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Investigating the effect of gold-palladium bimetallic nanoparticles on TiO2 and the catalytic activity in CO oxidation

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2013-04-29
http://hdl.handle.net/10539/12693

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Chapter 5

Conclusions

The numerous works on supported Au catalysts showed that these catalysts have superior activity for CO oxidation particularly at low or ambient temperatures as discussed in chapter 1. However, the high activity of these catalysts is governed by a lot of factors. In particular synthesis of the catalysts is crucial as there are various factors which play role in achieving highly dispersed active Au catalysts. Therefore the choice of preparation method and the choice of the support are also vital. The use of reducible supports such as TiO_2 enhances stability and activity of Au catalyst. It was also indicated that the small sized Au particles that are known to be highly active are best prepared via deposition-precipitation (DP) method. However, they rapidly deactivate at high temperatures due to particle sintering that results in formation large particle aggregates. To overcome the deactivation of the Au catalysts lot of researchers used modifiers and promoters. The use of bimetallic systems has also been studied.

In Chapter 2 of this work is presented a brief description of the deposition- precipitation (DP) method used to synthesize supported Au catalysts was presented. Furthermore the DP method was used to synthesize bimetallic catalysts in which Pd metal was incorporated as the second metal. The morphology and composition of these catalysts were characterized by techniques described in chapter 2. The activity of both monometallic and bimetallic catalysts was evaluated by CO oxidation reaction. The reaction conditions are described in chapter 2.

In this study, it was established that, to synthesize small Au particles, there are certain synthesis conditions had to be followed. It was found that during synthesis, factors such as Au loading, calcination temperatures, aging and pH affect the reproducibility of small sized Au particles. It was found that in order to obtain small sized Au particles uniformly dispersed on the support metal loading must be low. The XRD studies indicated that, as the Au loading was increased, the peak at 44.4° 2θ (corresponding to the Au (200) peak) grew broader indicating that there was decrease in particles size. TEM studies confirmed this finding, although the particle size obtained from XRD were larger.

BET studies showed an increase in surface area as the Au loading was increased. The increase in surface area suggests that there was a uniform dispersion of small sized particles. The obtained pore volume measurements decreased as Au loading increased suggesting the possibility of large Au particles blocking the pores. The 3% Au loading was found to be the optimum loading. Studies further indicated that the use of high pH results in small particles.

Preparation of Au catalysts at low pH, showed non-uniform dispersion of Au particles, as seen in TEM images in Chapter 3. There was clear evidence of big, black, lumpy particles on the TEM images observed at low pH suggesting that during synthesis an inhomogeneous distribution of ammonium across the sample may have occurred. The optimum pH obtained was pH 8 with particle size of 3.75 nm. However, pH 9 and 10 showed particles with 3.5 and 3.25 nm particle size respectively, which was smaller than the obtained particle size at pH 8. However, pH 8 displayed a bell curve indicating a normal distribution of the mean particle size distribution in which approximation of a sum of large random values clustered around one mean value can be made. High calcination temperatures affect the Au particle size with 200 °C showing the smallest sized Au particles. The similar effect on particle was also observed when the maturation or aging period of the catalyst was increased. This finding agrees with most of the researchers in the literature. Therefore the obtained optimum synthesis conditions of Au catalyst supported on TiO_2 in this study were: metal loading 3%, pH 8, calcinations temperature 200 °C and 3 days aging period.

SiO_2 was used as the support to evaluate the effect of the support on particle size of Au catalyst. The obtained particle size was 4.5 nm. However, it was observed that when pH was varied the particle size remained unchanged and surface area showed insignificant increase. However, change in pore volume was observed suggestion that Au particles were only occupying a small area. It was therefore established that the SiO_2 had an increasing effect on the Au particles size. HRTEM results showed that there was coalescence effect occurring where two particles were coming together to form one large particle. From this finding it is confirmed that the oxide support which in this study was TiO_2 has strong metal support compared to SiO_2. It can be concluded that TiO_2 as the support was able to suppress particle growth as small sized Au particles were obtained.

It has been established in this study that synthesis of Au-Pd/TiO_2 catalyst via DP method produced both Au and Pd metals separately attached on the support. Therefore DP method is

an inappropriate method for synthesizing bimetallic catalysts with Au and Pd. The XRD measurements showed that there was no PdO phase or Au-Pd alloyed formed. The absence of Pd peak from XRD diffractions resulted from low loading of Pd metal on the support. The presence of the Pd on the supported was confirmed by EDS study. Further studies by HRTEM confimed that the particles attached on the support had the interplanar spacing of 2.89 Å and 2.68 Å resembling both of Au and Pd metal respectively. However, both metals could not be distinguished by either colour or morphology suggesting that they occupy the same space and are therefore largely present as heterostuctured. Based on the obtained results it was concluded that the type of bimetallic system formed in this study was heterostructered bimetallic. Therefore it was established that synthesis of Au-Pd catalyst via DP method resulted in no formation of core-shell or alloyed Au-Pd particles on the support surface.

Catalytic evaluation measurements conducted, indicated that Au/TiO_2 had superior activity for CO oxidation. The superior activity was mostly observed at low temperatures with 95% CO conversion obtained at 200 °C. It was also established that the activity and stability of these catalyst deteriorated with increasing temperatures.TPD studies illustrated that less CO was adsorbed as temperature increased indicating that there was a decrease in adsorption sites. Therefore, the low activity observed at high temperatures was due to the availability of active sites. Furthermore the particle size increased as the temperatures increased.

The bimetallic catalysts showed low CO conversion compared with monometallic Au catalyst. Although the bimetallic catalysts showed low CO conversion compared to monometallic Au catalyst, there was an induction period observed for all Pd-containing catalysts. The highest CO conversion was observed for 25Au75Pd catalysts. The TPD studies conducted reveal that as the Pd loading increases there few active sites to adsorb CO. It was also observed that for both 25Au75Pd and 75Au25Pd catalyst the CO desorption peaks at 360 and 470 °C were absent. TEM results showed that as Pd loading increased the particle size decreased. Therefore it can be concluded that Pd metal was able to suppress particle growth. It was also obtained that as the temperature increased the stability and activity of the 25Au75Pd catalyst declined. A decrease in catalyst stability could be attributed to particle sintering. However, the cause of deactivation of bimetallic catalyst was not studied. Therefore incorporating Pd metal did not improve catalytic activity of Au catalyst.

5.2 Future Work

Future work that can be done on this work will be varying pH during synthesis of bimetallic catalyst. Additional characterization of the catalysts by Fourier transform infrared (FTIR) spectroscopy and X-ray photoemission spectroscopy (XPS) would be invaluable in aiding the understanding of catalyst surface properties and the nature of active sites in the catalysts which will enable to predict the catalytic mechanism of these catalysts . Deactivation studies need to be considered to examine the stability and robustness of the catalyst and establish their viability under real working conditions.