Description of the Kinetic Model

To determine the activity of the catalysts on a quantitative basis, a kinetic model was developed. In the following, this model is presented in detail.

Figure S1 shows the time-dependency for the reaction of phenol over a Ni-V$_2$O$_5$/SiO$_2$ catalyst at 250 °C and 100 bar. In the initial part of the experiment phenol converts to primarily cyclohexanol, which reached a maximum in the yield at approximately 3.5 h of reaction. The cyclohexane yield, on the other hand, increased continuously throughout the experiment, and with an increasing rate toward the end.
Figure S1: Conversion of phenol (X) and yields of cyclohexanone, cyclohexanol, and cyclohexane as a function of time over a Ni-V$_2$O$_5$/SiO$_2$ catalyst. The experiments were made with 1 g of catalyst in 50 g phenol. $T=250^\circ$C, $P=100$ bar.

The data in Figure S1 indicate a reaction mechanism in which hydrogenation of the aromatic ring occurs as a first step followed by deoxygenation, with cyclohexanol as the intermediate product and cyclohexane as the final product. Also, cyclohexanone and cyclohexene were observed in small amounts. The cyclohexanone yield reached a maximum of 1.7% after 1 h and then steadily decreases (cf. Figure S1). The cyclohexene yield was even less and on the order of 0.01%.

In the review by Shuikin and Erivanskaya$^1$ it is proposed that hydrogenation of phenol over Ni catalysts produces cyclohexanone as the primary product; however, the subsequent hydrogenation of cyclohexanone to cyclohexanol proceeds at a much higher rate, and therefore, cyclohexanone is seen in only low yields. Similarly, cyclohexene is formed through dehydration of cyclohexanol followed by quick hydrogenation to cyclohexane. Overall, the observations suggest the reaction scheme shown in Figure S2 (solid and not dashed arrows). This scheme has been proposed previously by other researchers for HDO of phenol over Pd/C,$^2,3$ Pt/C,$^4$ Ni/HZSM-5,$^5$ and Ni-MoS$_2$/Al$_2$O$_3$,$^6$ and thus appears to be generally accepted for low temperature hydrodeoxygenation.
The individual steps of Figure S2 were investigated in separate experiments to quantify the relative rates in one example with a Ni/ZrO$_2$ catalyst. Initially a 15 min short term isothermal experiment (see Section of Catalyst Testing for further details) was performed with 50 g of phenol, giving a phenol conversion of 26%. Cyclohexanone was loaded in the reactor in another short term isothermal experiment and over 4 min of reaction a conversion of 44% was observed. Cyclohexanol dehydration was quantified from the standard 5 h experiment where 99.8% conversion of phenol and a yield of 83% cyclohexane was found. Hydrogenation of cyclohexene was quantified from a 5 min short term isothermal experiment with cyclohexene, giving a conversion of 98.7%. Table S1 summarizes first order rate constants and turn over frequencies for the respective reactions from these experiments. This analysis revealed that the rates of hydrogenation of cyclohexanone and cyclohexene were significantly higher than the hydrogenation of phenol and dehydration of cyclohexanol.

**Table S1:** Experimental data for quantifying individual reaction steps in Figure S2 over a 5 wt%Ni/ZrO$_2$ catalyst. Turn over frequency (TOF) is calculated from a nickel crystallite size of 7 nm, a dispersion of 0.20 and normalized to a standard concentration of 1 mol/l as recommended by Kozuch and Martin.$^7$ The experiments were made with 1 g of catalyst and 50 g of feed. T=275 °C, P=100 bar.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$1^{st}$ order k [ml/(kg$_{cat}$ min)]</th>
<th>TOF [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol hydrogenation</td>
<td>1010</td>
<td>0.10</td>
</tr>
<tr>
<td>Cyclohexanone hydrogenation</td>
<td>7200</td>
<td>0.69</td>
</tr>
<tr>
<td>Cyclohexanol dehydration</td>
<td>330</td>
<td>0.03</td>
</tr>
<tr>
<td>Cyclohexene hydrogenation</td>
<td>43140</td>
<td>&gt;4.1</td>
</tr>
</tbody>
</table>

Because the rate of hydrogenation of both cyclohexanone and cyclohexene are relative fast
reactions and the yields of these compounds are low, the effective reaction scheme can be described through the dotted arrows in Figure S2, which gives the two following main reactions:

Reaction 1: \[ \text{Phenol} + 3\text{H}_2 \rightarrow \text{Cyclohexanol} \]

Reaction 2: \[ \text{Cyclohexanol} + \text{H}_2 \rightarrow \text{Cyclohexane} + \text{H}_2\text{O} \]

Assuming first order dependency of the hydrocarbon compounds leads to the following rate expressions:

\[ r_1 = k_1 \cdot C_{\text{Phenol}} \cdot P_{\text{H}_2}^n \]  \hspace{1cm} (S1)

\[ r_2 = k_2 \cdot C_{\text{C-hexanol}} \cdot P_{\text{H}_2}^m \]  \hspace{1cm} (S2)

Here \( r_i \) is the rate of reaction \( i \), \( k_i \) is the rate constant of reaction \( i \), \( C_i \) is the concentration of either phenol or cyclohexanol, and \( n \) and \( m \) are the reaction order of hydrogen in respectively reaction 1 and 2. The assumption of first order kinetics with respect to the hydrocarbons is made in the lack of a better estimate.

