**In-situ** hydrogen from aqueous-methanol for nitroarene reduction and imines formation over an Au-Pd/Al₂O₃ catalyst

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Materials

Nitrobenzene (> 99.0%) and Fe(NO$_3$)$_3$·9H$_2$O (> 98.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. 3-methylnitrobenzene (> 99.0%), 4-methylnitrobenzene (> 99.0%) and benzaldehyde (> 98.5%) were purchased from Shanghai Chemical Reagent Co. Ltd. Furfural (> 99.0%) was purchased from Shanghai Tingxin Chemical Reagent Factory. Cinnaldehydum (> 95%) was purchased from Shanghai Shuangxiang Auxiliary Factory. Methanol (AR/99.5%) was purchased from Quzhou Juhua Reagents Co. Ltd. H$_2$PdCl$_4$, HAuCl$_4$ and RuCl$_3$ were obtained from Hangzhou Kaida Metal Catalyst & Compounds Co. Ltd. γ-Al$_2$O$_3$ (80-120 mesh, ~250 m$^2$/g) was supplied by Zibo Boyang Chemical Co., Ltd. MgO (80-120 mesh, ~120 m$^2$/g) was prepared by precipitation of Mg(NO$_3$)$_2$·6H$_2$O. TiO$_2$ (80-120 mesh, ~200 m$^2$/g) was supplied by Nanjing Taiwei Science and Technology Co.Ltd.

Catalysts

The monometallic Pd/Al$_2$O$_3$ and Au/Al$_2$O$_3$ catalyst were prepared by incipient wetness impregnation of γ-Al$_2$O$_3$ with an aqueous solution of H$_2$PdCl$_4$ or HAuCl$_4$. The impregnation was followed by drying at 383 K for 5 h, and then calcining at 623 K for 5 h in air. The nominal loading of Pd and Au are both 3 wt-%.

The Au-Pd/Al$_2$O$_3$, Ru-Pd/Al$_2$O$_3$, Fe-Pd/Al$_2$O$_3$, Au-Pd/MgO, and Au-Pd/TiO$_2$ catalysts were prepared by incipient wetness co-impregnation of γ-Al$_2$O$_3$ or MgO or TiO$_2$ with aqueous solutions of HAuCl$_4$ and H$_2$PdCl$_4$, RuCl$_3$ and H$_2$PdCl$_4$, and Fe(NO$_3$)$_3$·9H$_2$O and H$_2$PdCl$_4$, respectively. The impregnation was followed by drying at 383 K for 5 h, and then calcining at 623 K for 5 h in air. The nominal loading of Pd is 3 wt-%, the atomic ratio of Au, Ru or Fe/Pd is 1.

The morphology of the reduced Au-Pd/Al$_2$O$_3$ catalyst was determined by a Tecnai G2 F30 S-Twin at an operating voltage of 300 kV. The CO-IR spectra of the Au-Pd/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalysts were detected by an in-situ FT-IR spectra instruments of NEXUS.
Catalytic reaction evaluation

The direct synthesis of imines from nitroarenes and carbonyl compounds was carried out in a fixed-bed reactor (a stainless-steel tube with an inner diameter of 8 mm). The typical procedure of the synthesis of nitrobenzene and furfural was described as the follows. 0.5 g of the catalyst (Au-Pd/Al₂O₃ etc.) was loaded in the isothermal region of the reactor, and then the catalyst was reduced in-situ at 553 K (a temperature ramp of 3 K.min⁻¹) for 2 h in flowing H₂ (99.999 %) with a rate of 20 ml.min⁻¹. The reactor pressure was then increased by adding Ar (99.999 vol-%) to 2.0 MPa to maintain reaction in liquid phase at 408 K. A mixed solution, composed of methanol 40 ml + water 10 ml + nitroarenes 1 ml + carbonyl compounds 1 ml, was fed at 0.1 ml.min⁻¹ into the reactor using a high-performance liquid chromatography pump (PK564AN-TG10-A2). The gases and condensates were separated in a stainless-steel vessel (about 20 ml) at the system pressure. The liquid effluent was collected when the reaction was carried out continuously for 4-5 h to obtain the steady state results, and analyzed by a GC-MS instrument (Agilent-6890 GC-5973 MS equipped with 30 m HP-5 capillary). The gas effluent was analyzed by an on-line GC instrument (Fuli 9790, Porapak Q & 13X molecular sieves columns) equipped with thermo conductive detector (TCD).

