Supporting Information

Synthesis of Renewable Acetic Acid from CO₂ and Lignin over Ionic Liquid-Based Catalytic System

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**Experimental section**

**Materials**
Anisole (99%) and dimethyl sulfoxide (DMSO, 99%) were provided by Beijing InnoChem Science & Technology Co., Ltd. Ruthenium carbonyl (Ru3(CO)12, 99%), ruthenium(III) iodide (RuI3, anhydrous Ru 20.5% min), hexarhodium hexadecacarbonyl (Rh6(CO)16, 98%), lithium tetrafluoroborate (LiBF4, 98%) and lithium iodide (LiI, 99%) were purchased from Alfa Aesar China Co., Ltd. Rhodium(III) iodide (RhI3, Rh, 18.5-21.3%) were purchased from J&K Scientific Ltd. 1-butyl-3-methylimidazolium chloride ([BMIm][Cl], 99%), 1-ethyl-3-methylimidazolium chloride ([EMIm][Cl], 99%), 1-hexyl-3-methylimidazolium chloride ([HMIm][Cl], 99%), 1-butyl-3-methylimidazolium bromide ([BMIm][Br] 99%), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF4], 99%), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIm][BF4], 99%), 1-buty-3-methylimidazolium bis(trifluoromethyl)sulfonylimide ([BMIm][NTf2], 99%), 1-butyl-3-methylimidazolium nitrate ([BMIm][NO3], 99%), tributylmethylammonium chloride ([N1444][Cl], 99%) were provided by Centre of Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS). Tetrahydrofuran (THF, 99.5%) was obtained from Energy Chemical. Lignin (Dealkaline) and 1,3-dimethyl-2-imidazolidinone (DMI, 99%) was purchased from TCI Shanghai Co., Ltd. All the chemicals were used as received.

**Instrumentation**
Liquid 1H and 13C NMR spectra were recorded on Bruck Avance III 400 HD NMR spectrometer. Liquid sample was analyzed by gas chromatography-mass spectrometry GC-MS (SHIMADZU-QP2010) with a packed column DB-5 MS. Gas sample was analyzed by GC-MS (7890A, Agilent) and GC (Agilent 4890D) equipped with a TCD detector and a packed column (Carbon molecular sieve TDX-01), using argon as the carry gas. High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) were performed on Bruker FT-ICR-MS (Solarix 9.4T). The lignin before and after reaction were determined by gel permeation chromatography (GPC, waters 1515) with a refractive index detector (RI, waters 2414) using Styrage HT3 (7.8×300 mm, waters, WAT044208) and HT4 (7.8×300 mm, waters, WAT044211). The column was eluted with N,N-dimethylformamide (DMF) at a flow rate of 1.0 mL/min.

**General procedure for the synthesis of acetic acid**
All the reactions were conducted in a Teflon-lined stainless steel autoclave (16 mL of inner volume) equipped with a magnetic stirrer. In a typical experiment, anisole (1 mmol), Ru3(CO)12 (0.1 mmol, based on the metal), RhI3 (0.1 mmol, based on the metal), LiI (2 mmol), LiBF4 (1 mmol), and [BMIm][Cl] (10 mmol) were sequentially added into a autoclave, and then the autoclave was sealed. CO2 (3 MPa) and H2 were charged successively into the autoclave until the total pressure reached 6 MPa at room temperature. Subsequently, the autoclave was moved to an air-bath of desired temperature (e.g., 180 °C) and stirred at 800 r.p.m for 12 h. After the reaction, the autoclave was cooled to room temperature, and then the residual gas was vented slowly and collected in a gasbag. 1, 3, 5-trioxane (0.019 g) as the internal standard and DMSO (2 mL) were added to the reaction solution, stirred vigorously and centrifuged. To determine the conversion and yield, the supernatant liquid was analyzed by 1H NMR in DMSO-d6, and the gas sample was analyzed by GC. In addition, the liquid and gas samples were also analyzed by GC-MS. Regarding the lignin (200 mg) as the reactant, the reaction procedure was similar to that described above. To get the lignin residue after reaction, the reaction mixture was centrifuged, and the filter residue was washed by water (5×1.5 mL) to remove the catalyst, and then the resulting lignin was dried in vacuum at 60 °C for 24 h over P2O5 desiccant. The fresh lignin and that after reaction were dissolved in DMF and filtrated by a 0.22 μm filter for the GPC analysis, respectively.
# Results and discussion

Table S1. Synthesis of acetic acid from anisole, CO2, and H2 using different catalytic systems.

