



High-performance, low Pd-loading microfibrillar-structured Al-fiber@ns-AlOOH@Pd catalyst for CO coupling to dimethyl oxalate



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ABSTRACT

Thin-sheet microfibrillar-structured Al-fiber@ns-AlOOH@Pd catalysts with low Pd-loading engineered from micro- to macro-scale are developed for the gas-phase CO coupling to dimethyl oxalate, providing unique combination of high activity/selectivity and good stability with high permeability and high thermal conductivity. The support of Al-fiber@ns-AlOOH is initially prepared via endogenous growth of boehmite nanosheets (ns-AlOOH) on 3D network of 60- μm Al-fiber. The palladium is then placed onto the surface of the ns-AlOOH rooted on the Al-fiber via incipient wetness impregnation method with a toluene solution of palladium acetate. As an example, the catalyst with a low Pd-loading of 0.25 wt% delivers ~66% CO conversion and ~94% DMO selectivity for a feed of $\text{CH}_3\text{ONO}/\text{CO}/\text{N}_2$ (10/14/76, vol%) with a gas hourly space velocity of $3000 \text{ L kg}^{-1} \text{ h}^{-1}$, and particularly, is stable for at least 200 h without deactivation. Our Al-fiber@ns-AlOOH@Pd catalyst demonstrates two times higher intrinsic activity (expressed by turnover frequency) compared to a traditional $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$. The existence of Pd-hydroxyl synergistic interaction is paramount to the enhanced catalytic performance for the CO coupling reaction, by nature, as the result of hydroxyl-promoted adsorption of bridged CO on the Pd surface.

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1. Introduction

Dimethyl oxalate (DMO) is an important raw material in chemical industry used as solvent, extraction agent, and intermediates of ethylene glycol, ethanol, vitamin B1, oxamide, dyes, pharmaceuticals, etc. [1–3]. The traditional production of oxalic ester is based on the esterification between oxalic acid and alcohol with inorganic acid catalysts (e.g., H_2SO_4) and the formed water needs to be removed by low boiling point solvent or excessive alcohol [4]. However, the use of mineral acid and large discharge of sewage have caused serious equipment corrosion and environmental pollution, obviously conflicting the basic concept of green chemistry [5]. Moreover, oxalic ester can be synthesized in liquid phase via aerobically-oxidative carbonylation of alcohol catalyzed by the $\text{PdCl}_2\text{-CuCl}_2$ catalyst [6], but this homogeneous process suffers from rapid deactivation, high pressure and catalyst/product separation issues. Thus, there is a pressing need to establish the clean and effective process using heterogeneous catalysts. In the past decade, the gas-phase CO oxidative coupling to oxalate has been attracting considerable attention because of many advantages, such as moderate reaction conditions, atom economy and non-oil

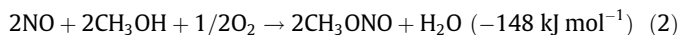
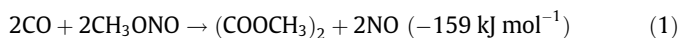
route [7,8]. In particular, considerably growing interest in hydrogenation of DMO for the production of ethylene glycol from non-oil resources is providing basic impetus for exploration on this process [9–11].

Under atmospheric pressure methyl nitrite (MN) gas couples with CO to produce DMO (Eq. (1)) and subsequently the MN is regenerated by recycling NO in the absence of catalyst (Eq. (2)). Clearly, the overall reaction (Eq. (3)) leads to an environmentally benign and chemical-looping process with MN as an active agent [12]. Various supported Pd catalysts have been investigated for the CO coupling reaction and the suitable support is $\alpha\text{-Al}_2\text{O}_3$ compared to silica, NaY zeolite and activated carbon, for which the exact reasons are still under discussion [12,13]. The generally accepted mechanism of the reaction is that active component Pd undergoes a redox cycle consisting of the oxidation of Pd^0 to generate $\text{Pd}(\text{OCH}_3)_2$ by unstable MN and the insertion of adsorbed CO into $\text{Pd}(\text{OCH}_3)_2$ to produce $\text{Pd}(\text{COOCH}_3)_2$ which finally yields DMO and Pd^0 [14–16]. Up to date, commercial production of DMO has been successfully realized in the fixed-bed reactor packed with $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$, but high Pd loading of 2 wt% (the state of the art) reduces the process economy [7,17]. In addition, due to the intrinsic nature of the randomly packed beds, the Al_2O_3 -supported pellet catalysts a few millimeters in size often suffer from high pressure drop, poor intraparticle/interbed mass/heat transfer and

