Electronic Supplementary Information

Outstanding catalytic performance of semi-hydrogenation of acetylene under front-end process by establishing “hydrogen deficient” phase

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1. Commercial Front-End and Tail-End Processes

As shown in Fig. S1, for front-end process, the stream flow into the reaction directly, while H₂ is removed first and then added by stoichiometry in front-tail process.
2. Catalyst characterization

X-ray diffraction (XRD) measurements of the catalyst samples were performed using a PANalytical-X'Pert PRO generator with Cu Kα radiation ($\lambda = 0.1541$ nm) that was operated at 60 kV and 55 mA. Diffraction patterns were recorded at a scanning rate of $2\text{min}^{-1}$ with a step angle of $0.02^\circ$.

Fig. S2 XRD patterns of different samples
Fourier transform infrared spectroscopy (FT-IR) characterization was recorded on a Fourier transform infrared spectrophotometer (Nicolet 6700).

![Infrared spectra of Pd-[Bmim][Cl]/Al₂O₃](image)

Fig. S3 Infrared spectra of Pd-[Bmim][Cl]/Al₂O₃

Thermogravimetric analysis (TGA) of Pd-[Prmin][Cl]/Al₂O₃ was conducted using METTLER-TOLEDO TA SDT 2960 between 30 and 600 °C in the mixture gas (5% H₂ and 95% Ar) with a heating rate of 10 °C/min.

![TGA curves of Pd-[Bmim][Cl]/Al₂O₃](image)

Fig. S4 TGA curves of Pd-[Bmim][Cl]/Al₂O₃
BET specific surface areas were measured using N\textsubscript{2} adsorption–desorption isotherms at liquid nitrogen temperature in a Micromeritics ASAP 2000 apparatus for the samples out gassed at 100 °C for 2 h. The BJH method was applied for determining the pore size distribution using the desorption data.

**Transmission electron microscope (TEM)** analysis was conducted to measure the diameter of palladium. However, due to the low loading amount of palladium, the particle of palladium cannot be found after several trials. Under this circumstance, we employ Soxhlet extractor to extract the Pd-IL phase, the set up is shown in Fig. S4. Firstly, the quartz wool was inserted in the pipe and 8 g 0.03Pd-30[Bmim][Cl]/Al\textsubscript{2}O\textsubscript{3} was poured into the pipe above the quartz wool. Then, about 150 mL acetonitrile was poured into the flask, and the flask was heated by temperature-controlled magnetic stirrer under 200 °C. Most of palladium was extracted (confirmed by XRF) from the support by repeated reflux within 24 h. Afterwards, the extracted solution was concentrated by rotary evaporation. The concentrated solution was filter by membrane (0.22 μm) before the characterization.

![Fig. S5 The diagram of Soxhlet extractor](image-url)
TEM analysis was conducted using a transmission electron microscope (TEM, Tecnai G2F30 S-Twin), operating at an acceleration voltage of 300 keV. Two drops of the concentrated solution were transferred to a thin carbon grid (Beijing Zhongjingkeyi Technology Co., Ltd.). The grids were allowed to dry before TEM characterization, the results are shown in Fig. S6.

Fig. S6 TEM of concentrated Pd-[Bmim][Cl] solution
3. Experimental Section

Materials

$\gamma$-Al$_2$O$_3$ was derived from Tianjin institute of chemical technology, PdCl$_2$ was purchased from Aladdin Co. [Bmim][Cl](1-butyl-3-methylimidazolium chloride) was purchased from Lanzhou institute of chemical physics.

Catalyst preparation

The support, $\gamma$-Al$_2$O$_3$, was crushed and sieved through 40-60 mesh sieves. PdCl$_2$ was used as Pd$^{2+}$ precursor. [Bmim][Cl] and H$_2$PdCl$_4$ (0.001g/mL) were added to the deionized water to make the impregnation solution. Pd/Al$_2$O$_3$ (0.03 wt% Pd) and Pd-[Bmim][Cl]/Al$_2$O$_3$ (0.03 wt% Pd and 30 wt% ionic liquid) were prepared by incipient-wetness impregnation method. The resulted materials were aged at room temperature for 12 h and then dried at 110°C overnight.

