

Editorial

New Trends in Gold Catalysts

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1. Background

Gold is an element that has fascinated mankind for millennia. The catalytic properties of gold have been a source of debate, due to its complete chemical inertness when in a bulk form, while it can oxidize CO at temperatures as low as ~200 K when in a nanocrystalline state, as discovered by Haruta in the late 1980s [1]. Since then, extensive activity in both applied and fundamental research on gold has been initiated. The importance of the catalysis by gold represents one of the fastest growing fields in science and is proven by the promising applications in several fields, such as green chemistry and environmental catalysis, in the synthesis of single-walled carbon nanotubes, as modifiers of Ni catalysts for methane steam and dry reforming reactions and in biological and electrochemistry applications. The range of reactions catalyzed by gold, as well as the suitability of different supports and the influence of the preparation conditions have been widely explored and optimized in applied research [2]. Gold catalysts appeared to be very different from the other noble metal-based catalysts, due to their marked dependence on the preparation method, which is crucial for the genesis of the catalytic activity. Several methods, including deposition-precipitation, chemical vapor deposition and cation adsorption, have been applied for the preparation of gold catalysts over reducible oxides, like TiO₂. Among these methods, deposition-precipitation has been the most frequently employed method for Au loading, and it involves the use of tetrachloroauric (III) acid as a precursor. On the other hand, the number of articles dealing with Au-loaded acidic supports is smaller than that on basic supports, possibly because the deposition of [AuCl₄][−] or [AuOH_xCl_{4-x}][−] species on acidic supports is difficult, due to their very low point of zero charge. Despite this challenge, several groups have reported the use of acidic zeolites as supports for gold. Zeolites are promising supports for Au stabilization, because of the presence of ion-exchange sites, such as NH₄⁺, that can be substituted by Au⁺ ions through the elimination of NH₄Cl [3]. Moreover, zeolites, due to their high thermal stability, the presence of a large surface area and micropores, may hinder Au sintering.

A very general phenomenon related to gold samples is the extreme dependence of the catalytic activity on the size of the Au particles, which also implies that sintering is very crucial for the long-term stability of the catalysts. These features make Au very different from classical catalysts based on transition metals, such as Pt or Pd, which are also active as larger particles and even as macroscopic single crystals. The achievement of a small particles size is not always an easy task, because of the low melting point of gold as compared to that for Pd and Pt. Another relevant aspect that must be considered, looking at the application of gold catalysts, is that both the activity and stability of these systems strongly depend on the structure of the support, as well as on the specific interaction between the gold and the support, giving rise to a synergistic effect. The size, composition, electronic structure and facet structure of gold and reducible oxides are important factors in determining their catalytic performance. In particular, creating Au-reducible oxide interfaces leads to enhanced catalytic performance. For example, metal-oxide interfaces (e.g., Au-TiO₂, Au-Fe₃O₄) have been found to enhance catalysis in CO oxidation [4]. The occurrence of a strong metal-support interaction through the formation of oxygen vacancies in reducible oxides, like TiO₂ and CeO₂, is unanimously recognized by the scientific community as one of the reasons for the enhanced activity [5,6]. Moreover, it should not be forgotten that TiO₂ as a reducible oxide can form sub-stoichiometric and fully-stoichiometric defects on the surface that are good nucleation sites for gold nanoparticles [7].

2. The Present Issue

I am honored to be the Guest Editor for the second time of a thematic issue published in the *Catalysts* journal.

I would like to thank especially Shu Kun Lin, President and Publisher, as well as Keith Hohn, Editor-in-Chief, and Mary Fan, Senior Assistant Editor. I am also grateful to Martyn Rittman, Production Editor, and to the entire staff of the *Catalysts* Editorial Office, who productively collaborated. Furthermore, I would like to thank all of the authors contributing their papers to this issue for their excellent work. It comprises three reviews and five research articles. As pointed out in the background, the meaning of this second issue is to underline the actual new trends in Gold Catalysts. With this aim, special attention has been paid to the various properties of gold nanoparticles, as well as to the most recent commercial and industrial applications, beyond the classical catalytic investigations.

In the first review article by Homma, the catalysis by gold for the synthesis of single-walled carbon nanotubes (SWCNTs) by chemical vapor deposition is discussed [8]. Interestingly, in spite of the low solubility of carbon in gold, nanoparticles smaller than 5 nm catalyze the synthesis of carbon tubular structures. Thanks to the inertness and high vapor pressure of gold, the diameter and chirality control of SWCNTs is achieved.

The second review by Heddle covers aspects related to the manifold interactions between gold nanoparticles and biological molecules [9]. Gold nanoparticles are well known as catalysts in organic chemistry, but much is unknown regarding their potential as catalysts of reactions involving biological molecules, such as proteins and nucleic acids. This is a very complex field, which remains open to important potential discoveries.

In the third review by Wu *et al.*, the progress in the synthesis, characterization and activity of Ni catalysts modified by gold for low-temperature steam reforming of methane is addressed [10]. Although there is a discrepancy between the results reported by different authors on the effect of gold on the catalytic activity of Ni-based catalysts, as a function of the support, preparation method and Au/Ni atomic ratio, it seems to be confirmed that the addition of gold improves the resistance of the Ni towards deactivation, due to coke deposition. These findings are fundamental in the design of new catalysts with a tailored gold effect on the activity and long-term stability.

