag{16}$$

$$a = \left(1 - \frac{n_{\text{Coke \& Poly}}}{n_{\text{Coke \& Poly, max}}}\right) \tag{17}$$

Where $\boldsymbol{k}$ is the vector of all reaction rates. The value of $n_{\text{Coke \& Poly, max}}$ is determined by taking the arithmetic average of the measured values of Coke & Poly when the distribution of the compounds did not change in any significant way.

2.5 Reaction Rates

$$
\begin{aligned}
r_1 &= k_1\ n_{\text{Syringol}} \\
r_2 &= k_2\ n_{\text{Syringol}}\ n_{\text{H}_2} \\
r_3 &= k_3\ n_{\text{Syringol}}\ n_{\text{H}_2} \\
r_4 &= k_4\ n_{\text{1,2-BD,3-MeO}} \\
r_5 &= k_5\ n_{\text{1,2-BD,3-MeO}}\ n_{\text{H}_2} \\
r_6 &= k_6\ n_{\text{1,2-BD,3-MeO}}\ n_{\text{H}_2} \\
r_7 &= k_7\ n_{\text{1,2,3-THB}} \\
r_8 &= k_8\ n_{\text{Guaiacol}} \\
r_9 &= k_9\ n_{\text{Guaiacol}}\ n_{\text{H}_2} \\
r_{10} &= k_{10}\ n_{\text{Guaiacol}}\ n_{\text{H}_2} \\
r_{11} &= k_{11}\ n_{\text{Guaiacol}} \\
r_{12} &= k_{12}\ n_{\text{MeOH}} \\
r_{13} &= k_{13}\ n_{\text{Catechol}}\ n_{\text{H}_2} \\
r_{14} &= k_{14}\ n_{\text{Catechol}} \\
r_{15} &= k_{15}\ n_{\text{Phenol}}
\end{aligned}
$$

