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

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Abstract

Thin-sheet microfibrrous-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 $\sim 66\%$ CO conversion and $\sim 94\%$ 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.

Keywords: structured catalyst; palladium catalysis; aluminum fiber; boehmite; synergistic interaction; CO adsorption; dimethyl oxalate.

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 oxidization of Pd⁰ to generate Pd(OCH₃)₂ by unstable MN and the insertion of adsorbed CO into Pd(OCH₃)₂ to produce Pd(COOCH₃)₂ which finally yields DMO and Pd⁰ [14-16]. Up to date, commercial production of DMO has been successfully realized in the fixed-bed reactor packed with Pd/ α -Al₂O₃, 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 Al₂O₃-supported pellet catalysts a few millimeters in size often suffer from high pressure drop, poor intraparticle/interbed mass/heat transfer and 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 microfibrinous 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 N_2 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/ $\alpha\text{-Al}_2\text{O}_3$ 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 $\text{K}\alpha$), 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 $\text{K}\alpha$ 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, the flow was switched from CO to the reaction gas (10% MN and 14% CO in N₂) and the DRIFTS spectra were continuously collected with 8 spectra min⁻¹ from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹ for 4 scans for 30 min. Moreover, for MN pulse reaction, the sample was cooled down to 100 or 150 °C in N₂ for taking a reference spectrum, exposed to 10% CO in N₂ at the same temperature for 30 min, and purged in N₂ at that temperature for 1 h. Subsequently, a gas mixture of 11.6% MN in N₂ was pulsed into the DRIFTS reaction cell with a pulse volume of 40 µL until 25 pulses were finished and the DRIFTS spectra were collected from 4000 to 600 cm⁻¹ at a resolution of 4 cm⁻¹ for 128 scans at 100 or 150 °C.

2.3. Reactivity tests

Catalyst testing in the CO coupling to DMO was carried out in a fixed-bed quartz tubular reactor (760-mm length) with feed gas containing of 10 vol% CH₃ONO (MN), 10-20 vol% CO and a balance of N₂ under atmospheric pressure. The MN was synthesized by dropping H₂SO₄ (50 vol%) into a mixture of sodium nitrite and methanol solution, collected into a steel cylinder and subsequently mixed with high-purity N₂ to obtain a mixture gas with N₂/MN volume ratio of 7.6. Three calibrated mass flowmeters were used to control the N₂, CO and the N₂/MN gas mixture, respectively. The circular chips of the Al-fiber@ns-AlOOH@Pd catalyst were packed layer-by-layer into the quartz tubular reactor while a thermocouple was placed in the middle of the catalyst bed for

in-situ monitoring reaction. The reaction temperature, gas hourly space velocity (GHSV), and CO to MN volume ratio were varied in range from 95 to 200 °C, 1500 to 160000 L kg⁻¹ h⁻¹, and 1.0 to 2.0, respectively. Notably, fiber-structured catalyst of 0.80 g packed in a 16-mm i.d. quartz tube reactor was employed at low GHSV in range from 1500 to 9000 L kg⁻¹ h⁻¹ while 0.08 g catalyst in an 8-mm i.d. quartz tube reactor at high GHSV ranged from 30000 to 160000 L kg⁻¹ h⁻¹. All data were collected after reaction at least 0.5 h to reach steady-state conditions. If not specified, the catalyst was in-situ activated by undergoing reaction at 200 °C for 2 h of a feed gas containing 10 vol% MN, 14 vol% CO and a balance of N₂ at a GHSV of 3000 L kg⁻¹ h⁻¹, prior to the reaction testing under appointed conditions. The compositions of the feed gas and effluent gas were monitored by an on-line gas chromatograph (GC) equipped with a TCD connected to a ShinCarbon ST packed column (DIKMA) and a flame ionization detector (FID) connected to an Innowax PEG-20M capillary column (HP). The main byproducts were identified, including dimethyl carbonate (DMC), methyl formate and methanol. The calculation of CO conversion, DMO selectivity and turnover frequency (TOF) was presented in the **Supporting Information**. In addition, the reference catalyst of Pd/ α -Al₂O₃ was diluted with quartz sand to the bed volume comparable with the fiber-structured Pd catalyst bed for the reaction testing (e.g., 0.80 g catalyst with 1.60 g quartz sand).

3. Results and discussion

3.1. Feature of microfibrillar structured Pd catalyst

Fig. 1 shows a top-down preparation strategy, structure and morphology of the representative catalyst engineered from micro- to macro-scale. **Fig. 1A** schematically illustrated the endogenous growth of nano-sheet AlOOH (ns-AlOOH) on the thin-sheet microfibrillar structure using 60- μ m Al-fiber (**Fig. 1B**) and subsequent dispersion of the Pd nanoparticles onto the ns-AlOOH surface to

form thin-sheet microfibrinous-structured Al-fiber@ns-AlOOH@Pd catalyst product (Fig. 1C).

