Strong effect of the surface properties of carbon supports in Au-catalyzed reactions

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Abstract: Support materials are well-known to affect catalytic performance of metal nanoparticles in metal-catalyzed reactions. We have recently demonstrated that surface properties of the carbon supports play a vital role in determining activity, selectivity and stability of Au catalysts. In this contribution, we will provide a detailed discussion on how and why the surface properties of carbon supports affect the performance of Au catalysts in the oxidation of 5-hydroxymethylfurfural, an important reaction for the production of bio-based polymers. Role of carbon support surface properties in other Au-catalyzed reactions, such as the gas-phase hydrogenation of butadiene, will be also mentioned.

Keywords: support surface effects, carbon materials, gold nanoparticles.

1. Introduction

Carbon materials are highly promising catalyst supports for metal nanoparticles, particularly for fuel cell catalysts and catalysis in the aqueous phase. Surface properties of carbon materials can greatly differ depending on the preparation method and post-treatments. For example, carbon surface can be easily functionalized by incorporating other elements, such as oxygen and nitrogen, which in turn would affect surface polarity and acid-base characteristics. These parameters are expected to strongly impact activity, selectivity and stability of supported metal catalysts. In this work, we investigated a series of similar 2–4 nm gold nanoparticles supported on high-surface-area graphite (HSAG) with different surface chemistries, but the same morphology, in the oxidation of 5-hydroxymethylfurfural (HMF) and hydrogenation of butadiene. We demonstrate that the surface properties of the carbon supports strongly impact the activity, selectivity, and stability of gold catalysts.

2. Experimental

A series of surface-modified high surface area graphite (HSAG, 500 m²/g, Timcal Ltd.) supports with different surface chemistries were obtained by functionalizing commercial HSAG, resulting in HSAG-ox (oxidation with HNO₃, 150°C), HSAG-H (reduction, 400°C), and HSAG-N (NH₃ treatment, 600°C). The four supports were characterized using XPS, N₂ physisorption, and mass- and acid-base titrations. Au catalysts were prepared by depositing 2-3 nm colloidal nanoparticles on these supports. The catalysts were characterized with TEM, XRD, ICP-MS and studied in the liquid-phase oxidation of HMF under basic conditions (Figure 1), as well as in gas-phase hydrogenation of butadiene.

![Figure 1. Oxidation of HMF to furandicarboxylic acid (FDCA).](image-url)

3. Results and discussion

Table 1 gives an overview of the surface properties (chemical composition, acid-base properties (point of zero charge, PZC; concentrations of acid and base sites)) and textural properties (surface area, pore volume and diameter) for the commercial and functionalized HSAG materials. A series of Au/HSAG-x
catalysts with similar particle sizes have been prepared by depositing 2-3 nm colloidal Au nanoparticles on these supports.

<table>
<thead>
<tr>
<th>Material</th>
<th>(S_{\text{BET}}), m(^2)/g</th>
<th>(V_{\text{pore}}), ml/g</th>
<th>(d_{\text{pore}}), nm</th>
<th>O/C (XPS)</th>
<th>N/C (XPS)</th>
<th>Acid sites, nm(^2)</th>
<th>Base sites, nm(^2)</th>
<th>PZC</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSAG</td>
<td>502</td>
<td>0.78</td>
<td>5.4</td>
<td>0.059</td>
<td>-</td>
<td>0.16</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td>HSAG-ox</td>
<td>443</td>
<td>0.64</td>
<td>5.8</td>
<td>0.145</td>
<td>0.005</td>
<td>0.54</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>HSAG-H</td>
<td>507</td>
<td>0.69</td>
<td>5.4</td>
<td>0.034</td>
<td>-</td>
<td>0.03</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>HSAG-N</td>
<td>506</td>
<td>0.70</td>
<td>5.5</td>
<td>0.013</td>
<td>0.009</td>
<td>-</td>
<td>0.09</td>
<td>9.9</td>
</tr>
</tbody>
</table>

Study of the Au catalysts for HMF oxidation showed that the activity (TOF\(Au\)) and the yield of FDCA strongly increased with the support PZC (Figure 2); on the other hand, Au catalysts supported on acidic HSAG (HSAG and HSAG-ox) were highly selective towards the intermediate HMFCa. Gold nanoparticles were substantially more stable on HSAG supports with lower concentration of surface oxygen groups, while Au nanoparticles on HSAG and HSAG-ox with oxygen-rich surfaces showed severe particle growth during reaction.

Figure 2. Activity and selectivity of Au/HSAG-x in HMF oxidation.

The observed differences in activity and selectivity between catalysts immobilized on modified HSAG supports primarily originate from the differences in the reactant and intermediate adsorption on the surface of the catalysts, as will be discussed in more detail in the conference contribution. Furthermore, a comparison of catalyst behavior as a function of carbon surface properties in a gas-phase reaction (hydrogenation of butadiene) will be given.

4. Conclusions

Surface properties of carbon materials have a strong impact on the performance of supported gold catalysts. A detailed discussion on the reasons behind such a strong impact, as well as guidelines for the rational design/choice of optimal carbon supports for highly active, selective and stable Au catalysts will be given in the conference contribution.

References