2.6 Set of Differential Equations for the Guaiacol-Network

$$\frac{d}{dt} n_{\text{Guaiacol}} = -r_8 - r_9 - r_{10} - r_{11} \tag{18}$$

$$\frac{d}{dt} n_{\text{Catechol}} = r_8 + r_9 - r_{13} - r_{14} \tag{19}$$

$$\frac{d}{dt} n_{\text{Phenol}} = r_{10} + r_{14} - r_{15} \tag{20}$$

$$\frac{d}{dt} n_{\text{MeOH}} = r_8 + r_{10} - r_{12} \tag{21}$$

$$\frac{d}{dt} n_{\text{H}_2} = 3\ r_{12} - r_9 - r_{10} - r_{13} \tag{22}$$

$$\frac{d}{dt} n_{\text{CH}_4} = r_9 \tag{23}$$

$$\frac{d}{dt} n_{\text{CO}_2} = r_{11} + r_{12} \tag{24}$$

$$\frac{d}{dt} n_{\text{Coke \& Poly}} = r_{11} + r_{14} + r_{15} \tag{25}$$

2.7 Reaction Network (Structural Formula)

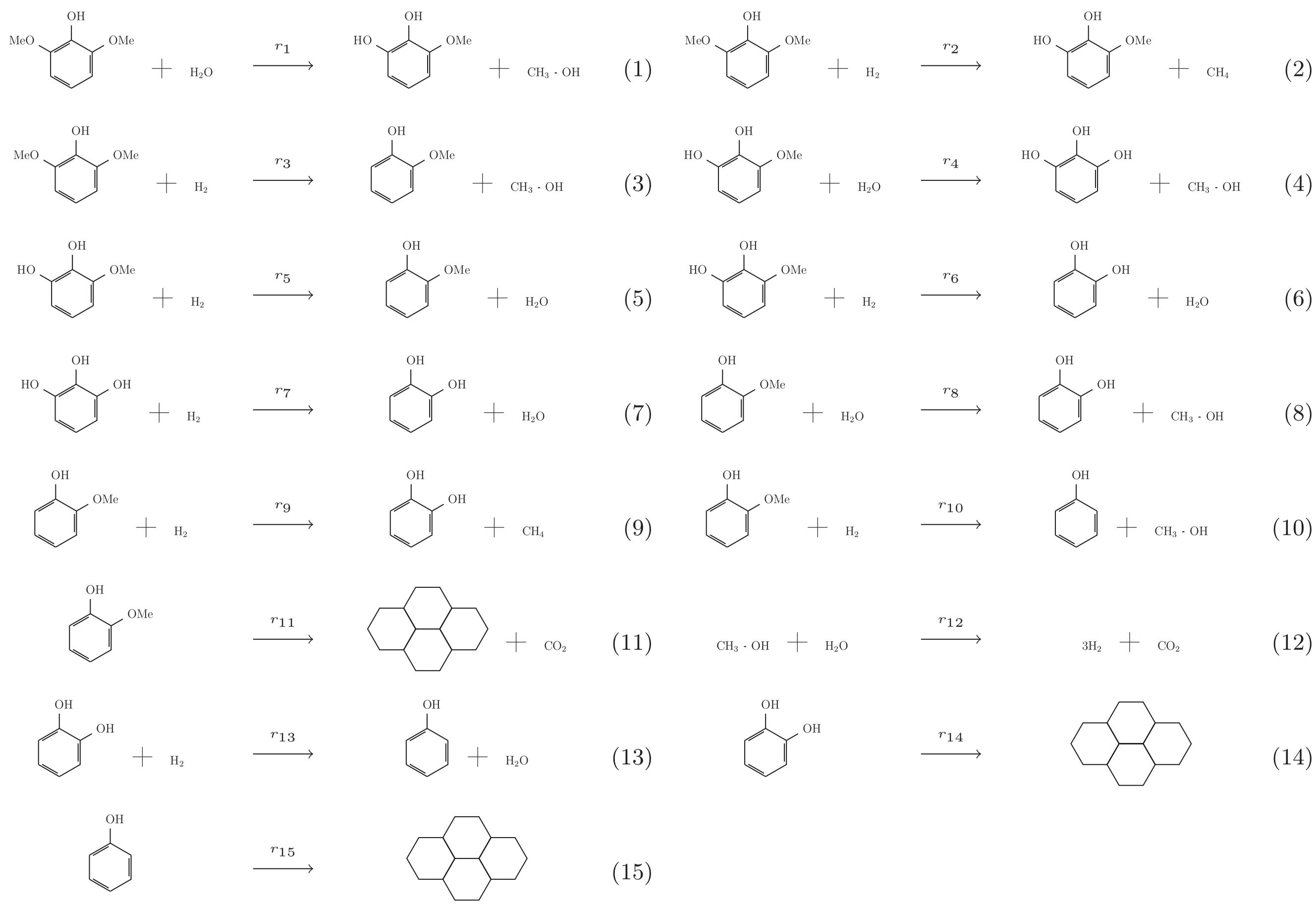

Figure S.5: Reaction network of syringol under hydrothermal conditions at 245 °C and usage of a supported Pt-catalyst.

3 Catalyst Analysis

3.1 XRD

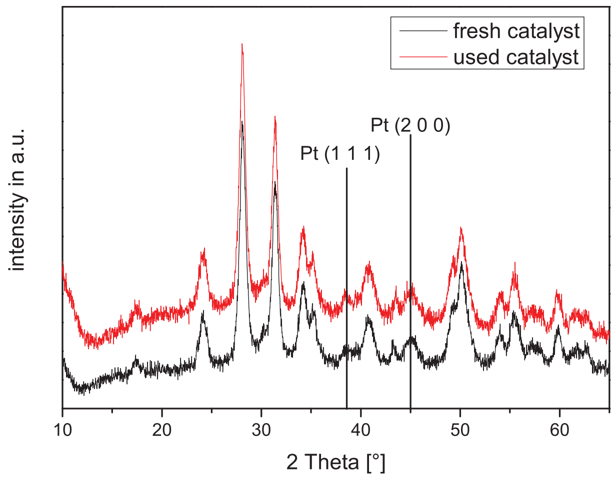

Figure S.6: XRD of the fresh and the used Pt/ZrO_2 catalyst. The catalyst has been used for 10 h under 245 °C in liquid water. The zirconia peaks between $2\,\Theta = 10° - 65°$ show no changes. The Pt (1 1 1) and (2 0 0) peaks on zirconia are indicated.