Reaction test

Partial acetylene hydrogenation was performed in a consecutive fixed-bed reactor equipped with a quartz reaction tube (6mm diameter, 300mm length) and the reaction scheme is shown in Scheme S1. 0.27g of catalyst was reduced by pure H$_2$ at 170 °C for 1 h. The gaseous mixture of the selective hydrogenation of acetylene was made by 66.7% N$_2$, 0.351% C$_2$H$_2$, 0.697% H$_2$, and 30.5% C$_2$H$_4$. In order to adjust the ratio of hydrogen to acetylene, the valve of another stream of hydrogen was open, and the ratio is controlled by the mass flow controller of hydrogen stream.
The compositions of the product were analyzed online by a gas chromatography equipped with a 50 m × 0.32 mm HP-PLOT capillary column and a FID detector. The C$_2$H$_2$ conversion and C$_2$H$_4$ selectivity for partial acetylene hydrogenation are defined as follows:

\[
\text{Acetylene conversion} = \frac{C_{C_2H_2,\text{inlet}} - C_{C_2H_2,\text{outlet}}}{C_{C_2H_2,\text{inlet}}}
\]

\[
\text{Ethylene selectivity} = \frac{C_{C_2H_4,\text{outlet}} - C_{C_2H_4,\text{inlet}}}{C_{C_2H_2,\text{inlet}} - C_{C_2H_2,\text{outlet}}}
\]
Fig. S7 Acetylene conversion and Ethylene selectivity for 0.03%Pd/Al₂O₃ under different reaction temperatures (conditions: Pressure=0.1MPa, GHSV≈6000h⁻¹, 0.33 vol.% C₂H₂, 1.65 vol.% H₂, 33 vol.% C₂H₄ in N₂)
<table>
<thead>
<tr>
<th>Reaction Results</th>
<th>Catalyst</th>
<th>Reaction Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>X\textsubscript{C2H2}=99.5% S\textsubscript{C2H4}=91%</td>
<td>T=120 °C, P=0.1 MPa GHSV= 6000 h\textsuperscript{-1} Hydrogen : Acetylene mole ratio=20:1</td>
</tr>
<tr>
<td>1\cite{2}</td>
<td>X\textsubscript{C2H2}=98% S\textsubscript{C2H4}=80%</td>
<td>T=65 °C, P=0.1MPa Space velocity =30,000 ml min\textsuperscript{-1} g\textsuperscript{-1} Hydrogen : Acetylene mole ratio=2:1</td>
</tr>
<tr>
<td>2\cite{3}</td>
<td>X\textsubscript{C2H2}=80% S\textsubscript{C2H4}=80%</td>
<td>T=105 °C,Flow rate=40 ml min\textsuperscript{-1} The reactant gas mixture (0.65vol% acetylene, 5vol% hydrogen, and 50.5vol% ethylene balanced with argon)</td>
</tr>
<tr>
<td>3\cite{4}</td>
<td>X\textsubscript{C2H2}=99% S\textsubscript{C2H4}=83%</td>
<td>T=115 °C space velocity = 60000 mL·g\textsuperscript{-1}·h\textsuperscript{-1} hydrogen : acetylene mole ratio=2:1</td>
</tr>
<tr>
<td>4\cite{5}</td>
<td>X\textsubscript{C2H2}=99% S\textsubscript{C2H4}=70-80%</td>
<td>T=120 °C space velocity =0.02 mol\textsubscript{C2H2}mol\textsubscript{H2}·s\textsuperscript{-1} Gas mixture: 0.6 kPa C\textsubscript{2}H\textsubscript{2}, 0.6 kPa C\textsubscript{3}H\textsubscript{8}, 49.3 kPa C\textsubscript{2}H\textsubscript{4}, 0.9 kPa H\textsubscript{2} and 48.6 kPa N\textsubscript{2}</td>
</tr>
<tr>
<td>5\cite{6}</td>
<td>X\textsubscript{C2H2}=99% S\textsubscript{C2H4}=83.8%</td>
<td>T=70°C,P=0.4MPa space velocity (GHSV) =10050 h\textsuperscript{-1} hydrogen : acetylene ratio=2:1</td>
</tr>
<tr>
<td>6\cite{7}</td>
<td>X\textsubscript{C2H2}=85.9% S\textsubscript{C2H4}=87.2%</td>
<td>T=45 °C,P=0.05MPa space velocity (GHSV) =10056 h\textsuperscript{-1} hydrogen : acetylene ratio=2:1</td>
</tr>
<tr>
<td>7\cite{8}</td>
<td>X\textsubscript{C2H2}=96% S\textsubscript{C2H4}=90%</td>
<td>T=100°C space velocity (GHSV)=3600ml g\textsuperscript{-1}·h\textsuperscript{-1} hydrogen : acetylene ratio=6:1</td>
</tr>
<tr>
<td>8\cite{9}</td>
<td>X\textsubscript{C2H2}=100% S\textsubscript{C2H4}=85%</td>
<td>T=160°C gas velocity=240000ml h\textsuperscript{-1}·g\textsuperscript{-1} hydrogen : acetylene ratio=20:1</td>
</tr>
<tr>
<td>9\cite{10}</td>
<td>X\textsubscript{C2H2}=96% S\textsubscript{C2H4}=92%</td>
<td>T=90°C space velocity (GHSV)=288000ml h\textsuperscript{-1}·g\textsuperscript{-1} hydrogen : acetylene ratio=10:1</td>
</tr>
<tr>
<td>10\cite{11}</td>
<td>X\textsubscript{C2H2}=95% S\textsubscript{C2H4}=80%</td>
<td>T=200°C Flow=30 cm\textsuperscript{3} min\textsuperscript{-1} hydrogen : acetylene ratio=10:1</td>
</tr>
<tr>
<td>11\cite{12}</td>
<td>X\textsubscript{C2H2}=100% S\textsubscript{C2H4}=83%</td>
<td>T=250°C space velocity (GHSV)=60000ml h\textsuperscript{-1}·g\textsuperscript{-1}</td>
</tr>
<tr>
<td>12\cite{13}</td>
<td>X\textsubscript{C2H2}=100% S\textsubscript{C2H4}=82%</td>
<td>T=100°C,P=0.4MPa space velocity (GHSV) =10050 h\textsuperscript{-1} hydrogen : acetylene ratio=2:1</td>
</tr>
</tbody>
</table>
4. Solubility measurement

