



Thin-sheet microfibrillar-structured nanoporous gold/Al fiber catalysts for oxidative coupling of methanol to methyl formate



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ABSTRACT

Active, selective, and stable nanoporous gold (NPG) catalysts supported on Al fiber, with enhanced heat transfer, have been developed for the oxidative coupling of methanol to methyl formate. The NPG/Al fiber catalysts are obtainable by galvanically depositing AuAg alloy on a thin-sheet microfibrillar structure using 50- μm Al fiber and subsequently dealloying by leaching Ag using HNO_3 aqueous solution. At 100 °C, NPG-7/Al fiber (Au loading: 7 wt%) catalyst is capable of achieving $\sim 100\%$ methyl formate selectivity with $\sim 25\%$ methanol conversion of a 10 vol% methanol feed at 5000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$. Gold loading can be reduced to 1 wt% with acceptable reactivity (35% conversion with 85% selectivity at 160 °C). The catalyst is stable for at least 300 h without NPG sintering. Lowering the Ag residual content of the NPG catalysts is essential for higher selectivity of methanol, by nature, due to the reduction in the amount of unselective surface O species.

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1. Introduction

Methyl formate is an important commodity chemical, used as a solvent, an environmentally friendly blowing agent, and a precursor for formic acid, formamide, and dimethyl formamide [1]. The current industrial process for methyl formate production is based on the homogeneous carbonylation of methanol in the presence of sodium methoxide catalyst (a caustic liquid base), using ultrapurified CO as feed gas (H_2O - and CO_2 -free) [2]. This method generally is linked to higher risk of environmental issues and faces serious problems in product separation, obviously conflicting with the concept of green chemistry [3]. There is thus an urgent need to develop greener methods, aimed at using solid catalysts under heterogeneous conditions.

In this context, the oxidative coupling of methanol (OCM) to methyl formate (MF) is attractive as a simple and environmentally benign process. In addition, the flourishing of a methanol economy generates a further impetus to explore the OCM process, which is superior to other routes for methanol conversion and utilization with regard to the extension of the methanol industrial chain. Several catalysts, including non-noble metal oxides (such as $\text{SnO}_2\text{-Mo}_2\text{O}_3$, $\text{V}_2\text{O}_5\text{-TiO}_2$, and $\text{Fe}_2\text{O}_3/\text{SiO}_2$) [4–7], heteropoly acids (HPAs) [8], and noble metal systems [9], have been extensively

investigated in the OCM reaction process. However, their practical application is particularly challenging. Besides concerns with catalytic performance, the thermal conductivity of the catalysts is also an important consideration because of the strong exothermicity of the OCM process. Metal oxide catalysts, as well as HPAs, are not active and/or selective enough from the industrial standpoint and their poor thermal conductivity will cause heat-transfer limitations. Graphene-supported Au–Pd nanocatalysts, with good heat conductivity, are reported to show excellent low-temperature activity and selectivity [9], delivering 90% conversion and 100% selectivity at 70 °C using a low methanol concentration of ~ 6 vol%.

Recently, nanoporous gold (NPG) has been attracting increasing attention because of its promising applications in a wide range of fields including catalysis [10,11], cell imaging [12,13], energy storage/transformation [14], and chemical sensors [15]. The NPG shows many special features such as high thermal/electrical conductivity, three-dimensional nanostructure, and much larger characteristic lengths in both ligament and nanopore diameters [16,17]. Owing to abundant surface defects and residual Ag, the bulk NPG offers excellent catalytic performance in some important reaction processes [10,11,17–19] such as OCM to MF. Most notably, bulk NPG exhibits high resistance to sintering compared to the Au nanoparticle catalysts, which is an important consideration in practical applications [14,15]. However, the high cost of bulk NPG hinders its practical application as a catalyst for OCM processes.

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In addition, conventional fabrication of NPG requires an initial alloy consisting of at least a noble constituent and a chemically dissolvable one. The Au–Ag system has been the most common alloy for fabricating NPG because of its complete solid solubility across all compositions, its mechanical compatibility (similar yield stress, thermal expansion, etc.) [16], and the marvelous interaction between Au and Ag for catalysis [20–23]. Bulk Au–Ag ingots, rods, wires, and sheets are produced by hammering, folding, or melting alloy constituents and subsequent annealing to relieve residual stress, and machining to produce desired dimensions [24–28]. Nevertheless, such methods are not directly compatible with conventional microfabrication processes, thus preventing their straightforward integration and limiting their versatility. Ideally, the alloy should be deposited by means of sputtering, evaporating, electroplating, or other easier methods that are established catalyst preparation technologies. For example, Ji et al. fabricated NPG wires by simultaneously electroplating a single-phase Au–Ag alloy on porous alumina substrates using potassium cyanide solutions of gold and silver, and subsequently releasing them by dissolving the alumina templates [29].

In this work, we demonstrate a microfibrillar-structured NPG catalyst system for OCM to MF. The NPG/Al fiber catalysts were obtained at a macroscale by galvanically depositing Au and Ag stepwise onto a thin-sheet three-dimensional (3D) network structure using 50- μm Al fiber, followed by alloying and dealloying. The resulting NPG/Al fiber catalysts were active, selective, and stable for OCM to MF under mild conditions, while showing high heat-transfer ability. The effects of catalyst preparation parameters (especially residual Ag content) and reaction conditions on catalyst performance were carefully investigated. X-ray photoelectron spectroscopy and O_2 temperature-programmed desorption (O_2 -TPD) were employed to elucidate the nature of Ag residue-controlled catalytic performance (especially the selectivity) for NPG/Al fiber catalysts.

