NANOSTRUCTERED CARBON CATALYSTS: EFFECT OF SURFACE CHEMISTRY AND POROSITY ON GOLD NANOPARTICLE ACTIVITY

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Introduction

The resurgence in carbon based materials for support of active metals has primarily centered on nanostructures and the ability to tailor properties as a means to optimize conversion efficiencies with reduced energy input. Unlike traditional porous graphitic materials, nanostructured carbons, such as carbide-derived carbons (CDC), carbon nanotubes (CNT) and graphene oxides (GO) enable greater utilization of sp^2-bonded carbon atoms and the ability to functionalize higher surface fractions to enhance interfacial interactions with metal particles. Since the initial discoveries by Haruta [1] and Hutchings [2] on the extraordinary activity of nanocrystalline Au particles on oxide supports, a major challenge remains in nanoscience to effectively manipulate and control molecular structures as a means to achieve optimal properties which can scale to functional materials. Control over metal particle size, structure, dispersion support interaction and stabilization are factors which are recognized as critical to successful development of these materials [3]. A particular area of interest is tailoring surface properties by use of ligand groups to promote favorable binding and to effectively direct dispersion of metal nanoclusters. Chemical ligands can exist as grafted entities, chemically bonded to the substrate, or distributed by means of dispersive forces influenced by the size of the substrate's pores. In this paper we present preliminary results on the growth and dispersion of low nanometer scaled Au particles (12-40 nm) on oxygen functionalized carbons produced from carbides (C_{CDC}) and bulk formed graphitic carbons (C_G). The objective is to obtain a systematic in-depth understanding of the role of surface moieties on activity of Au nanoparticles and its relationship to nanostructured carbon porosity.

Experimental

Two carbon sources were used in this investigation. One is a wood based carbon (SA-1500) provided by Meade-Westvaco and the second is a CDC derived from TiC. SA-1500 SSA is 1534 m^2/g with a micropore volume of 0.72 ml/g (determined by N_2 adsorption equilibria). Typical CDCs are synthesized by the selective extraction of metals/metalloids from metal carbides by high temperature chlorine etching, leaving behind the amorphous carbon with micro- or meso- pores [4]. We have successfully synthesized various CDCs with SSAs from 1000 to > 2000 m^2/g and pore sizes from 0.6 to >10 nm. Various structures with different SSAs and pore sizes can be obtained by changing the precursor, and can be further modified by varying the chlorination temperature, time, and other process variables. TiC is the most widely used precursor for CDC synthesis by reaction $TiC + 2Cl_2 = TiCl_4 + C$. Since $TiCl_4$ is a commonly used starting material for TiO_2 synthesis by hydrolysis and calcination, both porous carbon and TiO_2 can be produced in one process:
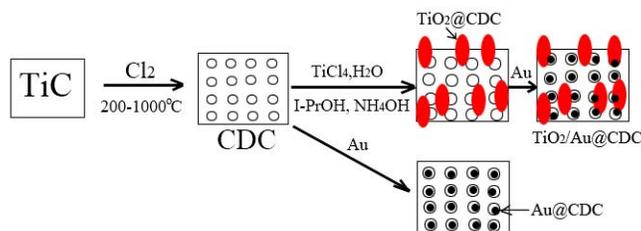
**Figure 1.** Schematic graph of catalytically active TiC-CDC

Functionalization of carbon: Carbon samples were quenched into 1:3 HNO_3:H_2SO_4 solution for ~2 hours. Sample was filtered with DI water for at least 3 times and dried at 100 ^{o}C. The sample is treated with 1-2 ml poly (diallyldimethyl-ammonium) chloride (PDADMAC, $C_8H_{16}NCl$, 20 wt%) polymer solution and ultrasonicated for 2 hours. Carbon sample was filtered and washed with DI water 3 times, followed by drying at 90 ^{o}C for 1 hour.

Loading TiO_2 nanoparticles on the carbons: 10g of carbon was added to $TiCl_4$/I-PrOH (~105ml), followed by 30 min vigorous stirring. The solution was filled with 300 ml DI water with 28.2 ml 10% NH_4Cl, followed by stirring for 30 min, vacuum filtration, drying at 100 ^{o}C for approximately 15 hours and calcination for 2-4 hours at 200 ^{o}C.

Synthesis of gold colloid: 0.0145 g hydrogen tetrachloro-aurate ($HAuCl_4$) and 10 ml DI water were mixed uniformly in a vial by stirring for 1 hour. The aqueous solution was heated to ~100 ^{o}C and 3 mL of sodium citrate (0.020g in powder) was added. The mixture was kept stirring until becoming dark red in color, then removed from the hot plate only to keep stirring for 2 hours. After cooling, the colloid was left to reach equilibrium in the refrigerator for future use.

Loading gold particles onto modified carbon or carbon/TiO_2: Gold and TiO_2 nanoparticles were deposited on carbon powders with loadings of ~3-15 wt%. The carbon modified sample with TiO_2 is added to the Au colloid solution with 1-2 hours of stirring. The solution is filtered and washed 3 times with DI water, followed by oven drying at 100 C.

