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Review

Recent advances in silver-based heterogeneous catalysts for green chemistry processes

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ABSTRACT

Silver-based heterogeneous catalysts play an important role in the catalytic elimination of environmental pollutants, production of clean energy, fuel distillation and the synthesis of highly value chemical intermediates. Most silver catalysts are mainly applied in the following four domains: chemo-selective oxidation, hydrogenation, photo-catalysis and electro-catalysis. The development of Ag-based heterogeneous catalysts would definitely contribute to the environment improvement and efficient utilization of energy resources. It would also help balance environment concerns with economic development. This mini-review gives an overview of recent progress in silver-based heterogeneous catalysts for four green chemical processes.

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1. Introduction

With increasing importance being placed on energy and environmental issues, more and more green chemical processes are urgently needed to meet the challenging green requirements, especially in the catalysis industry. So-called green chemistry approaches have significant potential not only for the reduction of byproducts and energy consumption, but also for the development of new methodologies toward previously unobtainable materials using existing technologies. Green chemistry promotes environmental and economic prosperity coupled with sustainable chemical methodologies. Catalysis is one of the key underpinning technologies on which new approaches to green chemistry are based. Recently, significant progress has been made in several key fields including green catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable feedstocks such as biomass. In all, it is necessary to design catalysts and catalysis processes with environmental considerations in mind.

Redox processes such as selective hydrogenation and oxidation are two of the key synthetic steps for the activation of a broad range of substrates. They are used for the production of either final products or intermediates. Molecular hydrogen and oxygen are good industrial options for hydrogenolysis and oxidation, respectively

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because of their high atomic economy. However, H_2 has to be activated on the surface of a heterogeneous catalyst prior to reaction under typical conditions. The O_2 however, is a di-radical in its groundstate and can participate in radical processes readily, even under very mild reaction conditions. However, the industrial application of the Ag based heterogeneous catalysts is scarce which is mainly confined to the epoxidation of ethylene, methanol oxidation to formaldehyde or other oxidation reactions [1]. Furthermore, Ag based catalysts, which own the catalytic reduction properties, also exhibit superb catalytic performances in the field of hydrogenation process, photocatalytic reaction and electro-catalysis. In this review, the interaction between silver and H_2/O_2 is given to better understand the silver-based heterogeneous catalysis.

Silver is a group IB transition metal with a $4d^{10}5s^1$ electronic layer structure. Silver-based materials with different morphology (nanobar, nanocubic, nanosphere etc.) have been a popular functional materials applied in many fields especially for heterogeneous catalysis due to its specific physical and chemical structure. However, compared with a research on gold nanoparticle catalysis, less attempts [1–12] have been focused on the catalysis of silver clusters or nanoparticles and structure–performance relationship of these catalysts. The performance of silver catalysts depends strongly on their surface structure and surface sites, which are very sensitive to the preparation method, pretreatment or reaction conditions, and the size of silver nanoparticles. Compared with other metals, such as nickel, palladium and platinum, silver is lack of affinity toward H_2 due to the filled d-band. Theoretical calculation [13–15] shows that the hydrogen interacts only very weakly with extended silver surfaces (single crystals, polycrystalline surfaces), and no dissociative chemisorption could occur at low temperature, which was attributed to the completely filled d-band of silver as well as the position of the d-band center relative to the Fermi level. However, pretreatment of silver in O_2 atmosphere would affect the interaction of silver with hydrogen. In other words, the activation of silver catalysts is often regarded as a result of the presence of various Ag-O interactions, for example, the molecular surface and subsurface oxygen atoms, etc. [16,17] In addition, due to its surface plasmon resonance (SPR) (When a noble metallic-nanoparticle is excited by light, the oscillating electric field of the light interacts with the conduction electrons.), a strong oscillation of these electrons happens when the incident photon frequency is resonant with the collective oscillation of the conduction electrons. Such resonance is called localized surface plasmon resonance. For metallic nanoparticles, the silver nanoparticles have also been applied widely in the field of photocatalysis.

In this review, a selection of the most recent advances in the field of silver-based heterogeneous catalysts for green chemistry process gives experimentalists a proper guide and overview to silver catalysis.

