Bimetallic Ag–Ir/Al$_2$O$_3$ catalysts prepared by electroless deposition: Characterization and kinetic evaluation

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A B S T R A C T

A series of alumina-supported Ag–Ir bimetallic catalysts having controlled and incremental coverages of Ag have been successfully prepared in an optimized electroless deposition bath. The starting monometallic Ir/γ-Al$_2$O$_3$ catalyst was highly dispersed (volume-surface mean diameter of 1.1 nm) with a narrow particle size distribution, as demonstrated by H$_2$ chemisorption and scanning transmission electron microscopy (STEM). While both catalytic (Ag on Ir) and autocatalytic (Ag on Ag) deposition were observed, coverages of Ag on Ir (measured by H$_2$ chemisorption) were successfully varied up to θ_{Ag} = 0.85 by varying Ag weight loadings up to 0.81 wt.%. In situ transmission Fourier transform infrared spectroscopy (FTIR) of CO adsorption demonstrated that the Ag is indiscriminately deposited on all types of Ir surface sites during the ED process. Kinetic studies of CO oxidation revealed that higher coverages of Ag resulted in higher turnover frequencies. Comparison of reaction orders in CO and O$_2$ on monometallic Ir and the most active bimetallic catalyst (θ_{Ag} = 0.37) suggests a bifunctional effect, where Ag provides a non-competitive source of adsorbed oxygen for reaction with CO adsorbed on Ir. In addition, further increases in TOF at higher Ag coverages argue for the presence of a geometric effect on smaller Ir ensembles.

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1. Introduction

An increasing number of investigations have shown the advantage of employing bimetallic alloys in catalysis to provide enhanced selectivity, stability, and/or activity [1–4] for a variety of reactions. These bimetallic catalysts are typically prepared by either co-impregnation or successive impregnation of both metal salts onto the catalyst support [5]. However, these traditional methodologies often provide inadequate control over structure, yielding catalysts containing both isolated, monometallic particles, and bimetallic particles with varying compositions [6,7]. This complex mixture results in poor control over the final catalyst performance, complicates catalyst characterization [8], and makes it very difficult to directly correlate the relationship between catalyst composition, characterization, and performance. Thus, new and reproducible methods are required for rational bimetallic catalyst design.

An alternate, industrially feasible method for the preparation of bimetallic catalysts is electroless deposition (ED), where a controlled chemical reaction is used for selective deposition of

reducible metal salts onto catalytic metal sites that have been activated by a reducing agent. Depending on the nature of the activated metal site, the process can involve deposition of the metal salt [A$^+$] from solution either onto the pre-existing metal [B^0] on the support (catalytic deposition) or onto the just reduced, deposited metal [A^0] (autocatalytic deposition) [9]. In principle, this ED method should result in the selective deposition of the secondary metal on the surface of a monometallic catalyst without formation of isolated crystallites of the secondary metal on the catalyst support. A more detailed description of this process has been published elsewhere [10].

The catalytic oxidation of carbon monoxide has been studied extensively due to its application for removing CO from the waste gas of automotive combustion [11,12], use in active filters of gas-masks [13], and for a variety of remote sensing applications [14–16]. The catalysts adopted consist mainly of oxides with variable oxidation state of the metal ions [17] and of supported noble metals on oxides [18,19]. Especially, the oxidation of CO on platinum group metals has been studied extensively, and the reaction mechanism has also been thoroughly investigated over these catalysts [20–25]. A high activity for CO oxidation at higher reaction temperatures (150–250 °C) can be obtained on Pt catalysts; however, the competitive adsorption of CO and O$_2$

decreases their low temperature activity [26,27]. On the other hand, more recently, oxide-supported Au nanoparticles have attracted considerable attention for the reaction of CO oxidation [28,29] due to their high catalytic activity at low temperatures [30]. Iridium, however, has not as often been considered as the catalyst for this reaction although it is situated among the same 5f orbital metals as Pt and Au. Therefore, this investigation explores the use of Ir-based bimetallic catalysts for the CO oxidation reaction. As the second metal, Ag was chosen due to the fact that silver metal has been extensively and successfully used for partial oxidation reactions, in which the silver–oxygen interaction is considered as a key step to explain the catalytic activity [31].

In this work, a series of Ag–Ir bimetallic catalysts has been synthesized to illustrate the effectiveness of the electroless deposition method to tune bimetallic surfaces for different catalytic purposes. The levels of Ag deposition have been intentionally limited to sub-monolayer coverages on the Ir surface, as verified by selective H_2 chemisorption and FTIR of CO adsorption on the Ir component of the Ag–Ir bimetallic surface. Catalytic CO oxidation on the ED-derived Ag–Ir/Al_2O_3 bimetallic catalysts are compared to those obtained for Ir and Ag monometallic catalysts prepared using traditional incipient wetness methods. It was found that the difference in the structures of these series of bimetallic catalysts affected their catalytic performance, especially in terms of intrinsic activity of Ir metal. The targeted and efficient Ag placement on the Ir surface in the ED-derived Ag–Ir/Al_2O_3 bimetallic catalysts induces dramatic changes in intrinsic activity.