2. Experimental

2.1. Catalyst preparation

A thin-sheet three-dimensional (3D) sinter-locked network structure using 50- μm Al fiber was employed as support, which was purchased from Shanghai Xincui Screen Manufacturing Co. Ltd. Prior to stepwise galvanic deposition, the microfibrillar-structured substrate was cleaned by immersing it in a sodium hydroxide (1 wt% NaOH) aqueous solution at room temperature to remove the Al_2O_3 film.

Gold and silver were stepwise deposited onto the Al fiber surface of the microfibrillar substrate with the aid of a galvanic exchange reaction. First, gold was galvanically deposited onto the cleaned Al fiber by impregnating it with an aqueous solution containing the specified amount of HAuCl_4 at room temperature. The solution gradually turned from bright yellow to colorless within 30 min. The resulting sample was washed with distilled water until no chloride ion was present to obtain the Au/Al fiber sample. Subsequently, silver was placed on the Au/Al fiber sample, again with the aid of the galvanic exchange reaction of Ag^+ with Al, by impregnating the Au/Al fiber with an aqueous solution containing the specified amount of AgNO_3 at room temperature. After that, alloying of Au and Ag deposited onto the Al fiber was performed by calcining the samples at 300 °C (if not specified) under inert helium for 2 h to give AuAg/Al fiber. Last, the AuAg/Al fiber samples were immersed into a 65% HNO_3 aqueous solution to selectively leach Ag from AuAg alloy for a desired time length (24 h if not specified) at room temperature while the passivation of the Al fiber surface automatically proceeded, thereby avoiding dissolving the Al fiber.

2.2. Catalyst characterizations

The catalysts were characterized by a scanning electron microscope (SEM, Hitachi S-4800; Japan) equipped with an energy-dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK). The specific surface area was determined from an N_2 adsorption isotherm at -196°C using standard Brunauer–Emmett–Teller (BET) theory on a Quantachrome Autosorb-3B instrument. The pore size distribution and total pore volume were determined using the Barrett–Joyner–Halenda BJH method. The X-ray photoelectron spectroscopy (XPS) was recorded on an Escalab 250xi spectrometer, using a standard Al $K\alpha$ X-ray source (300 W) and an analyzer pass energy of 20 eV. All binding energies were referenced to the adventitious C1s line at 284.6 eV. Temperature-programmed desorption (TPD) was performed on a Quantachrome ChemBET 3000 chemisorption apparatus with a TCD and an online mass spectrometer (Proline Dycor, AMETEK Process Instrument, USA). The amounts of Au and Ag for the NPG/Al fiber catalysts were determined quantitatively by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a USA Thermo IRIS Intrepid II XSP ICP spectrometer.

2.3. Reactivity tests

The gas-phase selective oxidation of methanol on the NPG/Al fiber catalysts with molecular oxygen was performed on a fixed-bed quartz tube reactor (600-mm length by 16-mm inner diameter) under atmospheric pressure. Circular chips (16.1-mm diameter) of the microfibrillar-structured NPG/Al fiber catalysts were punched down from their large sheet sample and packed layer up layer into the tube reactor. The catalyst used in testing experiments was 0.2 g. Note that a diameter 0.1 mm that is larger than the inner diameter of the tubular reactor was deliberately retained to avoid the appearance of a gap between the reactor wall and the edges of catalyst chips, thereby preventing gas bypass. A gaseous $\text{MeOH}/\text{O}_2/\text{N}_2$ mixture (2/1/17; 10 vol% methanol) was employed as feedstock. This feed was obtained by controlling oxygen (oxidant, 5 mL/min) and nitrogen (diluted gas, 85 mL/min) to pass through a methanol vapor saturator prior to being fed into the catalytic bed. Two calibrated mass flow controllers were used to control the oxygen and nitrogen gas. The methanol vapor saturator was immersed in a water bath precisely controlled at 20 °C. The product effluent, as well as the methanol concentration in the feed gas mixture, was analyzed online by an HP 6850 gas chromatograph equipped with a thermal conductivity detector (TCD) connected to Porapak Q and MS 5A parallel capillary columns (DICKMA). The gas pipeline and sampling six-way valve between the reactor outlet and the GC injector were heated to ensure that the effluent completely evaporated.

3. Results and discussion

3.1. Microfibrillar structure, Au–Ag galvanic deposition, and surface morphology

Fig. 1 shows the preparation strategy and structural features of the representative NPG-7/Al fiber catalysts from micro- to macroscale. The specific surface areas, mesopore surface areas (assumed to be contributed to the NPG surface area), and Au loadings of all the NPG/Al fiber samples are collected in Table 1. A thin-sheet microfibrillar structure consisting of 10 vol% 50- μm Al fiber and 90 vol% void volume, with irregular 3D networks (Fig. 1A and B), was employed as substrate. Stepwise deposition of Au and Ag onto the Al fiber was realized with the aid of galvanic exchange reaction (denoted as galvanic deposition [GD]; Fig. 1C-1 and C-2). Note that

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