Distinct Characteristics of Hydrogenation and Hydrodeoxygenation on Anatase TiO_2 Supported Au Catalysts

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Abstract: Gold nanoparticles are capable of activating the surface of anatase TiO_2 (TiO_2-A)， in contrast to that of rutile TiO_2, for selective hydrodeoxygenation of phenyl oxygenates. Hydrogen spill-over from gold nanoparticles after dissociation of molecular H_2 is the dominant mechanism for the reduction of TiO_2-A. Au/TiO_2-A catalysts were capable of hydrogenating isolated and conjugated C=C and C=O double bonds, but not aromatics including phenolics and phenol ether. The catalysts showed ubiquitous hydrogenation and hydrodeoxygenation characteristics for dihydroxybenzene (catechol, resorcinol, and hydroquinone), both in activity and in product selectivity. The associated sites on Au/TiO_2-A for these reactions will be elucidated.

Keywords: Titania supported gold, hydrodeoxygegnation, active sites.

1. Introduction

Heterogeneous catalytic hydrogenation is the most important industrial application of supported metal catalysts. Transition metal nanoparticles are known to catalyze the additive hydrogenation of unsaturated double bonds (e.g. C=C and C=O) and aromatics (e.g. benzene, alkylbenzene, and phenolics). Hydrodeoxygenation of aromatic oxygenates such as quaiacol and dihydroxybene over supported noble metal catalysts typically involves hydrogenative saturation of the aromatic ring over the metal surface, followed by dehydration over the acidic site of the support, and further hydrogenation of the olefin over the metal site to saturated hydrocarbons. Recently, we reported that Au/TiO_2-A catalyzed the selective hydrodeoxygenation of guaiacol and catechol only to phenolics as the end products.[1] The catalyst does not catalyze the hydrogenation of aromatics. This work was aimed at identifying and differentiating the active sites in hydrogenation and hydrodeoxygenation on the Au/TiO_2-A catalyst.

2. Experimental

Gold particles of 3 nm was supported on an anatase TiO_2 (40 nm particle size) in 0.4wt% Au loading according to a published procedure.[1] Hydrogenation of isolated and conjugated C=C and C=O double bonds, as well as dihydroxybenzene (catechol, resorcinol, and hydroquinone) and their derivatives was conducted at 3.0 MPa of H_2 pressure and 280°C in a batch reactor. Normal tetradecane was used as a solvent. A typical reaction was hold for 3 h at 700 rpm agitation.

3. Results and discussion

The catalytic results of the 0.4wt% Au/TiO_2-A catalyst in the hydrogenation of the three dihydroxybenzene substrates, i.e. catechol, resorcinol, and hydroquinone, are strikingly different. As shown in Figure 1, in contrast to catechol which was selectively hydrogenated only to phenol, hydroquinone was hydrogenated to products of partial and full saturation of the aromatic ring, while resorcinol was not converted under the same reaction conditions.

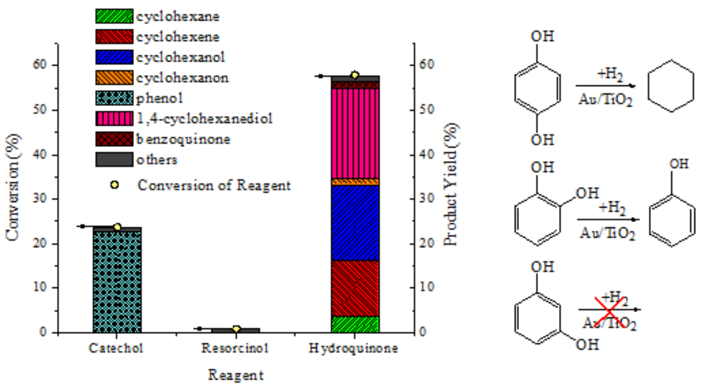

Figure 1. Hydrogenation of hydroquinone, resorcinol and catechol

Additional experiments showed that support played a critical role for the catalysts. Au nanoparticles supported on SiO_2, γ-Al_2O_3, and rutile TiO_2 were found inactive for the hydrogenation of hydroquinone. As expected, anatase TiO_2 alone was not an active catalyst. Evidently, anatase TiO_2 was the most critical as support for the Au catalyst. Experimental results on the hydrogenation of isolated and conjugated C=C and C=O bonds showed that the 0.4wt% Au/TiO_2-A was active for the hydrogenation of these unsaturated double bonds. However, the catalyst was not capable of hydrodeoxygenating primary alcohol.

4. Conclusions

The ubiquitous catalytic characteristics of the 0.4wt% Au/TiO_2-A catalyst are manifested by the results that it catalyzes the hydrogenation of isolated and conjugated C=C and C=C double bonds on the surface of Au nanoparticles, but the hydrodeoxygenation of catechol and guaiacol to phenol necessitates anatase TiO_2 as a support. Strikingly, the Au/TiO_2-A catalyst does not hydrogenate phenolics or phenol ether. Benzoquinone formed as a dehydrogenation intermediate from hydroquinone is a conjugated molecule of C=C and C=O and can therefore be hydrogenated sequentially to cyclohexane via various partial hydrogenation intermediates as shown in Figure 1.

References

1. J.B. Mao, J.X. Zhou, Z. Xia, Z.G. Wang, Z.W. Xu, W.J. Xu, P.F. Yan, K.R. Liu, X.W. Guo, Z. C. Zhang, **ACS Catal.**, *7* (2016) 695