Gold as a Catalyst

Brief Overview

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Abstract - **Gold catalysts have several advantages such as high catalytic activity, better selectivity and cost-effectiveness.However rapid deactivation of the gold catalysts is hindering further application of gold as a catalyst. This review paper summarizes main factors to influence catalytic activity of the gold catalysts, and potential causes and possible solutions for deactivation of the gold catalysts.**

Keyword - Gold Catalyst(s), Activity and Deactivation

I. INTRODUCTION

Traditionally, gold was considered as one of the most stable metals, consequently, was rarely attempted as a catalyst [1]. In 1987, Haruta *et.al* reported that very small gold particles supported on a few metal oxides are surprisingly active for the oxidation of the carbon monoxide at low temperature [2, 3]. This result overturned the conventional paradigm of the gold, and gained scientist's interest to exploring further application of gold as a catalyst [4, 5]. Currently, gold catalysts are one of the most widely studied catalysts in many oxidation reactions [6-8]. High catalytic activity with better selectivity of the gold catalysts not only reduces the cost for energy consumption in industry, but also it can solve many global environmental issues [9-11]. Many studies revealed that the gold catalyst would be excellent choice for reduction of the vehicle exhaust gases, removal of the volatile organic compounds (VOCs), ozone decomposition and the other pollution reduction reactions [4, 12-15].

Goldis the most abundant metal amongst the platinum group metals (PGMs). PGMs, especially platinum and palladium, have been the key catalysts for many important reactions. Unfortunately, scarcity of these metals is suppressing the development of many important industries [16-19]. Based on the achievement of acceptable technical performance, the use of gold has high potentials to replace the currently PGMs. The percentage of the gold in the catalyst is mostly very low. In most of reactions, the gold catalysts have exhibited excellent performance with only 1~3 w. % gold loading [6, 20, 21].

II. FACTORS AFFECTING THE GOLD CATALYSTS

Generally, the catalytic performance of the gold catalysts depends on physiochemical property of support, size and dispersion of goldparticles, oxidation states of gold and the properties of the gold-supportcontact surface, and thus strongly affected by preparation conditions such as nature of the support, morphology of the support, preparation method,pH and calcination temperature [22, 23].Following subsections describes the effect of these parameters in detail.

A. Effect of Nature of Support

Among the parameterswhich influence the catalytic performance of gold catalysts, the nature of the support ismost intensively studied [3, 7, 24-26]. Based on literature, nature of the support strongly affects the dispersion of gold particles, oxidation state of gold and gold-support interaction, which are directly correlated to the catalyticperformances of the catalyst[27, 28].

Different [12, 29-31] studies showed that gold catalysts supported on reducible metal oxides such as CeO_2, Co_3O_4, MnO_x and Fe_2O_3 are highly active for many oxidation reactions;whereas some insulated support such as Al_2O_3 and $SiO_2$are found to be less effective support for catalytic activity of gold catalysts on the same reaction[12, 32].

Catalytic activity difference between the gold catalysts supported on highly effective supports and less effective supports was found to be very large. One significant example is that the temperature for 50% conversion of propane on gold catalyst supported on alumina was found to be 200 $^{\circ}$C higher than that of gold catalyst supported on CeO_2[12].

B. Effect of Morphology of Support

Morphology, textural structure, crystal and particle size of the support also affects catalytic activity of the gold catalysts. Olea*et al* reported [33]that mesoporous supports for the gold catalysts are much more effective than microporous supports.Comparative studies also showed that the catalytic activity of the gold catalysts supported on nano sized ZrO_2 (particle size: 5~10nm) for CO oxidation six times higher than conventional ZrO_2[34]. Even larger effects have been found with CeO_2 that catalytic activity of the gold catalyst supported on nano sized $CeO_2$for CO oxidation 100 times was higher than the gold catalyst supported on conventional CeO_2 [35].

In summary, both catalytic activity differences between the gold catalysts supported on different supports and morphological properties of the support strongly affect the catalyticactivity of the gold catalysts.

C. Effect of Catalyst Preparation Methods

Three different preparation methods, such as impregnation [36, 37], co-precipitation [31, 38, 39] and deposition precipitation[12, 20, 21, 40] were mainlyused to prepare the gold catalysts.Among these three methods, impregnation method is not suitable for preparing of the gold catalyst, because of large gold particle size and a low affinity towards the metal oxides[4, 37, 41-43].

