Supporting information

Chemoselective hydrogenation of 3-nitrostyrene over Pt/FeOx pseudo-single-atom-catalyst in CO$_2$-expanded liquids

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Solubility measurement

The schematic diagram of a volume-variable optical solubility measurement apparatus is illustrated in Fig S1. The apparatus mainly consist of quartz windowed cell with a volume of 31.95 mL which can sustain pressure up to 30 MPa and temperature up to 80 °C, a volume-variable plug piston with volume range from 0 to 1.5 mL, a cold trap, and a high performance liquid chromatography (HPLC) pump. The view cell was heated by a water bath. In a typical experiment, a magnetic stirrer and a designated amount of 3-nitrostyrene was introduced to the cell, and the air in the view cell was replaced by CO$_2$. Then, the view cell was sealed and heated to the designated temperature in the water bath. The temperature and pressure in the cell were measured using a thermocouple with the accuracy of ± 0.1 °C and a pressure transducer (DG1300-BZ-A-2-40) with the accuracy of ± 0.01 MPa, respectively. CO$_2$ was added into the cell very slowly using the HPLC pump till an optical transparent single phase was formed. Subsequently, the pressure in the cell was gradually decreased by controlling the variable-volume piston until the cloud point was reached (Fig. S2). The cloud-point pressure P was recorded. For each condition, the solubility measurement was performed at least three times, and the data of cloud-point pressure at each experimental condition were averaged with the combined expanded uncertainty within ±0.04 MPa (level of confidence = 0.95, where k= 2). The amount of supercritical carbon dioxide used in each run was obtained using the volume of the view cell and the density of the carbon dioxide at the specific pressure and temperature from NIST Chemistry WebBook. The dissolved amount of 3-nitrostyrene in the hydrogenation reactor was estimated using its solubility in scCO$_2$, the volume of reactor and the density of the carbon dioxide at reaction conditions.
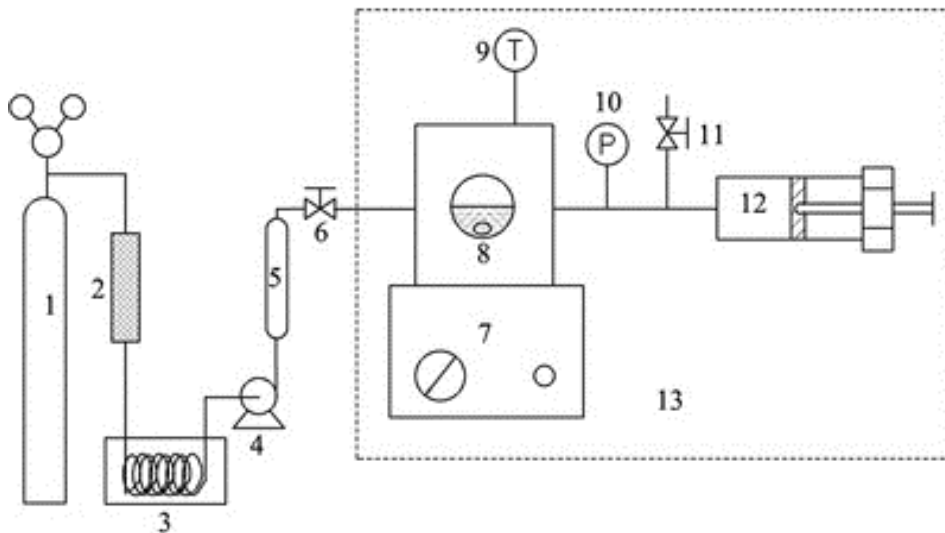
Fig. S1. Apparatus for solubility measurements.