![Chemical reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Promoter</th>
<th>Solvent</th>
<th>CO2/Total (MPa)</th>
<th>1 Conv(^b) [%]</th>
<th>2 Yield(^b) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>-</td>
<td>[BMIm][BF(_4)]</td>
<td>3/6</td>
<td>100</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>-</td>
<td>[HMIm][BF(_4)]</td>
<td>3/6</td>
<td>100</td>
<td>38</td>
</tr>
<tr>
<td>3(^c)</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>-</td>
<td>[BMIm][Cl], [HMIm][BF(_4)]</td>
<td>3/6</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>4(^d)</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>LiBF(_4)</td>
<td>[BMIm][Cl]</td>
<td>3/3</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5(^d)</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>LiBF(_4)</td>
<td>[BMIm][Cl]</td>
<td>0/3</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>6(^e)</td>
<td>Ru(<em>3)(CO)(</em>{12}), RhI(_3)</td>
<td>LiI</td>
<td>LiBF(_4)</td>
<td>[BMIm][Cl]</td>
<td>3/6</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) Reaction condition: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), cocatalyst (2 mmol), promoter (1 mmol), ionic liquids (10 mmol) or organic solvents (1.5 mL), anisole (1 mmol), CO\(_2\) (3 MPa) and total (6 MPa, at room temperature), 180 °C, and 12 h; \(^b\) Conversion and yield were determined by \(^1\)H NMR analysis with 1,3,5-trioxane as the internal standard; \(^c\) [BMIm][Cl] (5 mmol) and [HMIm][BF\(_4\)] (5 mmol); \(^d\) Without CO\(_2\) or H\(_2\), no acetic acid was produced, but CH\(_3\)I and phenol were detected; \(^e\) Without anisole, no acetic acid and CH\(_3\)I were detected.
Figure S1. The GC-MS spectra of liquid sample after the reaction of anisole, CO₂ and H₂. Reaction condition: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF₄ (1 mmol), [BMIm][Cl] (10 mmol), anisole (1 mmol), CO₂ (3 MPa) and total (6 MPa, at room temperature), 180 °C and 12 h.

Figure S2. Effects of reaction conditions (a–c) and results of recycling tests (d) over Ru₁₂(CO)₁₂ (0.1 mmol) and Rh₁₃ (0.1 mmol) (based on the metal) in [BMIm][Cl] (10 mmol) with LiI (2 mmol) and LiBF₄ (1 mmol): (a) time course of the reaction, CO₂ pressure (3 MPa) and total pressure (6 MPa), 180 °C; (b) effect of temperature, CO₂ (3 MPa) and total (6 MPa), 12 h; (c) effect of pressure, 180 °C, 12 h; (d) the reaction condition is the same as that of entry 3 in Table 1.
Figure S3. The GC-MS spectra of liquid sample after the reaction of anisole, $^{13}$CO$_2$ and H$_2$. Reaction condition: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF$_4$ (1 mmol), [BMIm][Cl] (10 mmol), anisole (1 mmol), $^{13}$CO$_2$ (2 MPa) and total (4 MPa, at room temperature), 180 °C and 24 h.
Figure S4. GC-MS spectra of the liquid sample of the reaction of anisole with CO\textsubscript{2} and D\textsubscript{2}. Reaction conditions: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF\textsubscript{4} (1 mmol), [BMIm][Cl] (10 mmol), anisole (1 mmol), CO\textsubscript{2} (2 MPa) and total (4 MPa, at room temperature), 180 °C and 24 h.

Note: The main molecular weight of acetic acid and phenol generated in the reaction were 61 and 95, indicating that D\textsubscript{2} indeed involved the formation of acetic acid and phenol. In addition, partial molecular ion peak m/z=60/62/63 and m/z=94/96 owing to the partial H/D exchange of acetic acid and phenol.
The NMR spectra of liquid sample after the reaction of anisole, $^{13}$CO$_2$ and H$_2$. Reaction condition is the same as that of Fig. S3. (a) $^1$H NMR; (b) $^{13}$C NMR.