2. Materials and methods

2.1. Catalyst preparation

The electroless deposition of Ag on Ir/Al_2O_3 was conducted using an aqueous bath of de-ionized (DI) water (made using Milli™-Q system), potassium silver cyanide, KAg(CN)$_2$ (54 wt.% Ag) supplied by Technic, Inc. as metal precursor, hydrazine (35 wt.% N_2H_4 solution, Sigma–Aldrich) as the reducing agent, and NaOH (EM pellets, 97% assay) to adjust pH. Metal salt/reducing agent molar ratios of 1:5 were used and the Ag deposition was conducted at room temperature (RT). Typically, the electroless bath volume was 100 ml for 0.5 g of base Ir/Al_2O_3 catalyst (1.0 wt.%; dispersion ~74% by H_2 chemisorption) prepared by the conventional incipient wetness (IW) method [32]. For this base Ir/Al_2O_3 catalyst, Ir metal ions were first impregnated onto a gamma–delta–theta phase alumina (specific surface area = 104 m^2/g, pore volume = 0.9 ml/g, provided by Toyota). This material was then dried at 60 °C in a vacuum oven for overnight and then reduced at 400 °C in 100 cm^3/min (STP) of flowing H_2 for 1 h before storing at ambient conditions. The initial potassium silver cyanide concentration in the ED bath was varied depending on the targeted weight loadings of the Ag metal. All baths were vigorously stirred to minimize any possible external mass transfer limitations and the solution pH was maintained at 11 ± 0.5 by careful addition of concentrated NaOH solution. Small aliquots of ED solution (<2 ml) were collected and filtered using a 5-μm mesh syringe filter at various time intervals of deposition to monitor the concentrations of Ag salts remaining in the bath during deposition. After the completion of ED (deposition times between 120 and 360 min), the slurry was filtered and washed repeatedly until all the remaining water soluble ligands (i.e., residual Ag(CN)$_2^-$ and CN$^-$) were removed. The wet sample cakes were dried under vacuum at room temperature and stored at ambient conditions. Thus, a series of the Ag–Ir/Al_2O_3 bimetallic catalysts with incremental Ag metal weight loadings and surface coverages on Ir was synthesized. A 1.0 wt.% Ag/Al_2O_3 monometallic catalyst was also prepared by incipient wetness

impregnation of AgNO$_3$ (⩾99%, Sigma–Aldrich) for comparison, followed by drying and reduction at 250 °C for 1 h under flowing H_2.

2.2. Atomic absorption spectroscopy (AA)

The elemental concentrations of Ag in the electroless solutions were determined by Atomic absorption spectroscopy (Perkin–Elmer model 3300) using standard methods. The compositions of the bimetallic catalysts were also measured following digestion of a ⩾40 mg sample in aqua regia at 120 °C for 4 h prior to AA analysis. A set of standards (known concentration of each specific element) was prepared to calibrate the instrument before the actual measurements were made. Both standards and samples were diluted using 5% (v/v) HNO$_3$ solution for better sensitivity and accuracy.

2.3. H_2 chemisorption studies

Hydrogen chemisorption measurements were performed using an automated AutoChem II 2920 from Micromeritics. Prior to chemisorption, samples (approximately 0.1 g) were reduced in flowing H_2 (50 ml/min) at 200 °C for 1 h followed by Ar (50 ml/min) purging at the same temperature for 1 h to remove chemisorbed hydrogen from the metal surface. The chemisorption experiments were done using pulse methodology by dosing a known volume of 10% H_2/Ar in 4-min intervals. H_2 that was chemisorbed on the samples was measured at 40 °C and atmospheric pressure, and the metallic dispersion and particle size were determined.

2.4. Fourier transform infrared spectroscopy

In situ FTIR spectra were recorded using a Nicolet Nexus 4700 spectrometer equipped with a mercury–cadmium–telluride B (MCT-B) detector cooled by liquid nitrogen. FTIR spectra were collected at room temperature in single beam absorbance mode with a resolution of 4 cm^{-1}. Catalysts samples of approximately 30 mg were prepared as self-supporting pellets with a diameter of 12 mm. All experiments were conducted in an externally heated cylindrical sample cell as described previously [33]. Briefly, a total gas flow of ~70 ml/min entered the cell in front of the pellet and exited behind the pellet. The samples were reduced in H_2 for 1 h at 200 °C, cooled to 25 °C in He, exposed to 1% CO in He, and then flushed with pure He to remove weakly bonded CO species and gas-phase CO. All spectra were referenced to an initial background spectrum taken in He prior to CO exposure.

The curve fitting of these FTIR spectra was performed using different fitting models (e.g., Gaussian, Lorentzian, log-normal) to obtain the peak position, width, height, and area of the overlapping peaks. Initially, the individual peak parameters (i.e., position, full width at half maximum (FWHM), and height) were chosen based on visual inspection of the experimental spectrum for the Ir/Al_2O_3 monometallic sample. Then, the residual between the overall fit and raw spectrum was minimized by minimizing the square root of the sum of square errors in an iterative fashion. The peak deconvolution using spectral curve fitting was continued for other samples in a similar fashion. It was found that Gaussian line shapes effectively modeled all of the peaks.

2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy measurements were made on selected samples using a Kratos AXIS Ultra DLD XPS system with a monochromatic Al Kα source operated at 15 keV and 150 W and a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to the surface normal and the pass energy