Characterization and CO oxidation tests: Samples of carbon loaded with gold/titania were characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010F attached with an energy dispersive x-ray spectroscopy (EDS) detector from EDAX. The activity of the catalyst materials was measured by means of exposing a sample catalyst to a known concentration of chemical adsorbate (Figure 2). The system is a closed-circuit design and circulates a gas mixture through a bed of sample catalyst at fixed airflow velocities.
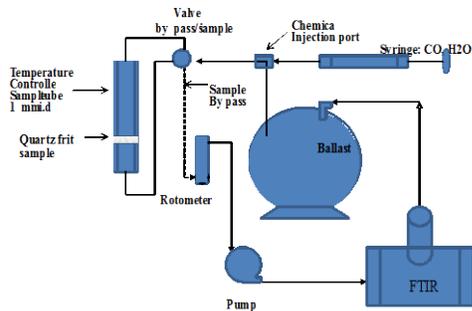
Figure 2. CO catalytic activity tests: Closed circuit recirculation apparatus

Results and Discussion

Au-C_G with enhanced catalytic activity toward CO. TEM image in Figure 3 displays a relatively uniform distribution of gold particles. The Au size and dispersion largely depend on the modification of gold colloid and C_G support. Most importantly, a more uniform distribution can be obtained by depositing gold particles at a smaller size.
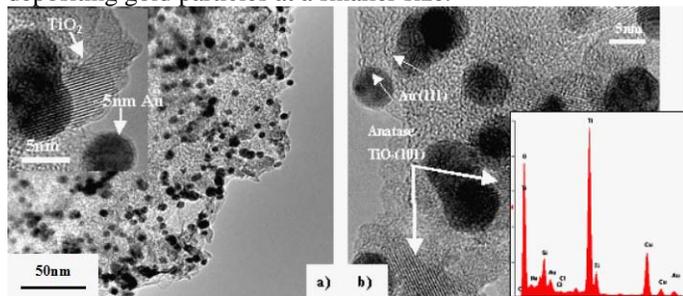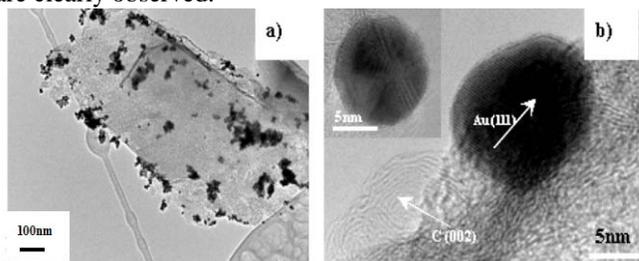

Figure 3. TEM images of 3wt% Au (5nm particles) and 10wt% TiO_2 (10 nm particles) on C_G-SA1500. Inset is an EDS spectrum.
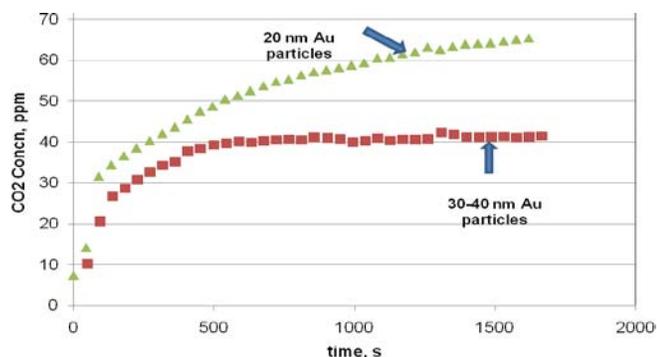
Figure 4. CO_2 concentration as a function of time. SA1500 (C_G/Au-3 wt%). The initial CO concentration is 1000 ppm. Humidity: 25% RH temperature 100 C.

As displayed in Figure 4, the decreased size of gold particles obviously improved the corresponding CO activity. When the size decreased from 30-40 nm to ~20 nm, the converted CO_2 concentration increased from 43 to 70 ppm (~ 4 and 7 % conversion).

Au particles loaded on C_{CDC} without TiO_2. The C_{CDC} was annealed at 1000 ^{o}C before it was used as a support. From the HRTEM image in Figure 5, the graphite fringes of C_{CDC} (002) are clearly observed.

Figure 5. TEM images of 3wt% Au (~12 nm) without TiO_2 on CDC.

The better graphite structure (CDC) strongly improved the stability of Au particle size/dispersion compared to the amorphous active carbon C_G. The ~12 nm gold particles were relatively uniformly distributed (Figure 5a). The CO activity of Au/C_{CDC} support showed a substantial improvement, (Figure 6), increasing the CO_2 concentration to around 210 ppm (21% conversion). The enhanced activity obviously confirmed that the C_{CDC} support is helpful for CO oxidation. However, the CO_2 concentration decreased continually when the time was over 500s, which means the catalyst is not very stable and needs to be further improved.
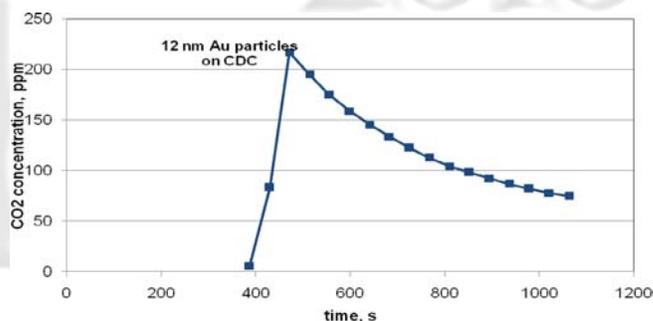
Figure 6. CO_2 concentration as a function of time.CDC (3 wt%) at 100 ^{o}C. The initial CO concentration is 1000 ppm. Humidity: 25% RH.

Conclusions

CDC nanostructured carbons demonstrate the potential for enhanced catalytic performance compared to bulk source graphite. CDC catalytic activity implies greater utilization of active Au sites resulting from increased microporosity.

References
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