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non-regular flow pattern, which result in compromised catalyst effectiveness [18,19].



In the chemical process industry, structured catalysts and reactors (SCRs) are paving the way to the holy grail with their unprecedented enhancements and improvements in both catalyst performance and reactor engineering [20,21]. On the catalyst level, structured catalysts are qualified with high activity [22], selectivity [23] and stability against coke and sintering [24,25], and can reduce the catalyst usage without sacrificing its activity [26,27]. On the reactor level, structured reactor internals allow themselves to enhance heat/mass transfer under low pressure drop with uniform flow patterns and residence times [28–30], and optimize the reactor design and operation based on the decoupling of hydrodynamics and reaction kinetics by computer-aided calculation [31]. Since the CO coupling to DMO is a strongly exothermic and fast reaction, it is desirable to dissipate reaction heat in catalyst bed and move the products away from the active sites rapidly. Hence, for both academic research and commercial applications it is pivotal to adopt SCRs in the CO coupling reaction process. To accomplish this goal, alumina-coated cordierite monoliths catalyst is prepared by common coating for the CO coupling reaction, which exhibits six-fold higher Pd efficiency than that of the reference pellet catalyst [5,32]. However, such coating technique on structured materials faces the risks of nonuniformity and exfoliation of the coating layer as well as the binder contamination, which is too cumbersome to control and scale up [33–35].

As previously reported, the monolithic Al-fiber@ns-AlOOH core-shell composite has been developed by endogenous growth of 2-dimensional (2D) boehmite nanosheets (ns-AlOOH) on a 3-dimensional (3D) Al-fiber network with the aid of the fundamental oxidation reaction between Al metal and H₂O ($2\text{Al} + 4\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + 3\text{H}_2$) [36]. This new approach shows substantial potential for forming novel structured catalysts and reactors with unique combination of enhanced heat/mass transfer, low pressure drop and high surface area to volume ratio. It is thus worthwhile to explore a cost-effective, high-performance structured Pd catalyst for the gas-phase CO coupling to DMO, by employing such Al-fiber@ns-AlOOH composite as support. In this work, uniform honeycomb-like shell of 2D AlOOH nanosheets were grown and disorderedly aligned onto a thin-sheet 3D network microfibrillar structure using 60- μm Al-fiber by steam-only oxidation at 120 °C. Pd was then placed onto the structured ns-AlOOH by impregnation method to obtain the product catalyst named as Al-fiber@ns-AlOOH@Pd. Besides high selectivity and good stability, the resulting novel Al-fiber@ns-AlOOH@Pd (0.25 wt%, ICP-AES) catalyst delivered the intrinsic activity two times higher than the traditional Pd/ α -Al₂O₃ catalyst for the CO coupling reaction. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments on CO adsorption, MN adsorption and CO/MN reaction were carried out to reveal the nature of intrinsic activity improvement.

2. Experimental

2.1. Catalyst preparation

Thin-sheet (~1.3 mm in thickness) 3D network structure consisting of 10 vol% 60- μm Al-fiber (99.9 wt% purity) and 90 vol% voidage was utilized as the substrate, which was taken from Shanghai Xincal Net-structured Material Co. Ltd. (China). Circular

chips (for example, 16 mm in diameter; about 1.0 g) punched down from their large felt were ultrasonically degreased in analytically pure acetone for 10 min, etched using NaOH (0.1 wt%) aqueous solution for 2 min and thoroughly washed using deionized water. After that, the pretreated substrate chips were packed layer-by-layer into a quartz tube (i.d. of 16 mm) in steam flow at 120 °C for 6 h and dried at the same temperature for 2 h in N₂ flow.

