



High catalytic activity for formaldehyde oxidation of AgCo/APTES@MCM-41 prepared by two steps method



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ABSTRACT

We reported here a novel synthesis procedure to prepare a highly active bimetallic AgCo/APTES@MCM-41 catalyst. Complete oxidation of formaldehyde was achieved at temperature as low as 90 °C over the bimetallic catalysts with Ag/Co = 3/1 (mass ratio). N₂ isotherms, small-angle XRD results suggested that both Ag and Co species were well dispersed on the support, and the pore structure of the support was not destroyed after introducing the active metal. The formation of the strong metal–metal interaction (SMMI) between Ag and Co in the bimetallic catalysts due to the electron transfer between each other resulted in the high Co³⁺/Co²⁺ ratio and good low-temperature reducibility. And more surface active oxygen species (O_{surf}) formed on the surface of the bimetallic catalysts. All these factors gave rise to the high formaldehyde catalytic oxidation activity in AgCo bimetallic catalysts. The possible structure changes of bimetallic catalysts and the reaction path for the complete oxidation of formaldehyde over AgCo bimetallic catalyst was also proposed.

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1. Introduction

Volatile organic compounds (VOCs) are chemicals that exist in the gaseous state at standard temperature and pressure. Formaldehyde (HCHO) is a serious pollutant of the indoor air, which is often released in room decorating and refurbishing process, as well as in furniture production. Conversion of HCHO into H₂O and CO₂ using heterogeneous catalysts has proven to be an efficient and practical technology for controlling HCHO emission for indoor air purification [1]. The success of this approach greatly relies on the properties of the catalyst. The desired catalyst should be able to work at lower temperatures and has higher catalytic activity [2]. Different types of catalysts, such as supported noble metals (Pt, Ph, Pd, Au and Ag) [3] and some metal oxides (Co₃O₄, CeO₂, TiO₂, MnO_x and so on) [4] have been studied for the HCHO catalytic oxidation.

During the past decade, the design and synthesis of bimetallic materials have attracted considerable attention because they show multiple functionalities and prominent catalytic activity, selectivity and stability over monometallic nanomaterials [5]. The bimetallic catalytic system can potentially achieve chemical transformations that are unprecedented with monometallic catalysts because different components of the catalysts have a particular function in the

overall reaction mechanism [5,6]. It often shows the electronic and chemical properties that are distinctly different from those of the parent metals, offers the opportunity to obtain novel catalysts with enhanced activities. Bimetallic catalysts have been widely utilized in many catalysis processes. For example, the activity can be sharply increased from 0% to 100% at 300 K for CO oxidation on bimetallic catalysts with Au/Ag = 8/1 compared with single silver catalyst [7].

However, to the best of our knowledge, the catalytic properties of supported bimetallic catalysts for formaldehyde catalytic oxidation have not yet been studied. First principle studies have indicated that the synergistic effect on the performance of heterometallic nanocatalysts is subject to the surface electronic states, which are greatly altered by the change of catalysts for the geometric parameters, particularly related to the local strain and effective atomic coordination number on the surface [8]. With an excellent redox capacity due to its mixed-valence states, the transition metals Co catalysts as support and active species all exhibit the considerable activities, especially when Co exists as Co₃O₄, such as in the oxidation of CO [9] and Fischer–Tropsch synthesis and so on [10]. In our previous work, silver has been found to be active for HCHO oxidation and the addition of Ag resulted in the formation of the new HCHO adsorption sites at low temperatures [11]. However, the general HCHO complete decomposition into CO₂ was observed at temperature of 150 °C or higher over Ag/MCM-41 catalysts. It has been reported that the Ag–Co bimetallic catalysts can exhibit the improved catalytic performances in some reactions [12,13].

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Luo et al. [13] believed that the cooperative action existed in Ag–Co catalysts on account of the silver promoted the reduction of cobalt oxide which at last resulted in the high activity for CO, acetone, pyridine oxidation and CO–NO reaction. For Ag-promoted Co-ZSM-5 catalyst [12], the results showed that Ag can change the redox nature of cobalt species. The bimetallic Ag–Co/CeO₂ catalyst also showed superior activity due to the synergetic effect [14]. It seems that bimetallic AgCo catalysts would be activated in HCHO catalytic oxidation due to the existence of two kinds of active species. The investigation of the formation of synergistic effect between Ag and Co will be very significant to investigate whether the synergistic effect is formed and how the synergistic effect between Ag and Co is created.

It has been known that the metal oxides are widely used as support to disperse the active metal species due to their strong metal–support interaction (SMSI) [15]. However, their low surface areas limit the well dispersion of active metal species. Since bimetallic catalysts are composed of two different metal atoms, the atomic distribution can greatly influence the final architectures of nanocatalysts, which could have a significant impact on their catalytic performance [16]. Here it was our first time to report a functionalized mesoporous silica MCM-41 supported AgCo catalyst (AgCo/APTES@MCM-41) for the HCHO catalytic oxidation. The large number of active species would be loaded with less aggregation and good distribution on the functionalized silica MCM-41 due to its unique mesoporous structure in comparison to metal oxides and pure MCM-41. The obtained AgCo/APTES@MCM-41 bimetallic catalysts exhibited a superior catalytic activity for HCHO oxidation into CO₂ and H₂O with 100% conversion at relatively low temperature of ~90 °C, that was considerably lower than pure Ag catalyst. To determine the underlying reason for the promoting effect between Ag and Co, detailed investigations of the catalyst structures were conducted. Nitrogen sorption, XRD and TEM were employed to observe the physical pore channel structure and the dispersion of the active species on the support. The electronic property of the AgCo catalysts was monitored using the binding energy (BE) derived from XPS. H₂-TPR experiments were conducted because reducibility was an important factor influencing the catalytic activity of a sample. These characterizations could clearly elucidate the modification of surface physical and chemistry and the synergistic effect of the bimetallic AgCo catalysts in the HCHO catalytic oxidation reaction.