Fig. S7 presents the schematic diagram of the experimental apparatus, which is similar to previous publication\cite{14}. It mainly consists of a 316-L stainless steel reactor with a magnetic stirrer(39.8 mL), a gas reservoir(500 mL), a vacuum pump, a water bath, and two pressure sensors (Rosemount 3051) with an accuracy of 0.03 kPa in the experimental pressure range.

For each experimental run, about 8 g ionic liquid was placed in the reactor. The reactor was closed and kept under vacuum (1 kPa) at the 100 °C to degas the absorbent as well as to test the gas leak. Then a certain amount of gas was introduced to the gas reservoir supplied by the gas cylinder. The inlet gas valve was open until the pressure reached the about 103 kPa. To ensure that the temperature equilibrium had been reached, both reactor and reservoir were placed in oil bath for about 1 h, and the original pressure/temperature was recorded. The equilibrium process begins with opening the gas inlet valve (the valve should be closed immediately) to make the gas transfer from gas reservoir to reactor. Finally, when the pressure of reactor was constant, the soluble equilibrium was arrived and the pressure/temperature of reservoir and reactor was recorded. Therefore, the solubility of gas can be calculated and the formulas were as follows:

\[ V_{Ra} = V_R - m_{IL} \times \rho_{IL} \]  \hspace{1cm} (3-1)

\[ n_{R1} = \frac{P_{R1} \times V_{R1}}{R \times T_{R1}} \]  \hspace{1cm} (3-2)

\[ n_{R2} = \frac{P_{R2} \times V_{R2}}{R \times T_{R2}} \]  \hspace{1cm} (3-3)
\[ n_{s1} = \frac{P_{s1} \times V_{s}}{R \times T_{s1}} \] (3-4)

\[ n_{s2} = \frac{P_{s2} \times V_{s}}{R \times T_{s2}} \] (3-5)

\[ S = \frac{(n_{s1} - n_{s2}) - (n_{r2} - n_{r1})}{m_{IL}} \] (3-6)

\[ V_{R3}: \text{Actual volume of reactor} \]
\[ V_{R}: \text{Original volume of reactor} \]
\[ V_{S}: \text{Volume of reservoir} \]
\[ P_{R1}: \text{Pressure of reactor before adsorption} \]
\[ P_{S1}: \text{Pressure of reservoir before adsorption} \]
\[ P_{R2}: \text{Pressure of reactor when the adsorption is balanced} \]
\[ P_{S2}: \text{Pressure of reservoir when the adsorption is balanced} \]
\[ T_{R1}: \text{Temperature of reactor before adsorption} \]
\[ T_{R2}: \text{Temperature of reactor when the adsorption is balanced} \]
\[ T_{S1}: \text{Pressure of reservoir before adsorption} \]
\[ T_{S2}: \text{Pressure of reservoir when the adsorption is balanced} \]
\[ n_{R1}: \text{Mole amount of gas in reactor before adsorption} \]
\[ n_{R2}: \text{Mole amount of gas in reactor when the adsorption is balanced} \]
\[ n_{S1}: \text{Mole amount of gas in reservoir before adsorption} \]
\[ n_{S2}: \text{Mole amount of gas in reservoir when the adsorption is balanced} \]
\[ m_{IL}: \text{Mass of ionic liquid} \]
\[ \rho_{IL}: \text{Density of ionic liquid} \]
\[ S: \text{Solubility of gas} \]
Fig. S8 The set-up for measuring the gas solubility

References