

Ag-Pt bimetallic nanoparticles reduction catalysts: Effects of their metal alloying composition and H₂ evolution studies

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In the advancing field of nanotechnology, metallic nanoparticles (NPs) have gained a tremendous interest as heterogeneous catalysts and been well established as the subject of a wide research due to their promising use in catalysis.¹⁻³ Herein, we present a kinetic study of reduction reactions on Ag, Au, Pt metallic and Ag-Pt bimetallic alloy NPs that were synthesized in aqueous suspensions without using any stabilizer. Owing to the synergistic and alloying effects between the metals in Ag-Pt alloy NPs, those have shown superior catalytic performance in the reduction of 4-nitrophenol to 4-aminophenol by NaBH₄. In the bulk, an alloy of Ag and Pt has not been observed because of the vast immiscibility of these metals, whereas in the nanosized regime, the prepared Ag-Pt alloy NPs have not only shown higher catalytic efficiency than their mono-metals but also eliminated the induction time which was observed in the pure Ag NPs case. Kinetics studies of hydrogen evolution on all NPs were conducted in order to follow the reduction mechanism of the fastest Ag-Pt catalyst. High-resolution transmission electron microscopy (HR-TEM) and X-Ray powder diffraction (XRD) studies show that the silver-rich Ag-Pt alloy NPs have a spherical linked shape and confirm the structure of an alloy with the size of ~4.0 nm. Ag-Pt alloy NPs are also relatively low-cost catalysts as their one particular metal ratio composition presented the highest catalytic activity with a relatively low content of Pt. Supporting gold nanoparticles have shown to be extremely active for many industrially important reactions, including oxidations. Two representative examples are the oxidation of alcohols and alkenes, that are substrates of industrial interest, but whose oxidation is still challenging. This review deals with

these reactions, giving an insight of the first studies performed by gold based catalysts in these reactions and the most recent developments in the field. Heterogeneous catalysis by gold nanoparticles is now a “hot topic,” as it can have applications in several industrially and environmentally important oxidation reactions. Catalytic oxidations can be classified into two types complete (or total) oxidation, used for catalytic destruction of various toxic compounds, and selective oxidation, used for organic compounds in fine chemistry, aiming at the synthesis of desired chemical products.

Gold catalysts proved to be efficient for both types of oxidations, including oxidation of CO, hydrogen production by water-gas shift (WGS), hydrogen purification by selective oxidation of CO in the presence of H₂ (preferential oxidation, PROX), oxidative decomposition of volatile organic compounds (VOCs), selective oxidation of alcohols, hydrocarbons and sugars, among many others. Colloidal Au can be synthesized in solution in the presence of an excess of stabilizing (capping) agents/ligands or surfactants (which can be as thiols, amines, polymers, phosphines, etc). This provides control of the size and shape of the formed nanoparticles, preventing them from agglomerating. Colloids prepared by reduction of chloroauric acid by citric acid, NaBH₄, or other reducing agents, can be used to prepare gold on carbon or oxide supports, by deposition from the colloid, to give good dispersions of gold. Usually, a stabilizing agent is used in excess in order to effectively stabilize the nanoparticles. Then the colloids are deposited on the surface of the support to synthesize a heterogeneous catalyst. Thus, the stabilizing agent present in the colloidal solution might also form bonds with the support, and that can be detrimental as it might (partially) block the active metal sites (Donoeva and De Jongh,). Also, the

presence of stabilizing agents on the surface makes it more complicated to interpret catalytic results, since one does not know the effects they might have on the reaction (Niu and Li,). Polyvinylpyrrolidone (PVP) is one of the most commonly used stabilizing agents. Impregnation (IMP) is the classical method used to prepare supported metal catalysts and consists of simply impregnating a support with a solution of a metal salt. This usually involves suspending the support in a larger volume of solution, from which the solvent is then removed. An alternative variation is the so-called incipient wetness (IW) technique, in which the pores of the support are filled with the solution. Common gold precursors like chloroauric acid (HAuCl_4) or auric chloride (AuCl_3 or Au_2Cl_6) are usually used but complex salts, such as potassium aurocyanide (KAu(CN)_2) and the ethylenediamine complex $[\text{Au(en)}_2]\text{Cl}_3$, are also alternatives. Traditional supports are silica, alumina and magnesia, but titania, alumina, boehmite (AlO(OH)), ferric oxide ($\alpha\text{-Fe}_2\text{O}_3$) and magnesium hydroxide can also be used. After drying, the precursor needs calcination at temperatures as high as 800°C . Reduction by hydrogen at 250°C , aqueous oxalic acid at 40°C or aqueous magnesium citrate is also needed. However, Datye

and co-workers reported an alternative impregnation method for supporting gold on alumina using HAuCl_4 (Xu et al). Since impregnation under acidic conditions leads to poor dispersion of Au and the resulting catalysts are not very active, a two-step procedure has been developed: In the first step, gold chloride was adsorbed on alumina from an acidified solution. After washing off the excess gold precursor, the solid was treated with strong base to convert the chloride to an adsorbed hydroxide. Drying and calcining at 400°C yielded a catalyst with gold particles having an average diameter of 2.4 nm, with good activity, and stability to hydrothermal sintering

This new method is a successful impregnation preparative route for gold catalysts, allowing them to have durability at least until 600°C , since no chloride is present. The influence of the pH on the particle size of Au is remarkable, as above pH 6, the main species of Au in solution are transformed from AuCl_4^- to $[\text{Au(OH)}_n\text{Cl}_{4-n}]^-$ ($n = 1-3$), and the mean particle diameters of Au in the calcined catalysts become smaller than 4 nm. Several authors claim that a pH ranging from 7 to 8 is preferable depending on the oxide support.