2. Experimental

2.1. Catalyst preparation

The AgCo bimetallic catalysts were synthesized by two steps method similarly as previously reported by Mou et al. in prepared AuAg bimetallic catalysts [7]. Firstly, the purchased MCM-41 was functionalized with 3-aminopropyltrimethoxysilane (APTES, H₂N(CH₂)₃Si(OEt)₃, Acros), 2 g commercial silica support (Shanghai Zhuoyue Chemical Agent Co. (China)) to a 200 mL ethanol solution containing 10.0 g of APTES. The mixture was refluxed for 24 h to graft APTES on the silica surface. Then the samples were washed with ethanol and dried at 60 °C then denoted as APTES@MCM-41. The surface functioned MCM-41 (1 g) was added to the silver nitrate (AgNO₃) solution then reduced with 0.2 M sodium borohydride (NaBH₄) aqueous solution. After Ag nanoparticles were anchored on the APTES@MCM-41, cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O) solution was added and also reduced with NaBH₄. The whole loading amount of metal was controlled to 8 wt% in the preparation process. The actual total metal loading is about 5% obtained by ICP measurement. Unless otherwise mentioned, the Ag/Co mass ratios discussed below are the nominal values as in the precursor solution, and they are similarly consistent with the

composition measured by ICP-AES (see Table 1). After calcination at 500 °C in air for 6 h, the AgCo/APTES@MCM-41 was obtained. Monometallic Ag/APTES@MCM-41 and Co/APTES@MCM-41 were also prepared in a similar way. All of the bimetallic and monometallic catalysts were pre-treated in O₂ atmospheres at 500 °C for 2 h before catalyst characterization and catalytic evaluation experiments.

2.2. Catalyst characterization

The ICP-AES was used to determine the actual content of silver and cobalt in the synthesized samples, which was performed on an OPTIMA 2000.

Specific areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method in Quantachrome quadrasorb SI. Before measurement, the samples were treated by degassing at 300 °C for 4 h. The pore diameter distributions were calculated from desorption branches using the BJH (Barrett–Joyner–Halenda) methods.

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a Rigaku powder diffract meter using CuK α radiation ($\lambda = 0.1542$ nm) and operating at 40 kV and 200 mA. The patterns were taken over the 2θ range from 0.5° to 6° for small-angle XRD and from 10° to 80° for wide-angle XRD and a position-sensitive detector using a step size of 0.02°.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a Tecnai G² F30 S-Twin operating at 100 and 200 kV. Energy dispersive X-ray fluorescence spectrometer (EDX-700 Shimadzu) was used for elemental analysis of the catalysts.

UV–vis diffuse reflectance spectra were recorded in the air on a SHIMADZU UV-2450 UV–vis spectrophotometer. Reference spectra were collected with pressed polytetrafluoroethylene (PTFE) disks. The following parameters were used to collect data: 5.0 spectra band width, 0.5 nm data pitch, 800–190 nm measurement range, and 200 nm/min scanning speed.

X-ray photoelectron spectroscopy was measured using an X-ray photoelectron spectrometer (ESCALAB250, Thermo VG, American) with a monochromatic X-ray source of AlK α (1486.6 eV) under ultra-high vacuum. The binding energies were calibrated internally by the carbon deposit C 1s binding energy (BE) at 284.6 eV.

H₂-TPR was carried out on the Quantachrome automated chemisorption analyzer. A 0.05 g sample was pre-treated with O₂, and then cooled to room temperature in a flow of Ar in a fixed-bed reactor. For the H₂-TPR study, it was exposed to a flow of 30 mL/min H₂/Ar (10 vol.% H₂) mixture. The temperature was programmed with a constant heating rate of 10 °C/min.

2.3. Catalytic evaluation

HCHO oxidation activity measurements were carried out in a fixed-bed flow reactor at atmospheric pressure and with 0.2 g catalyst. The total flow rate was 30 mL/min. Gaseous HCHO was generated by flowing Ar over trioxymethylene (99.5%, Acros organics) in an incubator kept in an ice water mixture. The flow rate passing through the reactor in all the experiments were controlled at 30 mL/min by a mass-flow meter. And the feeding stream consists of a mixture of 500 ppm HCHO, 20 vol.% oxygen and balanced Ar. The effluents from the reactor were analyzed by on-line gas chromatograph (GC 7890II, Techcomp, China) equipped with FID detectors. To determine the exact concentration of producing carbon dioxide, a nickel catalyst converter was placed before the FID detector and used for converting CO₂ quantitatively into methane in the presence of hydrogen. In typically runs, the reaction data were obtained after HCHO oxidation was performed for 1 h in order to achieve the steady state. No other

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