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<tr>
<td>Citation</td>
<td>Applied Catalysis B-environment, 232, 299-305</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2018-09-15</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/79275">http://hdl.handle.net/2115/79275</a></td>
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<td>Supplementary_information.pdf (Supplementary information)</td>
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Reverse Water Gas Shift Reaction Using Supported Ionic Liquid Catalysts

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Estimation of equilibrium of water gas shift reaction (WGSR)

WGSR is written as

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]

Therefore, change in Gibbs free energy at \( t \) (\( \Delta G^t \)) can be written as

\[ \Delta G^t = \Delta H^t - t\Delta S^t \]

where \( \Delta H^t \) and \( \Delta S^t \) are change in enthalpy and entropy at \( t \), respectively.

By using thermodynamic parameter of each molecule, \( \Delta H^t \) and \( \Delta S^t \) are written as

\[
\Delta H^t = H^t_{\text{CO}_2} + H^t_{\text{H}_2\text{O}} - H^t_{\text{CO}} - H^t_{\text{H}_2} \\
\Delta S^t = S^t_{\text{CO}_2} + S^t_{\text{H}_2\text{O}} - S^t_{\text{CO}} - S^t_{\text{H}_2}
\]

Each thermodynamic parameter can be calculated by using molar heat capacity at constant pressure \( (\overline{C_p}) \)

\[
H^t = H^{298.15} + \int_{298.15}^{t} \overline{C_p} \, dt \\
S^t = S^{298.15} + \int_{298.15}^{t} \frac{1}{t} \overline{C_p} \, dt
\]

Further, \( \overline{C_p} \)'s of each molecule are known to be related to temperature by following empirical equations. (J. Larminie, A. Dicks, Fuel Cell Systems Explained, second Ed., John Wiley & Sons Ltd, West Sussex, England, 2003.)

\[
\begin{align*}
\text{H}_2\text{O (steam)} & \quad \overline{C_p} = 143.05 - 58.040T^{0.25} + 8.2751T^{0.5} - 0.036989T \\
\text{H}_2 & \quad \overline{C_p} = 56.505 - 22222.6T^{-0.75} + 116500T^{-1} - 560700T^{-1.5} \\
\text{CO} & \quad \overline{C_p} = 69.145 - 0.022282T^{0.75} - 2007.7T^{-0.5} + 5589.64T^{-0.75} \\
\text{CO}_2 & \quad \overline{C_p} = -3.7357 + 3.0529T^{0.5} - 0.041034T + 2.4198 \times 10^{-6}T^2
\end{align*}
\]
According to above relationship, thermodynamic parameters at 443.15 (K) (170 °C) can be calculated as

$$
\begin{align*}
\Delta G_{f}^{298.15} \\
\Delta S_{f}^{298.15}
\end{align*}
$$

In this results, $\Delta G_{f}^{443.15}$ can be calculated as $-22.66 \text{ kJ mol}^{-1}$. ($\Delta G_{f}^{443.15}$ for RWGS is 22.66 kJ mol$^{-1}$)

Now, when initial partial pressure of H$_2$ and CO$_2$ are 6 MPa and 2 MPa, respectively, equilibrium constant ($K^t$) can be written as

$$
K^t = \frac{(2 - x)(6 - x)}{x^2}
$$

where $x$ (MPa) is partial pressure of H$_2$O and CO at equilibrium.

Simultaneously, equilibrium constant ($K^t$) is related to $\Delta G_{f}^t$ as follows.

$$
\Delta G_{f}^t = -RT \ln K^t
$$

where $R$ is gas constant. When $t$ and $\Delta G_{f}^t$ are 443.15 K and $-22.66 \text{ kJ mol}^{-1}$, $x$ can be calculated as ca. 0.15 MPa, suggesting that ca. 7.5 % of CO$_2$ will be converted to CO until reaching to equilibrium. Concerning volume of autoclave (40 mL), amount of evolved CO at equilibrium is ca. 2.7 mmol, which is corresponding to TON = 135 in case of SILP-Cl (1.6) (1.0 g of SILP-Cl includes ca. $2.02 \times 10^{-2}$ mmol of Ru.).

<table>
<thead>
<tr>
<th>gases</th>
<th>$H_{298.15}$/J mol$^{-1}$</th>
<th>$H_{443.15}$/J mol$^{-1}$</th>
<th>$S_{298.15}$/J K$^{-1}$ mol$^{-1}$</th>
<th>$S_{443.15}$/J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$(steam)</td>
<td>-241827</td>
<td>-236891</td>
<td>188.83</td>
<td>202.3101</td>
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<tr>
<td>H$_2$</td>
<td>0</td>
<td>4218.305</td>
<td>130.59</td>
<td>142.1127</td>
</tr>
<tr>
<td>CO</td>
<td>-110529</td>
<td>-106294</td>
<td>197.65</td>
<td>209.2213</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>-393522</td>
<td>-387711</td>
<td>213.80</td>
<td>229.6046</td>
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※ $H_{298.15}$ and $S_{298.15}$ are referenced from ref.
DRIFTS of SILP-Cl(1.6) which was heat treated under various gas conditions.

SILP-Cl (1.6) was heat treated at 170 °C under N₂, H₂ or H₂/CO₂ atmosphere and DRIFTS was measured for each sample. The results are shown in Figure S1.

![Graph showing DRIFTS results](image)

Figure S1. The results of DRIFTS measurement of SILP-Cl (1.6). (a) before heat treatment, (b) treated under N₂ (Pₙ₂ = 2 MPa) at 170 °C for 10 h, (c) treated under H₂ (P_H₂ = 6 MPa) at 170 °C for 2 h and (d) treated under CO₂/H₂ (P_CO₂/Pₙ₂ = 2 MPa /6 MPa) at 170 °C for 10 h. Since catalyst is reduced to be Ru metal at high temperature under pure H₂ atmosphere and carbonyl peak in DRFTS becomes small, time of heat treatment was set at 2 h.

Figure S1 clearly shows shift of CO vibration peaks to lower wavenumber after heat treatment. After heat treatment under N₂, CO vibration peaks was shown at 2051 cm⁻¹ and 1981 cm⁻¹ (Figure S1 (b)). These peaks can be assigned to [RuCl₃(CO)₂]⁻. After heat treatment under H₂ atmosphere, additional peaks were found at 2023 cm⁻¹ and 1939 cm⁻¹ (Figure S1 (c)). These peaks can be
assigned to [RuHCl₂(CO)₂]−. Finally, even after heat treatment under CO₂/H₂ mixed gas conditions, peaks are shown at same position to Figure S1 (c) with different intensity.