(1) CO_2 cylinder; (2) filter; (3) cooling coil; (4) HPLC pump; (5) surge tank; (6) needle valve; (7) magnetic stirrer; (8) view cell; (9) thermocouple; (10) pressure sensor; (11) vent valve; (12) volume-variable plug piston; (13) water bath.
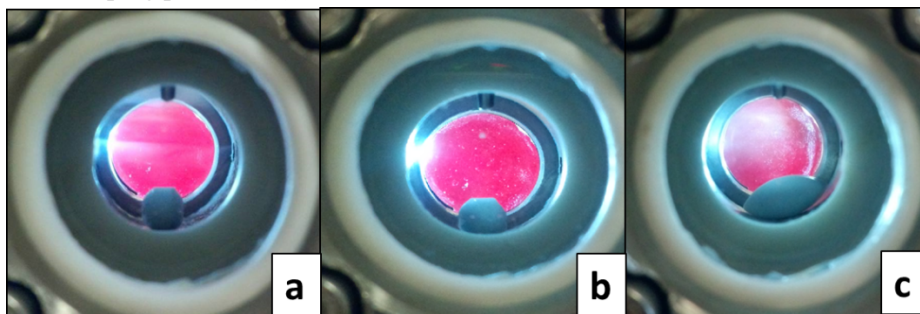

Fig. S2 Phase observation of CO_2-substrate (through the view cell at 40 °C (a) 8.5 MPa (b)10.2 MPa (c) 10 MPa
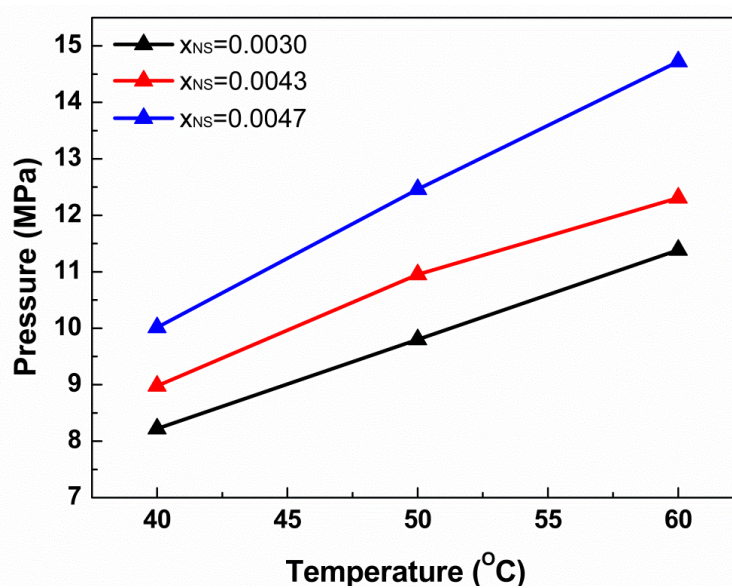

Fig. S3 P−T phase diagram for the system NS+ CO_2 at different concentrations.

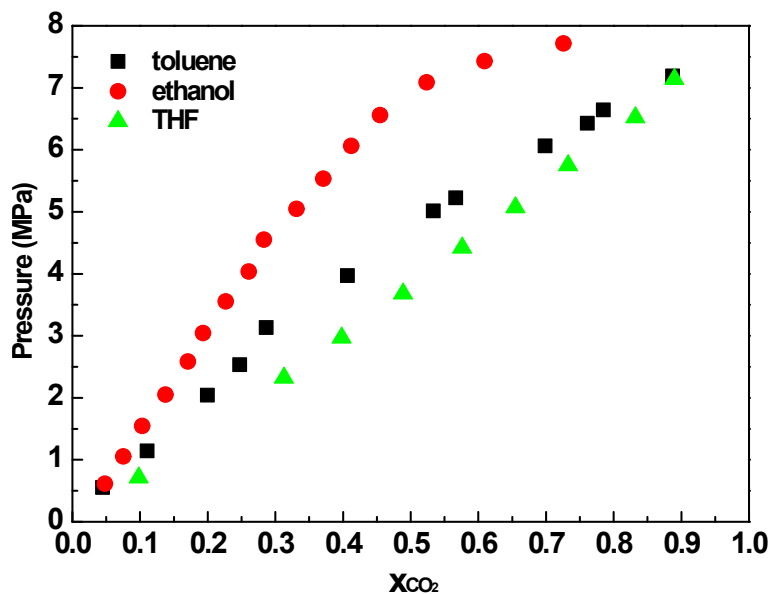# Phase equilibrium of CO_2+toluene, CO_2+ethanol, CO_2+THF at 40 °C

Fig. S4 The molar fraction of CO_2 in different organic solvents at 40 °C and different pressures. The data was taken from literatures [1-3].