As all the experiments were performed with the same and constant pressure of hydrogen, the hydrogen pressure can in the current case be included in the rate constant and thereby give the following lumped rate expressions:

\[ r_1 = k'_1 \cdot C_{\text{Phenol}} \]  \hspace{1cm} (S3)

\[ r_2 = k'_2 \cdot C_{\text{C-hexanol}} \]  \hspace{1cm} (S4)

Here \( k'_1 \) is the rate constant for the hydrogenation reaction and \( k'_2 \) is the rate constant for the deoxygenation reaction. By defining \( X_1 \) as the degree of conversion in reaction 1 relative to the initial phenol concentration and \( X_2 \) as the degree of conversion in reaction 2 relative to the initial phenol concentration a stoichiometric table can be set up as shown in Table S2.

Using the expressions for the molar amounts of phenol and cyclohexanol established in Table S4.
Table S2: Stoichiometric table for effective reaction scheme shown in Figure S2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phenol</th>
<th>Cyclohexanol</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>(N_{0,\text{Phenol}})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>(-N_{0,\text{Phenol}} \cdot X_1)</td>
<td>(N_{0,\text{Phenol}} \cdot X_1 - N_{0,\text{Phenol}} \cdot X_2)</td>
<td>(N_{0,\text{Phenol}} \cdot X_2)</td>
</tr>
<tr>
<td>Out</td>
<td>(N_{0,\text{Phenol}} \cdot (1 - X_1))</td>
<td>(N_{0,\text{Phenol}} \cdot (X_1 - X_2))</td>
<td>(N_{0,\text{Phenol}} \cdot X_2)</td>
</tr>
</tbody>
</table>

S2, the concentrations can be found as:

\[
C_{\text{Phenol}} = C_{0,\text{Phenol}} \cdot (1 - X_1) \quad (S5)
\]

\[
C_{C\text{-hexanol}} = C_{0,\text{Phenol}} \cdot (X_1 - X_2) \quad (S6)
\]

Here \(C_{0,\text{Phenol}}\) is the initial concentration of phenol.

The reaction takes place in a batch reactor, for which the mole balances are:

\[
\frac{dX_1}{dt} = k'_1 \cdot (1 - X_1) \cdot \frac{W}{V} \quad (S7)
\]

\[
\frac{dX_2}{dt} = k'_2 \cdot (X_1 - X_2) \cdot \frac{W}{V} \quad (S8)
\]

Here \(W\) is the mass of catalyst and \(V\) is the volume of liquid in the reactor, which were assumed constant in the derivation and equal to the initial values. On this basis, the algebraic solution to Eq. S7 and S8 is:

\[
X_1 = 1 - \exp\left(-k'_1 \cdot \frac{W}{V} \cdot t\right) \quad (S9)
\]

\[
X_2 = 1 - \frac{k'_1 \cdot \exp\left(-k'_2 \cdot \frac{W}{V} \cdot t\right) - k'_2 \cdot \exp\left(-k'_1 \cdot \frac{W}{V} \cdot t\right)}{k'_1 - k'_2} \quad (S10)
\]

\(X_1\) is identical to the conversion of phenol and from Table S2 it can be seen that \(X_2\) is equivalent to the yield of cyclohexane.

The assumption of constant volume induces an uncertainty in the calculations since the liquid volume expands as phenol is converted into cyclohexanol/cyclohexane and water is evolved, while
on the other hand some of the liquid evaporates into the gas phase. Based on stoichiometry and the specific volumes of the pure compounds, the liquid volume can be estimated to increase by 18% when phenol is completely converted to cyclohexanol and by 43% when phenol is completely converted to cyclohexane and water. Thus, the liquid volume can be described as:

\[
V = V_0 \cdot (1 + 0.18 \cdot (X_1 - X_2) + 0.43 \cdot X_2)
\]  
(S11)

This does not take evaporation into account. By substituting this expression into Eq. S5-S8 the equation system can be solved numerically. On average this increased the values of \(k'_1\) and \(k'_2\) in the order of 5%.

However, through a flash calculation using Specs v. 5.62 using the Soave-Redlich-Kwong equation of state combined with the association equation of state (CPA model\(^9,10\)), the equilibrium between the gas phase and the liquid phase at 275 °C and 100 bar was calculated for a mixture of 45 mole% \(\text{H}_2\), 22 mole% phenol, and 11 mole% of cyclohexane, cyclohexanol, and water (corresponding to a case with \(X_1 = 50\%\) and \(X_2 = 25\%\) in the current setup). This showed that 45% of the phenol, 45% of the cyclohexanol, 60% of the cyclohexane, and 90% of the water was in the gas phase at the specified conditions. Overall, the two phenomena induce changes in the liquid volume during the reaction, but with opposite effect. The low degree of change observed when using the expanding volume in Eq. S11 in the model indicates that the effect of the changing volume is limited and therefore the assumption of constant volume does not appear to cause a marked error. Thus, for all calculations of the kinetic parameters, the algebraic expressions of Eq. S9 and S10 have been used.

Finally the kinetic model was fitted to the data of Figure S1, as shown in Figure S3. The dotted lines indicate the fit of the kinetic model to the experimental data. Generally the calculated values of \(X_1\) and \(X_2\) were within ±6% and ±2%, respectively, of the experimental data which is acceptable considering the simplicity of the model and the incorporated assumptions. The good correlation between model and experiments further supports the validity of the implemented assumptions.
**Figure S3:** Fit of the kinetic model to the experimental data from a test with Ni-V$_2$O$_5$/SiO$_2$. The experiments were made with 1 g of catalyst in 50 g phenol. $T=250\, ^\circ\text{C}$, $P=100\, \text{bar}$.

**References**