3.2 SEM Pictures

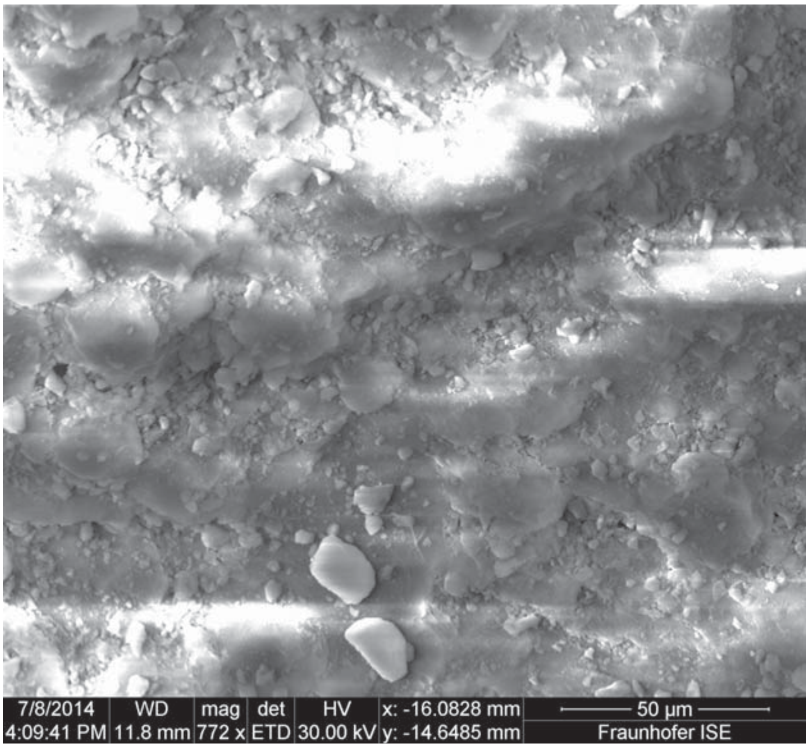

Figure S.7: SEM picture of the fresh γ-Al_2O_3 catalyst. A fractured surface with larger coherent areas. The brighter parts of the picture appear due to charges accumulating on the non-conductive material.

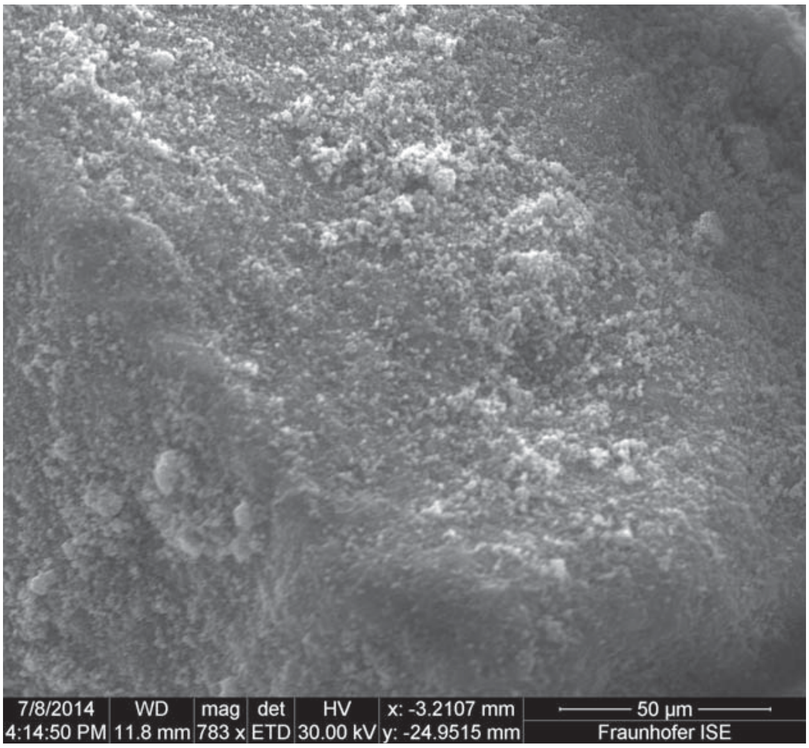

Figure S.8: SEM picture of the fresh TiO_2 catalyst. A fractured surface with very small coherent areas.