Note: In the $^1$H NMR spectrum, the proton signal of $^{13}$COO group on the acetic acid molecule splits into two peaks by the coupling with $^{13}$C atom. In the $^{13}$C NMR spectrum, the signal of CH$_3$ group became weaker and splits into dual peaks, which is caused by the coupling with the adjacent $^{13}$C atom in the $^{13}$COO group. Both $^1$H NMR and $^{13}$C NMR spectra confirmed that the COO group in acetic acid molecule is from CO$_2$, i.e., CO$_2$ is transferred into the acetic acid product in the reaction.

Figure S5.
Figure S6. The GC-MS spectra of gaseous sample after the reaction of anisole, $^{13}$CO$_2$ and H$_2$. The reaction condition is the same as that of Fig. S3.
Figure S7. The GC-MS spectra of liquid sample after the reaction of anisole, CO and H₂. Reaction condition: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF₄ (1 mmol), [BMIm][Cl] (10 mmol), anisole (1 mmol), CO (3 MPa) and total (6 MPa, at room temperature), 180 °C and 12 h.
Figure S8. GC-MS spectra of liquid sample of the reaction of anisole with $\text{H}_2^{18}\text{O}$, $\text{CO}_2$ and $\text{H}_2$. Reaction conditions: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF$_4$ (1 mmol), [BMIm][Cl] (10 mmol), anisole (1 mmol), $\text{H}_2^{18}\text{O}$ (1 mmol), $\text{CO}_2$ (3 MPa) and total (6 MPa, at room temperature), 180 °C and 12 h.

Figure S9 GC spectrum of gaseous sample of the reaction of anisole with $\text{CO}_2$ and $\text{H}_2$. The reaction conditions were the same as those of entry 3 of Table 1.
Figure S10. The GC spectrum of gaseous sample after the reaction of anisole, CO and H₂. The reaction condition is the same as that of Fig. S7.
Figure S11. HR-ESI-MS spectra of the mixture of Ru catalyst, Rh catalyst, LiI, LiBF$_4$ and [BMIm][Cl] with CO$_2$ and H$_2$. Conditions: Ru catalyst (0.5 mmol, based on the metal) and Rh catalyst (0.5 mmol, based on the metal), LiI (2 mmol), LiBF$_4$ (1 mmol), [BMIm][Cl] (4 mmol), CO$_2$ (3 MPa) and total (6 MPa, at room temperature), 180 °C and 2 h. (a) ESI-MS (+); (b) ESI-MS(-); (c) Magnifications of the selected region of the ESI-MS(-) spectrum.
Figure S12. HR-ESI-MS spectra of the mixture of Ru catalyst, Rh catalyst, LiI, LiBF₄ and [BMIm][Cl] with ¹³CO₂ and H₂. Conditions: Ru catalyst (0.5 mmol, based on the metal) and Rh catalyst (0.5 mmol, based on the metal), LiI (2 mmol), LiBF₄ (1 mmol), [BMIm][Cl] (4 mmol), ¹³CO₂ (1 MPa) and total (2 MPa, at room temperature), 180 °C and 3 h. (a) ESI-MS (+); (b) ESI-MS (-), (c) Magnifications of the selected region of the ESI-MS (-)spectra.

