Supporting information

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

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Therefore, change in Gibbs free energy at *t* (K) (ΔG_f^t) can be written as

$$\Delta G_f^t = \Delta H_f^t - t\Delta S_f^t$$

where ΔH_f^t and ΔS_f^t are change in entalpy and enthropy at *t*, respectively.

By using thermodynamic parameter of each molecule, ΔH_f^t and ΔS_f^t are written as

$$\Delta H_f^t = H_{CO_2}^t + H_{H_2O}^t - H_{CO}^t - H_{H_2}^t$$

$$\Delta S_f^t = S_{CO_2}^t + S_{H_2O}^t - S_{CO}^t - S_{H_2}^t$$

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 enpirical equations. (J. Larminie, A. Dicks, Fuel Cell Systems Explained, second Ed., John Wiley & Sons Ltd, West Sussex, England, 2003.)

H_2O (steam)	$\overline{C_p} = 143.05 - 58.040T^{0.25} + 8.2751T^{0.5} - 0.036989T$
H_2	$\overline{C_p} = 56.505 - 22222.6T^{-0.75} + 116500T^{-1} - 560700T^{-1.5}$
CO	$\overline{C_p} = 69.145 - 0.022282T^{0.75} - 2007.7T^{-0.5} + 5589.64T^{-0.75}$
CO_2	$\overline{C_p} = -3.7357 + 3.0529T^{0.5} - 0.041034T + 2.4198 \times 10^{-6}T^2$

According to above relationship, thermodynamic parameters at 443.15 (K) (170 °C) can be calculated as

gases	$H^{298.15}$ /J mol^{-1}	$H^{443.15}$ /J mol^{-1}	$S^{298.15}$ /J K^{-1} mol^{-1}	$S^{443.15}$ /J K^{-1} mol^{-1}
H_2O(steam)	−241827	−236891	188.83	202.3101
H_2	0	4218.305	130.59	142.1127
CO	−110529	−106294	197.65	209.2213
CO_2	−393522	−387711	213.80	229.6046

※ $H^{298.15}$ and $S^{298.15}$ are referenced from ref.

In this results, $\Delta G_f^{443.15}$ can be calculated as −22.66 kJ mol^{-1}. ($\Delta G_f^{443.15}$ for RWGSR 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_2O and CO at equilibrium.

Simultaneously, equilibrium constant (K^t) is related to ΔG_f^t as follows.

$$\Delta G_f^t = -Rt \ln K^t$$

where R is gas constant. When t and ΔG_f^t are 443.15 K and −22.66 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. 2.02×10^{-2} mmol of Ru.).

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 N_2, H_2 or H_2/CO_2 atmosphere and DRIFTS was measured for each sample. The results are shown in Figure S1.

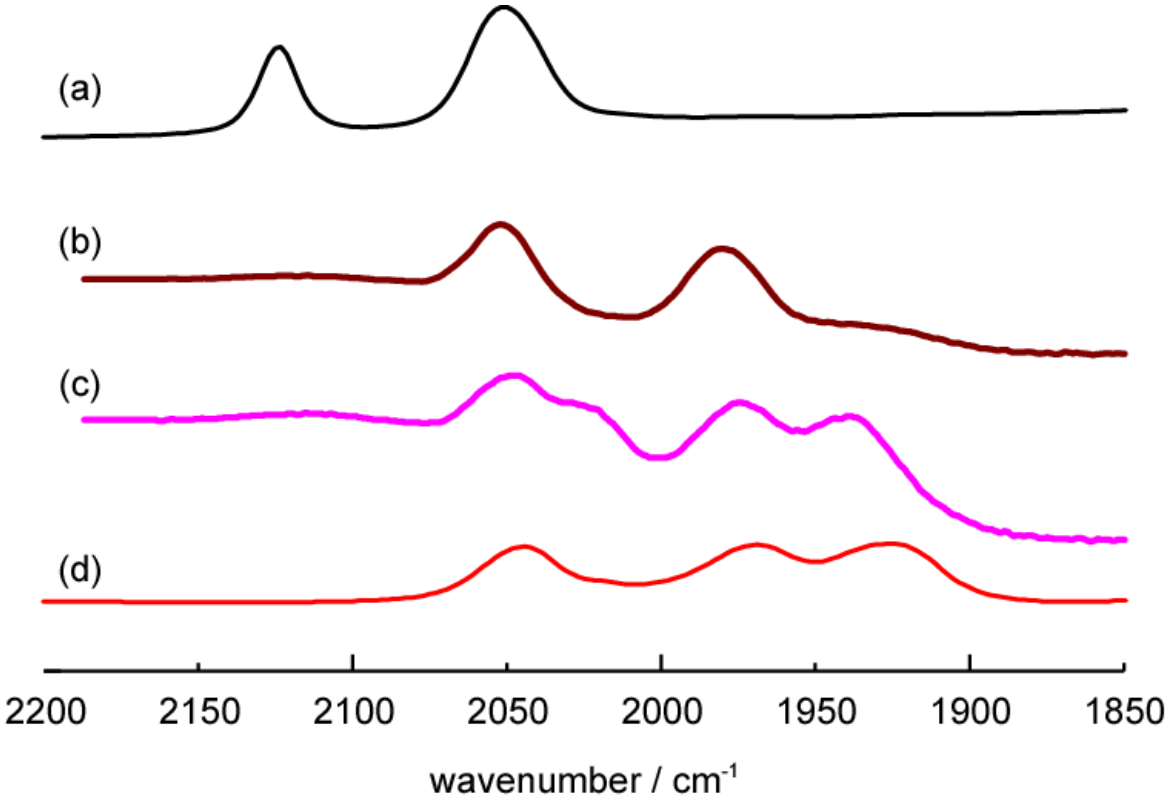

Figure S1. The results of DRIFTS measurement of SILP-Cl (1.6). (a) before heat treatment, (b) treated under N_2 (P_{N2} = 2 MPa) at 170 °C for 10 h, (c) treated under H_2 (P_{H2} = 6 MPa) at 170 °C for 2 h and (d) treated under CO_2/H_2 (P_{CO2}/P_{N2} = 2 MPa /6 MPa) at 170 °C for 10 h. Since catalyst is reduced to be Ru metal at high temperature under pure H_2 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 N_2, CO vibration peaks was shown at 2051 cm^{-1} and 1981 cm^{-1} (Figure S1 (b)). These peaks can be assigned to $[RuCl_3(CO)_2]^-$. After heat treatment under H_2 atmosphere, additional peaks were found at 2023 cm^{-1} and 1939 cm^{-1} (Figure S1 (c)). These peaks can be

assigned to $[RuHCl_2(CO)_2]^-$. Finally, even after heat treatment under CO_2/H_2 mixed gas conditions, peaks are shown at same position to Figure S1 (c) with different intensity.