2. Environmental catalysis

2.1. Green oxidation catalysis

Silver-based materials are an outstanding catalyst for many catalytic oxidation reactions, such as ethylene epoxidation [18], formaldehyde synthesis [19], NO_x abatement [20], the selective catalytic oxidation of ammonia [21], partial oxidation of benzyl alcohol [22], the oxidative coupling of methane [23], the oxidation of styrene [24], the selective oxidation of ethylene glycol [25] and CO oxidation [26–30]. The surface and subsurface oxygen atoms found by Ertl and Schlögl were investigated to be the active sites for Ag catalysts in many oxidation reactions [31–34], and different pre-treatment atmosphere and temperatures affect the formation of subsurface oxygen and activated silver catalysts. It is understood that oxygen pre-treatment at high temperature results in the formation of subsurface oxygen that then activates silver catalysts [35,36]. The role of different silver species has also been studied, and Ag^0 as an active species was found to enhance the catalytic activity at low temperature (<140 °C). In contrast, Ag^+ could be the active species at temperatures about 140 °C on Ag/Al_2O_3 for the selective oxidation of ammonia to nitrogen [21]. The conversion of NO to N_2 was enhanced on the reduced silver species resulting from thermal-induced changes in silver morphology for NO_x abatement [20].

The catalytic oxidation of CO to CO_2 at low temperature is an important subject for environmental protection. It has widespread applications in air purification for buildings or vehicles and in reformer gas for fuel cell plants [26–30]. The Ag/TiO_2 catalysts have shown 50% CO conversion at 60 °C. Higher activities for CO oxidation at 100 °C over Ag/Mn/perovskite have also been obtained. Even 90% CO conversion at 126 °C could be obtained via Ag/α-MnO_2 [26]. Recently, Au-Ag alloy catalysts prepared by a unique deposition-precipitation method or the post-graft method showed better catalytic activity for CO oxidation at room temperature [27–29]. Liu et al. [30] reported that highly dispersed silver catalysts with mesostructured silica supports by a one pot synthesis approach exhibited 100% CO conversion at room temperature. Zhang et al. [37] studied the influence of pretreatment conditions on the catalytic performance of CO oxidation over Ag/SiO_2 and concluded that oxygen-containing Ag species might be the active species and silver particle size ca. 4.5–5.5 nm would be favorable for the low temperature CO oxidation. In addition, Hu et al. [38] developed the Ag/OSM-2 catalyst with a cryptomelane type structure via a reflux approach for the selective oxidation of CO in the hydrogen rich steam. In long term stability testing under realistic reaction conditions, 100% CO conversion can be maintained for 250 h at 120 °C with 90% selectivity.

Formaldehyde is an important chemical intermediate and is extensively used for the synthesis of value-added chemicals such as ethylene glycol, glycolic acid, dyes, and drugs. The synthesis of anhydrous formaldehyde via the direct dehydrogenation of methanol is a promising approach, and the development of highly efficient catalysts is of great importance. Silver-based catalysts seem to be a good choice for the direct dehydrogenation of methanol [39–42]. The $Ag\text{-}SiO_2\text{-}Al_2O_3$ material prepared by our group seems to be a powerful catalyst for the selective oxidation of methanol with excellent stability in methanol oxidation and no appreciable deactivation or structural changes even after reaction for more than 140 h [19]. It is noted that methanol adsorption on the surface of pure silver is insignificant but is facilitated by the presence of small amounts of oxygen in the reaction mixture. It is commonly accepted that there are various oxygen species formed on the silver surface after the adsorption of oxygen [43,44] such as weakly bound atomic species (O^α), bulk dissolved species (O^β) and strongly bound species (O^γ). Oxygen—usually termed the subsurface oxygen species—is the most stable species at high reaction temperatures and dehydrogenates methanol to anhydrous formaldehyde.

Many types of silver catalysts are used in the process of direct dehydrogenation of methanol to anhydrous formaldehyde. A catalyst made of silver gauze with an additional, electrolytically deposited silver layer [45] shows 84% formaldehyde yield at 800 °C and an elevated pressure in the gas–vapor mixture. Similar results can also be obtained (78%) when the dehydrogenation of steam-diluted methanol is performed at 620 °C in the presence of silver on copper gauze [43]. In addition, eutectic Ag_3Cu_2 alloy granules (0.8–2.4 mm) were also tested as a catalyst in the dehydrogenation of nitrogen diluted methanol [44]. However, sintering of the alloy is observed when a high formaldehyde yield (60%) is attained. A more stable $Ag_{97}Cu_2Si$ catalyst giving a 58% formaldehyde yield