Palladium was placed onto the microfibrillar-structured composite supports obtained above by incipient wetness impregnation with a toluene solution of palladium acetate. The resulting samples were subsequently dried at 100 °C for 2 h and calcined in air at temperature ranged from 200 to 600 °C for 2 h to obtain the catalyst product with Pd loading varied from 0.06 to 1.0 wt%. For reference, a Pd/ α -Al₂O₃ catalyst (Pd loading of 0.3 wt%) was also prepared by the same preparation method.

2.2. Catalyst characterizations

The catalysts were characterized by scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscope (TEM, FEI TECNAI G² F30 instrument at 300 kV), X-ray diffraction (XRD, Rigaku Ultima IV diffractometer, Cu K α), thermogravimetric analysis (TG, NET2SCH STA449F3) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ICP Thermo IRIS Intrepid II XSP). The X-ray photoelectron spectroscopy (XPS) was recorded on an Escalab 250xi spectrometer, using a standard Al K α X-ray source (300 W) and analyzer pass energy of 30.0 eV. All binding energies were referenced to the adventitious C1s line at 284.6 eV. Specific surface area (SSA) was determined from N₂ adsorption isotherm at –196 °C using standard Brunauer–Emmett–Teller (BET) theory. The pore size distribution was determined using the Barrett–Jovner–Halenda (BJH) method calculated by the adsorption isotherms.

CO pulse adsorption experiments were performed on a Quantachrome ChemBET 3000 chemisorption apparatus with a thermal conductivity detector (TCD) to determine the Pd dispersion by assuming a CO/Pd ratio of 1. The sample of 100 mg was prereduced with 10 vol% H₂ in N₂ (50 mL/min) at 150 °C for 2 h, purged in He (90 mL/min) at that temperature for 1 h and cooled down to 35 °C in He. Subsequently, a gas mixture of 10% CO in He was pulsed, with a pulse volume of 250 μL , to the reactor every 3 min until the CO peak intensity remained unchanged.

Temperature programmed desorption (TPD) technique was employed to study the hydroxyl desorption behavior of the samples, using a Tianjin XQ TP-5080 chemisorption instrument with a TCD. The sample of 100 mg packed into a quartz tube reactor was purged in He at 150 °C for 1 h and subsequently heated to 600 °C. H₂-temperature programmed reduction (H₂-TPR) was conducted using the same equipment with 100 mg of sample in each trial. Before the H₂-TPR measurement, the sample was flushed with He at 200 °C for 1 h and then cooled down to room temperature. After this pretreatment, H₂-TPR was performed with a gas mixture of 5% H₂ in N₂. In all cases, the flow rate of gas fed to the reactor was maintained at 40 mL/min while the temperature of sample was ramped at 10 °C/min.

In situ DRIFTS experiments were carried out using a Bruker Tensor 27 spectrometer equipped with a Harrick Scientific HVC-DRP-4 reaction cell. The sample without diluents placed into the cell was prereduced in H₂ at 150 °C for 2 h and flushed with N₂ at 200 °C for 1 h. For CO or MN adsorption experiments, the sample was cooled down to 35 °C in N₂ for taking a reference spectrum, exposed to pure CO or 11.6% MN in N₂ at 35 °C for 30 min and purged in N₂ at that temperature for 1 h. Following this, the DRIFTS spectra were collected from 4000 to 600 cm^{–1} at a resolution of 4 cm^{–1} for 128 scans in range from 35 to 150 °C. For CO and MN coupling reaction, the sample was cooled down to 150 °C in N₂ for taking a reference spectrum and exposed to 10% CO in N₂ at 150 °C for 30 min. Then,

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