Thermodynamic calculation

The VLE data for the ternary systems (toluene, CO_2 and H_2) were simulated at the experimental conditions by using the PR-BM equation of state with van der Waals mixing rules and binary interaction parameters[4, 5]. The critical parameters were obtained from the Aspen library. The Aspen regression was used to calculate the binary interaction parameters by fitting the experimental VLE data in the literature [6-8] for the binary system.

The PR equation of state (EOS) is expressed as:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)}$$

Where

$$b = \sum_i x_i b_i$$

$$a = \sum_i \sum_j x_i x_j \left(\alpha_i \alpha_j \right)^{0.5} \left(1 - k_{ij} \right)$$

$$\alpha_i = 0.45724 \left(\frac{R^2 T_{ci}^{\;2}}{P_{ci}} \right) \alpha \left(T_{ri}, \omega_i \right)$$

$$b_i = 0.0778 \frac{RT_{ci}}{P_{ci}}$$

$$\alpha(T_{ri}, \omega_i) = \exp^2 \left[n_i (1 - T_{ri}^{\;d_i}) \right]$$

$$d_i = 1 + \frac{h_i}{2}$$

$$n_i = 1 - \frac{1}{d_i}$$

$$h_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

The objective function used for fitting is given by eq. 1 with a convergence criterion of less than 10^{-4} for liquid phase compositions. Table S1 summarizes the binary interaction parameters used in the simulation. The simulated VLE data for the $CO_2 + H_2 + C_7H_8$ ternary system at (40 °C) are shown in Table S2. To better understand the effect of CO_2 on the H_2 solubility, the H_2 solubility in CO_2-expanded C_7H_8 is compared with the H_2 solubility in pure C_7H_8. The H_2 solubility enhancement factor (E) [9] is defined as

$$E = \frac{x^{CXL}}{x^{neat\ solvent}}$$

Where x^{CXL} and $x^{neat\ solvent}$ represent the mole fractions of the permanent gas component (H_2) in the CXL and neat solvent, respectively. It is noteworthy that the H_2 solubility in pure solvent is compared to H_2 solubility in CXL solvent at the same temperature and gas phase H_2 fugacity

Table S1. Binary Interaction Parameters kij used in the PR EOS

Compounds	Temperature(°C)	k_{ij}
CO_2-C_7H_8	40	0.101
H_2-C_7H_8	40	0.357
H_2-CO_2	40	0.195

$$AAD\% = \frac{1}{n}\sum_i \left| \frac{x_i^{cal} - x_i^{exp}}{x_i^{exp}} \right| \times 100\% \tag{1}$$

P、T — pressure(MPa), temperature(K); v — molar volume，ml/mol; P_{ci}、T_{ri}、T_{ci}、ω_i — critical pressure, reduced temperature($T_{ri} = T/T_{ci}$), critical temperature and acentric factor of component i; x_i — mole fraction of component i; The mass fraction m_i was calculated from x_i.

The volume expansion of a CO_2-expanded organic solvent is defined[10] as:

$$\Delta V(\%) = \frac{V(P,T,x_1) - V(P^0,\ T)}{V(P^0,\ T)} \times 100\ \%$$

$V(P^0, T)$ is the total volume of a pure organic solvent at the specific temperature and reference pressure (usually at 1 atm). $V(P, T, x_i)$ represents the total volume of a CO_2-expanded organic solvent with the CO_2 mole fraction of x_i.

Table S2 Vapor–liquid equilibrium data for the system $CO_2(1)$ + $H_2(2)$ + toluene(3)

Pressure (MPa)	x_1	x_2	y_1	y_2	x_{neat}	E
6	0.263	0.012	0.534	0.463	0.011	1.09
6.6	0.314	0.013	0.587	0.410	0.011	1.18
7.5	0.391	0.014	0.653	0.343	0.011	1.27
8.5	0.479	0.015	0.712	0.284	0.011	1.36
9	0.525	0.016	0.737	0.258	0.011	1.45
9.5	0.574	0.017	0.761	0.234	0.011	1.55
10	0.626	0.018	0.782	0.212	0.011	1.64
11	0.744	0.024	0.818	0.175	0.012	2.00
12	0.888	0.056	0.852	0.136	0.013	4.31

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