Supporting Information

(Pd-CuCl₂)/γ-Al₂O₃: a high-performance catalyst for carbonylation of methyl nitrite to dimethyl carbonate

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Fig. S1. XRD patterns of (a) CuCl$_2$ and (b) (Pd-CuCl$_2$)/γ-Al$_2$O$_3$ catalyst.

Fig. S2. Nitrogen adsorption-desorption isotherms of (a) (Pd-CuCl$_2$)/γ-Al$_2$O$_3$ catalyst, (b) (Pd-CuCl$_2$)/α-Al$_2$O$_3$ catalyst, (c) (Pd-CuCl$_2$)/MgO catalyst and (d) Pd/γ-Al$_2$O$_3$ catalyst at 77 K.
Table S1. The texture properties of as-synthesized catalysts with different supports.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>(Pd-CuCl₂)/γ-Al₂O₃</th>
<th>(Pd-CuCl₂)/α-Al₂O₃</th>
<th>(Pd-CuCl₂)/MgO</th>
<th>Pd/γ-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>S_{BET} (m²/g)</strong></td>
<td>40.5</td>
<td>5.7</td>
<td>9.8</td>
<td>71.1</td>
</tr>
<tr>
<td>Pore volume (cm³/g)</td>
<td>0.21</td>
<td>0.02</td>
<td>0.03</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Fig. S3. Cu 2p XPS spectra of (a) fresh and (b) engaged of (Pd-CuCl₂)/γ-Al₂O₃ catalysts.
**Fig. S4.** *In situ* DRIR spectra of CO on (Pd-CuCl₂)/γ-Al₂O₃ catalyst at 120 °C, range from 2400 cm⁻¹ to 1800 cm⁻¹.

**Fig. S5.** *In situ* DRIR spectra of CO and MN on (Pd-CuCl₂)/γ-Al₂O₃ catalyst at 120 °C, range from 3000 to 1850 cm⁻¹.
Fig. S6. *In situ* DRIR spectra of the reaction between CO and MN after sweeping by N₂ over (Pd-CuCl₂)/γ-Al₂O₃ catalyst at 120 °C, range from 2600 to 1800 cm⁻¹.

The *in situ* DRIR spectra of the reaction between CO and MN over (Pd-CuCl₂)/γ-Al₂O₃ catalyst after sweeping by N₂ are shown in Fig. S6. The small peaks appeared at 1998 and 1932 cm⁻¹ are assigned to adsorbed CO on metallic Pd(0) in bridge (Pd₂–CO). The large peaks at 2118 and 2138 cm⁻¹ (not the bimodal peaks of CO in gas) have been detected, which can be ascribed to the C–O stretching vibrations of CO adsorbed on Pd(II). According to the results of *in situ* DRIR experiments, most of CO are adsorbed on Pd(II), while only a few of CO are adsorbed on Pd(0) during the reaction process of CO and MN, which is consistent with the results of XPS characterization.
Fig. S7. GC diagrams on FID of methyl nitrite and organic products over (a) Pd/γ-Al₂O₃ catalyst, (b) (Pd-CuSO₄)/γ-Al₂O₃ catalyst and (c) (Pd-CuCl₂)/γ-Al₂O₃ catalyst at 0.1 MPa and 120 °C.
The organic products over as-synthesized catalysts are methanol, methyl formate (MF), dimethoxymethane (DMM), DMC and dimethyl oxalate (DMO). The products of methanol, MF, and DMM come from the decomposition of methyl nitrite (MN) [reactions (1) and (2) shown as follows]. The products of DMC [reaction (3) shown as follows] and DMO [reaction (4) shown as follows] come from the carbonylation of MN. The selectivity to DMC is calculated based on CO. Thus, the byproduct based on CO of as-synthesized catalysts is only DMO. The selectivities to DMC over Pd/γ-Al₂O₃ and (Pd-CuSO₄)/γ-Al₂O₃ catalysts not containing Cl⁻ are much lower than that over (Pd-CuCl₂)/γ-Al₂O₃ catalyst containing Cl⁻, which can be directly observed in GC diagrams (Fig. S7).

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\begin{align*}
4\text{CH}_3\text{ONO} & \xrightarrow{\text{catalyst}} 2\text{CH}_3\text{OH} + \text{HCOOCH}_3 + 4\text{NO} \\
2\text{CH}_3\text{ONO} + \text{CH}_3\text{OH} & \xrightarrow{\text{catalyst}} (\text{CH}_3\text{O})_2\text{CH}_2 + 2\text{NO} + \text{H}_2\text{O} \\
\text{CO} + 2\text{CH}_3\text{ONO} & \xrightarrow{\text{catalyst}} (\text{CH}_3\text{O})_2\text{CO} + 2\text{NO} \\
2\text{CO} + 2\text{CH}_3\text{ONO} & \xrightarrow{\text{catalyst}} (\text{COOCH}_3)_2 + 2\text{NO}
\end{align*}
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