Deposition-precipitationmethod has been the most preferred preparation method for a wide range of various supports. This method is easy to keep all the active components, remained to be active and uniform distribution of gold [1, 37, 40].

Bamwendet al [37]reported that catalytic activity of the gold catalystprepared by deposition-precipitationis much higher than that of platinum based catalystfor CO oxidation.Whereas, gold catalystsprepared bythe impregnation method had showed less catalytic activity with respect toplatinum catalyst. Another comparative study showed that the temperature for the complete conversion of tolueneby Au-Cecatalyst prepared by co-precipitation is 200 °C higher than for the Au-Ce catalyst prepared by deposition-precipitation [29].

In summary, deposition precipitation method can be considered as the most appropriate preparation method to obtain highly active gold catalysts.

D. Effect of Calcination Temperature

Calcination is one of the basic steps in the catalyst preparation. Main role of the calcination for the gold catalysts is to produce a strong interaction between gold particles and supports [44-46]. Some impurities which remained on the catalysts can be also removed by calcination [47].

It has been found that calcination temperature is also very important parameterto influence the catalytic activity of the gold catalysts[48, 49].A proper calcination temperature leads to higher catalytic activity of the catalysts; however if the calcination temperature is too high, the gold particle size would become large, and the catalytic activity of the gold catalysts would decrease consequently[48].

The effect of the calcination temperature has been studied by many researchers [24, 49-52]. They concluded that there is optimum calcination temperature for the preparation of the gold catalysts. Until reaching the optimum calcination temperature, catalytic activity of the gold catalysts increases with increasing of the calcination temperature. If the calcination temperature is higher than the optimum calcination temperature, catalytic activity of the gold catalysts would rapidly decrease with increasing of the calcination temperature. It has been suggested that the optimum calcination temperature is different for the different support and the different reaction system [24, 52].

Some researchers recommended that calcination in hydrogen is more beneficial than calcination in air for activity of the gold catalysts. Main advantages of the calcination in hydrogen are (1) Producing a stronger gold-support interaction and less sintering ;(2) hydrogen removes chloride ion as HCl, so it can be prevented from chloride poisoning [47]. However the calcination in air is commonly used in most of the literatures, maybe because it is more convenient.

E. Effect of pH

One of the critical and difficult processes during the preparation of the gold catalysts is to control the pH of the solution properly. Because the pHvalue significantly affects the final dispersion of gold,removal of impurities, and consequently the catalytic activity of the gold catalysts[53, 54].

It was suggested that at lower values of pH, hydrolysis of the Au-Cl bond is very week [54]. Moreover the surface of the support is positively charged, and so it can adsorb more of negatively charged gold species. Therefore it produces not only a larger particle size, and also higher concentration of the chloride on the surface [53, 54]. If the value of pH is very high, the gold loading would be very low [53].

Several comparative studies on effect of the pH value were conducted. From the findings, it can be concluded that the pH range of 8~9 is the optimum pH value to obtain highly active gold catalyst [6, 53, 55, 56].

F. Effect of Other Parameters

In some cases, magnesium citrate has been added to the solution to obtain smaller goldparticles. There are several explanations for the role of magnesium citrate. According to Haruta et.al[54, 57], citrate not only acts as reducing agent, but also acts as a sticking agent which blocks the coagulation of the gold particles. According to Kung et.al [53], it is very useful to avoid the formation of gold clusters after drying and it can remove the chloride ions. In sum, better dispersion of gold particles can be achieved, and consequentlythe better catalytic performance of the gold catalysts can be obtained by adding magnesium citrate.

Effect of thermal pretreatment in different condition before the reaction has been also studied in the recent years. It was suggested that pretreatment of the catalysts in different gases affects the interaction between gold species and support, and consequently affects the catalytic activity of the reaction [58-60]. Comparative results showed that pretreatment of gold catalysts with reducing gases such as hydrogen in nitrogen, carbon monoxide in helium could produces much higher catalytic activity with respect to pretreatment with air only[24, 61].

One of the important concerns for the gold catalysts is storage of the catalysts. Because of sensitivity of the gold catalysts to light, it was strongly recommended that not only exposure of the gold to light should be minimized during the preparation of the gold catalysts, but also the catalysts should be stored in the dark, ambient condition[62]. Comparative result on deactivation of the gold catalysts during the storage in different condition revealed that the deactivation of the catalysts stored in the bright condition is much faster and much higher than the catalysts stored in the darkcondition [63].