The conversion of nitrobenzene (X_{NO₂}) and carbonyl compounds (X_{C=O}) were calculated from the GC-MS instrument analysis with the external standard method. The products (Imines, aniline, N-methylaniline, alcohols, and amines) composition in the liquid phase were obtained using the normalization method. The selectivity of imines based on carbonyl compounds was calculated according to the equation (1).

\[ S = \frac{\text{Imines in products}}{\text{Imines in products} + \text{by-products derived from carbonyl compounds in products}} \times 100\% \quad (1) \]

The formation rate of imines was calculated, from the conversion of carbonyl compounds and the selectivity of imines based on carbonyl compounds, according to the equation (2).
The equation (2) is given as:

\[ r = \frac{1}{52} \times \frac{\rho}{M} \times 0.1 \times X_{C=O} \times S \times \frac{1}{m_{\text{cat}}} \times 100\% \]  

In the equation (2), the 1/52 means the volume concentration of carbonyl compounds, \( \rho \) means the density of carbonyl compounds, \( M \) means the molecular weight of carbonyl compounds, 0.1 is the feeding rate of the mixed solution, \( X_{C=O} \) means the conversion of carbonyl compounds, \( S \) was calculated from equation (1), \( m_{\text{cat}} \) means the amounts of the catalyst.

**Table S1.** Experimental results for the hydrogenation of nitrobenzene, styrene, acetone and cyclohexanone using methanol as hydrogen source.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entries</th>
<th>Catalyst</th>
<th>Unsaturated substrates</th>
<th>Hydrogenation rate (( \mu \text{mol.g}^{-1}.\text{min}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene</td>
<td>17.9</td>
</tr>
<tr>
<td>2</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Styrene</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene (1) + Styrene (2)</td>
<td>(1) 12.4, (2) 1.9</td>
</tr>
<tr>
<td>3</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene (1) + Acetone (2)</td>
<td>(1) 13.3, (2) n.r.</td>
</tr>
<tr>
<td>4</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene (1) + Cyclohexanone (2)</td>
<td>(1) 13.8, (2) n.r.</td>
</tr>
<tr>
<td>5(^{[b]})</td>
<td>Au-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene (1) + Styrene (2)</td>
<td>(1) 37.8, (2) 29.1</td>
</tr>
<tr>
<td>6</td>
<td>Fe-Pd/Al(_2)O(_3)</td>
<td>Nitrobenzene (1) + Styrene (2)</td>
<td>(1) 14.9, (2) 12.5</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Experimentals were carried out in a fixed bed reactor at 408 K and 2.0 MPa (Ar pressure), the load Au-Pd/Al\(_2\)O\(_3\) catalyst was 0.5 g, a mixed solution (methanol 40 ml + water 10 ml + substrates 1 ml) was fed at 0.1 ml.min\(^{-1}\).\(^{[b]}\) Molecular H\(_2\) was used as the reducing reagent.

Table S1 shows the experimental results of selective hydrogenation nitrobenzene, with the presence of styrene, acetone or cyclohexanone in the same system. The rates for the hydrogenation of nitrobenzene and styrene, using methanol as hydrogen source over the Au-Pd/Al\(_2\)O\(_3\) catalyst, are 17.9 and 2.8 \( \mu \text{mol.g}^{-1}.\text{min}^{-1} \), respectively. The rates for the hydrogenation of nitrobenzene, with styrene, acetone and cyclohexanone
presented in the same system, are 12.4, 13.3 and 13.8 μmol.g⁻¹.min⁻¹, respectively, the hydrogenation rates of styrene, acetone and cyclohexanone are only 1.9, 0 and 0 μmol.g⁻¹.min⁻¹, respectively. However, the rates for the hydrogenation of nitrobenzene and styrene in the same system are 37.8 and 29.1 μmol.g⁻¹.min⁻¹, respectively, using H₂ as reductives over the Au-Pd/Al₂O₃ catalyst, and the rates for the hydrogenation of nitrobenzene and styrene are 14.9 and 12.5 μmol.g⁻¹.min⁻¹, respectively, using methanol as hydrogen source over the Fe-Pd/Al₂O₃ catalyst. These results suggested that the hydrogenation of nitrobenzene, with the presence of styrene, acetone or cyclohexanone in the same system, using methanol as hydrogen source over the Au-Pd/Al₂O₃ catalyst possess an significantly higher selectivity than using H₂ as hydrogen source over the Au-Pd/Al₂O₃ catalyst or using methanol as hydrogen sources over the Fe-Pd/Al₂O₃ catalyst. The results also indicated that the generation of hydrogen from methanol, by means of aqueous-phase reforming or dehydrogenation, could be an effective way to provide limited hydrogen for the selective hydrogenation of nitro- group with the presence of –C=O, etc. in the same system. Therefore, we chose methanol as hydrogen source and Au-Pd/Al₂O₃ as the catalyst for the direct synthesis of imines from nitroarenes and carbonyl compounds.
Table S2. Experimental results for the hydrogenation of nitrobenzene using methanol as hydrogen source over different catalysts.[a]