Note: To elucidate active species in the reaction, the above mixture was analyzed with electrospray-ionization (ESI-MS) mass spectrometry. HR-ESI-MS (+) spectrum of the mixture shows that the positive ions mainly include 1-butyl-3-methyl-imidazolium cation ([BMIm]+, m/z=139.1) and aggregates of [BMIm]-containing ions such as, ([BMIm]₂•Cl]+ with m/z=313.2, ([BMIm]₂•BF₄]+ with m/z=365.2, ([BMIm]₃•I]+ with m/z=405.2, ([BMIm]₃•Cl₂]+ with m/z=487.3, [Li(BMIm)₂•Cl]²⁻ with m/z=529.3, ([BMIm]₃•ClI]+ with m/z=579.2 etc.. Magnification of some selected regions of the ESI-MS(+) spectrum shows a range of small peaks, which could be attributed to distinct Rh-complexes ([Rh(BMIm)₂(CO)I₄]+ (m/z=916.8) and ([Rh(BMIm)₃(CO)LiCl]⁺ (m/z=1090.9). As shown in negative ion ESI-MS spectrum, some kinds of ruthenium species were detected: [Ru(CO)I₃]- (m/z=510.6), [Ru(CO)I₃]²⁻ (m/z=255.3), [Ru(CO)I₃]³⁻ (m/z=170.2); [Ru(CO)₂I₃]- (m/z=538.6), [Ru(CO)₂I₃]²⁻ (m/z=269.3), [Ru(CO)₂I₃]³⁻ (m/z=179.5); [Ru(CO)₃I]- (m/z=566.6); [Ru(CO)₃I]²⁻ (m/z=283.3), [Ru(CO)₃I]³⁻ (m/z=188.9); [Ru(CO)₂I₂Li]- (m/z=390.7); [Ru(CO)₂I₂Li]⁻ (m/z=418.7); [Ru(CO)₃I₂Li]- (m/z=446.7); [Ru(CO)₄Li]⁻ (m/z=474.7). In addition, some Rh complexes also were detected in the negative ion ESI-MS spectrum, which could be attributed to [RhI]- (m/z=610.5), [RhI₂(CO)Cl]⁻ (m/z=419.7), [RhICl]⁻ (m/z=392.7), and [RhI₂(CO)]⁻ (m/z=638.5). Moreover, the HR-ESI-MS spectra of the ¹³C labeling experiments indicated that some carbonyl groups that coordinated with the Ru* or Rh* were sourced from ¹³CO₂ as the reaction proceeded.
**Figure S13.** $^1$H NMR spectra of [BMIm][Cl] and the mixture of RhI$_3$ and [BMIm][Cl]. (a) [BMIm][Cl]: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.03 (s, 1H), 8.22 (s, 1H), 8.09 (s, 1H), 4.24 (t, 2H), 3.91 (s, 3H), 1.67 (m, 2H), 1.08 (m, 2H), 0.70 (t, 3H); (b) the mixture of RhI$_3$ and [BMIm][Cl] treated at 180 °C: $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.53 (s, 1H), 7.90 (s, 1H), 7.81 (s, 1H), 4.20 (t, 2H), 1.74 (m, 2H), 1.21 (m, 2H), 0.84 (t, 3H).

**Figure S14.** $^{13}$C NMR spectra of [BMIm][Cl] and the mixture of RhI$_3$ and [BMIm][Cl]. (a) [BMIm][Cl]: $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 136.79, 123.34, 122.23, 48.08, 35.55, 31.35, 18.54, 13.02; (b) the mixture of RhI$_3$ and [BMIm][Cl] at 180 °C: $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 136.53, 123.31, 122.08, 48.25, 35.77, 31.28, 18.58, 13.13.
Figure S15. The $^{13}$C NMR spectra of CH$_3$I and the mixture of RhI$_3$, CH$_3$I and [BMIm][Cl]. (a) CH$_3$I; (b) the mixture of RhI$_3$, CH$_3$I and [BMIm][Cl] at 25 °C. Note: In the $^{13}$C NMR spectrum of the mixture of RhI$_3$, CH$_3$I and [BMIm][Cl], the signal at -23.94 ppm that attributed to the CH$_3$ group of CH$_3$I disappeared accompanied by the appearance of a new signal at 26.18 ppm, which may be caused by the strong interaction between the RhI$_3$ and CH$_3$I.
Figure S16. The $^1$H NMR spectrum of liquid sample after the reaction of lignin (Dealkaline), CO$_2$ and H$_2$. Reaction condition: Ru catalyst (0.1 mmol, based on the metal) and Rh catalyst (0.1 mmol, based on the metal), LiI (2 mmol), LiBF$_4$(1 mmol), [BMIm][Cl] (10 mmol), lignin (200 mg), CO$_2$ (3 MPa) and total (6 MPa, at room temperature), 180 °C and 12 h.

Figure S17. The GPC traces of the lignin before and after reaction. The reaction conditions are the same as that of entry 3 of Table 1.

Note: Fig. S17 shows the GPC traces of the lignin (Dealkaline) before and after reaction. It can be seen that the GPC traces before and after the reaction were similar and there was no detectable depolymerisation product.
References