III. POTENTIAL CAUSES OF DEACTIVATION OF GOLD CATALYSTS

The main problem of using gold as a catalyst is its instability. Namely, deactivation of the gold catalysts is more rapid than the other platinum group catalysts [64, 65]. Although, the origin of the deactivation has yet not been clearly understood, it has been concluded that deactivation of the catalyst might result from the following aspects:

- Growth of the gold particle size by sintering;
- Poisoning of the catalysts by chloride;
- Blocking of the active sites by unreactive species;
- Reduction of oxidized gold species.

Each of these aspects is discussed below.

A. Growth ofGold Particle Size by Sintering

At higher temperature, the goldparticles can easily sinter, leads to the agglomeration of the gold particles, and consequently growth of the gold particle size [66, 67]. As gold particle size is the most important for the catalytic activity of the gold catalysts. Therefore, an increase in gold particle size could lead to a decrease catalytic activity of the gold catalysts.

B. Poisoning of the Catalyst by Chloride

So far, chloride containing precursors have been generally used for preparation of the gold catalysts. However residual chloride is very detrimental that could act as a catalyst poisoning. It has been found that chloride not only accelerates the agglomeration of the gold particles, but also it inhibits the catalytic activity of the gold catalyst by poisoning the active site of the catalysts [42, 56, 68].

C. Blocking of Active Sites by Unreactive Species

During the oxidation of hydrocarbons water and other unreactive species are formed, that could easily block the active sites of the catalyst, a potential reason for the decrease in the catalytic activity of the catalyst [69-71]. In addition, presence of many unwanted species, such as chloride, can also block an active sites of the catalysts[54, 68].

D. Reduction of Oxidized Gold Species

Another reason for deactivation of the gold catalyst is reduction of oxidized gold species that play a key role for the high catalytic activity of the gold catalysts. Studies on the oxidation state of the gold showed that both of metallic gold and oxidized gold species were present in the fresh gold catalyst. However, only metallic gold species or very little amount of oxidized gold species, are present in the deactivated gold catalyst [70, 72].

IV. POSSIBLE SOLUTIONS FOR DEACTIVATION

A. Using Mixed Oxides as a Support

Sintering of the gold particles can be inhibited by strong interaction between the gold and the support[6, 73]. It has been strongly suggested that mixed oxides could be more preferable as a support that one could stabilize the gold particles against sintering, and another one could bring high catalytic activity for the catalyst[74, 75]. Geisel et.alinvestigated the effect of mixedoxides as a support to the performance of the gold catalysts on CO oxidation. They used single metal oxide and mixed metal oxide as a support for the catalyst preparation. They found that the catalyst supported onmixed metal oxideexhibits higher catalytic activity and better stability as compared to gold catalyst supported on single metal oxide[23].

B. Removing Of Chloride When Chloride Containing Precursors Is Used

As it is mentioned above, chloride is very harmful for both activity and stability of the catalysts. Although most of chloride are hydrolyzed, and removed through washing water, some chloride still remains on the catalyst. One effective method to completely remove the chloride would be washing with ammonia solution[76, 77]. But when using ammonia, safety problem should be concerned. Another way is calcination of the catalyst in hydrogen which is mentioned above.

C. Using Chloride-Free Precursors

Preparing the gold catalysts from the chloride-free precursors would be the most desirable method to enhance stability and catalytic activity of the gold catalysts. There is sufficient evidence that some chloride-free precursors are very potential for preparation of gold catalysts. One significant example is that small particle sizes and high catalytic activity has been obtained for the catalyst prepared by impregnation using chloride-free precursors [33, 54, 78]. However this method produces large particle size and low catalytic activity for the gold catalysts prepared by using chloride containing precursor [41, 54].

V. SUMMARY

Currently gold catalyst has become one of the most widely studied catalysts, due to its high activity for many oxidation reactions at low temperature, better selectivity and cost-effectiveness. Numerous studies showed that nature of the support, preparation method, pH, calcination temperature and other pretreatment conditions strongly affect surface property of the catalyst, oxidation state, size and dispersion of gold particles, and ultimately affect catalytic performance of the gold catalysts.The main problem for using the gold as a catalyst is that the deactivation of the gold catalysts is faster than the other platinum group catalysts, which might result from growth of particle gold sizeby sintering, poisoning of the catalysts by chloride, blocking of the active sites by unreactive species and reduction of oxidized gold species. It has been suggested that stability of the gold catalyst can be enhanced by using mixed oxide as a support, removing of chloride and (or) using chloride-free precursors.

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