<table>
<thead>
<tr>
<th>Entries</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Hydrogenation rate (μmol.g⁻¹.min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au-Pd/Al₂O₃</td>
<td>46.7</td>
<td>92.2</td>
<td>17.9</td>
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<tr>
<td>2</td>
<td>Ru-Pd/Al₂O₃</td>
<td>43.5</td>
<td>90.0</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>Fe-Pd/Al₂O₃</td>
<td>54.1</td>
<td>88.7</td>
<td>20.7</td>
</tr>
<tr>
<td>4</td>
<td>Pd/Al₂O₃</td>
<td>11.8</td>
<td>97.4</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>Au/Al₂O₃</td>
<td>0</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Au-Pd/MgO</td>
<td>44.2</td>
<td>94.1</td>
<td>16.9</td>
</tr>
<tr>
<td>7</td>
<td>Au-Pd/TiO₂</td>
<td>65.4</td>
<td>94.9</td>
<td>25.1</td>
</tr>
</tbody>
</table>

[a] Experimentals were carried out in a fixed bed reactor at 408 K and 2.0 MPa (Ar pressure), the load catalyst was 0.5 g, a mixed solution (methanol 40 ml + water 10 ml + nitrobenzene 1 ml) was fed at 0.1 ml.min⁻¹.

The results from Table S2 suggested that the formation rate of imines from nitrobenzene and furfural are highly dependent upon the hydrogenation rate of nitrobenzene. Bimetallic supported Au-Pd, Ru-Pd, and Fe-Pd catalyst shows the higher hydrogenation rate of nitrobenzene.

Figure S1. Schematic representation of the hydrogenation of nitrobenzene with hydrogen generated in-situ from the aqueous-phase reforming of methanol
**Figure S2.** Schematic representation of the hydrogenation of nitrobenzene with hydrogen generated in-situ from the dehydrogenation of methanol.

**Figure S3.** Deactivation profiles of the synthesis of imine from nitrobenzene and furfural on Au-Pd/Al₂O₃ catalyst with hydrogen from aqueous-methanol. Reaction conditions were the same as the entry 1 of Table 1.

As shown in Fig. S3, the formation rate of imine from nitrobenzene and furfural on the Au-Pd/Al₂O₃ catalyst was highly decreased at 1-4 h (this is the initial reaction stage, which was not represent the steady state of the catalyst), but it was only slightly decreased at 4-60 h (the experimental results in this paper was all obtained at 4-5 h). In addition, the selectivity of imine based on furfural was maintained at 98.8-99.8% versus time on stream for 60 h. These results suggested that the Au-Pd/Al₂O₃ catalyst was quite stable for the proposed reaction, but we suggested that the stability of the catalyst still need further improvement.
**Figure S4.** CO-IR spectra of the Au-Pd/Al₂O₃ and Pd/Al₂O₃ catalysts

Fig. S4 gives the CO-IR spectra of the Au-Pd/Al₂O₃ and Pd/Al₂O₃ catalysts. The adsorption of CO on the Pd/Al₂O₃ gave rise to at least two distinctive $\nu_{c=0}$ bands. The first peak appearing at 2068 cm⁻¹ is attributed to linearly adsorbed CO on one Pd atom, and the second, at around 1800-1990 cm⁻¹ (a broad peak at 1923 cm⁻¹), is assigned to CO bridging on two or more Pd atoms. The other peaks at 1384, 1560, and 1643 cm⁻¹ could be attributed to the $\nu_{c=0}$ bands on the Al₂O₃ support, and the peaks at 2114 and 2173 cm⁻¹ are assigned to gas phase $\nu_{c=0}$ bands. Over the Au-Pd/Al₂O₃ catalyst, the band of the linearly adsorbed CO at 2068 cm⁻¹ is shift to a high wavenumber at 2074 cm⁻¹. The peaks at 1923 and 1973 cm⁻¹ are attributed to bridgingly adsorbed CO on the Pd (111) and Pd (100), respectively.

**DFT calculations:** The first-principles DFT calculations are performed using the DMol³ module in Materials Studio.[1, 2] The generalized gradient approximation (GGA) with PW91 functional [3] is used to describe the exchange-correlation (XC) effects. The double numerical plus polarization (DNP) basis set are used in expanded electronic wave functional. In this study, the periodic supercells of (3, 3) Au(111), Pd(111), and Au(111), Pd(111) with a surface Pd and Au atoms. The Brillouin zone is
sampled by $2 \times 2 \times 1$ $k$ points using the Monkhorst-Pack scheme. All of atoms are fully relaxation during the geometry optimization.

**Reference**