Among the research articles herein presented, three papers deal with the synthesis, characterization and catalytic activity of gold-supported catalysts [11–13]. In particular, Genty and coworkers have investigated the influence of gold on X_6Al_2HT (where $X = Mg, Fe, Cu, Zn$) hydrotalcite-like (HT) catalysts for CO and toluene total oxidation [11]. An interesting way to obtain mixed oxide catalysts is the use of hydrotalcite precursors. Indeed, HT compounds are a class of layered, double hydroxides that, after calcination treatment, form mixed oxides with high specific surface areas and porosity, as well as good thermal stability [14]. Many studies have established that nanosized Au over reducible oxide catalysts has a remarkable catalytic activity for oxidation reactions [15]. However, in the literature, only a few works have discussed the VOC oxidation activity of Au on HT-like catalysts [16]. In the quoted article, Genty *et al.* have demonstrated the beneficial effect of gold on the oxidation activity of CO and toluene over X_6Al_2HT compounds [11]. A correlation between catalytic properties and reducibility was observed.

Catalytic results discussed in the present issue clearly point out that metal oxide-supported gold systems are receiving growing attention as catalysts for catalytic applications, both from academic and industrial points of view. However, if gold-based catalysts are ever to find commercial applications on a large scale, their long-term stability must be improved. The investigation of the procedures leading to the preservation of the catalytic performances of gold catalysts supported on zirconia and sulfated zirconia have been investigated in detail by Signoretto *et al.* [12]. Three potential causes of deactivation, namely particle growth by the sintering of gold nanoparticles, metal leaching and the formation of un-reactive species, which inhibit the reaction, have been recognized. The catalysts' deactivation has been evaluated under different conditions: (1) storage conditions; (2) with time on stream for the water-gas shift reaction (WGS); and (3) with time on stream for furfural oxidative esterification. The beneficial effect of sulfated zirconia in gold stabilization has been highlighted. In fact, even if sulfates are not present in the final catalyst, they act in the synthesis step increasing both, surface area and gold dispersion. Moreover, the calcinations pretreatment is an essential procedure for improving stability of Au/ZrO₂ catalysts.

Sanada *et al.* reported on the synthesis and catalytic activity of thermally-stable Au nanoparticles on ultrastable Y (USY) zeolites [13]. Au was successfully loaded on the NH₄-form Y-type zeolite to yield 1.7 nm-sized Au₂O₃ along with the formation of NH₄Cl. Interestingly, the formation of 1.8–3.7 nm Au particles was observed after thermal treatment at 773–973 K. Partial oxidation of benzyl alcohol in the liquid phase was employed as the test reaction. The catalytic activity of the Au/USY zeolites showed good correlation with the Au dispersion. The highest activity was attained with the Au/USY treated at 773–973 K. This study has demonstrated the potential use of the NH₄-form of USY zeolites for supporting Au.

The importance of the Au-support interaction in the stabilization of Au nanoparticles was addressed by Park and co-workers [17]. They presented a comparative study of various defects formed on TiO₂ (110), such as sub-stoichiometric and stoichiometric defects. The role of such defects as nucleation sites for the initial adsorption of Au was demonstrated by using two different approaches: scanning tunneling microscopy (STM) and density functional theory (DFT). Among intrinsic defects, oxygen vacancy has been the focus of intense investigations on the reduced surfaces of TiO₂ [18,19]. It may be regarded as the simplest form of surface defect, created upon the loss of oxygen. However, a growing number of experiments have indicated that the presence of oxygen vacancy is not the only major characteristics of reduced TiO₂ surfaces. Besides oxygen vacancy, the experimental and theoretical studies all point to the significance of Ti interstitials and their role in forming surface defects during re-oxidation [7]. These defects can influence surface chemical reactivity with their distinct bonding geometry, local electronic structures and charge re-distribution at various sites around the defects. For gold chemisorption, bonding of Au is greatly enhanced at the sub-stoichiometric strand defect by electron transfer to Au and the formation of anionic Au^{δ-}. These findings highlight the importance of surface restructuring driven by Ti interstitials and locally-modified chemical reactivity.

Another important aspect, which, in my opinion, should deserve further research studies, concerns the optical properties and optical sensing applications of gold nanostars. An important example is herein reported by Chirea [20]. Gold nanostars are multibranching nanoparticles with multiple plasmon resonances, of which the lower energy ones, corresponding to the nanostar tips and core-tip interactions, are the most sensitive to environmental changes [21,22]. The electrocatalytic properties of gold nanostars could be also strongly influenced by their sensitivity to environmental changes. Their unusual shape could bring different contributions to the electron transfer processes, due to different sizes existent in their structure. In the present work, Chirea demonstrated that gold nanostars (AuNS) of a 70-nm tip-to-tip distance could be excellent electrocatalysts, if covalently self-assembled as dense layers on 1,5-pentanedithiol-modified electrodes. These findings make them great candidates for the fabrication of energy storage devices, electrochemical sensors or biosensors.

In conclusion, I personally feel that the present issue “New Trends in Gold Catalysts” is of great interest and relevance, as it covers all of the new aspects of gold catalysis, from those typical of environmental catalysis to new applications in biology, for sensors and electro-catalysis.

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