A typical microfibrinous structure consisting of 10 vol% 60- μm Al-fiber and 90 vol% void volume, with characteristic irregular 3D open networks (Fig. 1D), was employed as mother substrate. With the aid of steam-only oxidation between Al and H_2O ($2\text{Al} + 4\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + 3\text{H}_2$) at 120 °C, the ns-AlOOH (Fig. 1E; ~ 12 nm in thickness) was formed and disorderedly aligned to form a uniform honeycomb-like shell along with the Al-fiber core (insert of Fig. 1E). As a result, the specific surface area (SSA) was sharply increased to $13.1 \text{ m}^2 \text{ g}^{-1}$ for the as-obtained composite from less than $1 \text{ m}^2 \text{ g}^{-1}$ for the mother substrate. The ns-AlOOH shell was about $0.7 \mu\text{m}$ (insert of Fig. 1E), corresponding to an appropriate AlOOH mass fraction of 7.5 wt% (92.5 wt% Al-fiber). The formation of boehmite (i.e., AlOOH) was solidly confirmed by XRD (JCPDS-74-1895; Fig. 1F, pattern b) and DRIFTS spectra (Fig. S1) in comparison with the mother Al-fiber as a reference (Fig. 1F, pattern a).

As-prepared microstructured Al-fiber@ns-AlOOH composite (only after the endogenous growth of ns-AlOOH on Al-fiber in 120 °C steam), was directly used as the catalyst support. The Al-fiber@ns-AlOOH@Pd catalysts were obtained by the incipient wetness impregnation method with a toluene solution of palladium acetate and subsequent calcination in air at 300 °C if not specified. Our representative catalyst of Al-fiber@ns-AlOOH@Pd (0.25 wt% Pd, ICP-AES) possessed a SSA of $13.2 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.023 \text{ cm}^3 \text{ g}^{-1}$ (including the mass of Al-fiber). In addition, such catalyst showed a BJH mesopore size of 2-10 nm, evidenced by the step at P/P_0 of 0.4-0.6 on the N_2 adsorption-desorption isothermal (Fig. 1G). The optical photograph and SEM image showed that our representative catalyst preserved well the macroscopic monolith, honeycomb-like shell and nanosheet structure (Fig. 1C,H). The XRD patterns and DRIFTS spectra for the Al-fiber@ns-AlOOH@Pd catalyst clearly indicated that the boehmite feature still remained

unchanged even after supporting Pd (Fig. 1F, pattern c, and Fig. S1). Notably, no diffraction peaks of Pd nanoparticles was detectable, indicating a high dispersion feature (Fig. 1F, pattern c); indeed, the TEM image clearly showed that Pd was highly dispersed onto the ns-AlOOH with average particle size of only 1.8 ± 0.3 nm (Fig. 1I) and HRTEM image revealed the interval between two lattice fringes of Pd nanoparticles was 0.228 nm, corresponding to the Pd(111) facet (Fig. S2). Moreover, Pd dispersion (D) was determined to be 54% by means of CO pulse adsorption and Pd particle size (d) thus was estimated to be ~ 2.1 nm (according to $d = 1.12 / D$ [37]), which was basically consistent with the TEM results (Fig. 1I, Table 1).

3.2. CO coupling to DMO over Al-fiber@ns-AlOOH@Pd catalyst

3.2.1. Effects of catalyst preparation and activation parameters

Fig. 2 shows the CO conversion and DMO selectivity for the CO coupling to DMO reaction process against the Pd loading, catalyst/support calcination temperature and catalyst activation. The effect of Pd loading was addressed by testing the catalysts using a feed of 10 vol% MN and 14 vol% CO in N₂ at 150 °C and a GHSV of 3000 L kg⁻¹ h⁻¹, with the results as shown in Fig. 2A. Clearly, CO conversion was increased remarkably from 56.3% to 66.9% with increasing the Pd loading from 0.06 to 0.3 wt% and then plateaued at $\sim 67\%$ (close to the theoretical maximum CO conversion of 71.4%) with further increasing the Pd loading up to 1.0 wt%. With the increase in the Pd loading from 0.03 to 1.0 wt%, DMO selectivity decreased progressively from 96.1% to 94.3% (Fig. 2A), being probably attributed to the increase of Pd particle size resulted from the increase of Pd loading accordingly [8,38,39]. Indeed, with the increase of Pd loading from 0.03 to 1.0 wt%, the Pd dispersion estimated by CO pulse adsorption decreased from 67% to 32%, and conversely, the Pd particle size increased gradually (Table 1). Considering the balance between catalytic performance

and catalyst cost, the promising catalyst should be the one with Pd loading of 0.3 wt% (theoretical). Notably, the theoretical Pd loading for catalysts in the posterior parts was 0.3 wt% and the real one was determined to be 0.24-0.26 wt% by ICP-AES analysis while denoting it as Al-fiber@ns-AlOOH@Pd-0.25.

Fig. 2B shows the effect of calcination temperature of Al-fiber@ns-AlOOH support on the performance of Al-fiber@ns-AlOOH@Pd-0.25 catalyst for the CO coupling to DMO reaction process. Clearly, the DMO selectivity (~96.0%) was almost immune to the support calcination temperature but the CO conversion declined gradually from ~67% to ~61% with increasing the support calcination temperature up to 600 °C. Interestingly, the nanosheet morphology could be intactly retained with the increase of support calcination temperature while the SSA declined slightly from 13.1 to 10.2 m² g⁻¹ [36]. It is generally known that boehmite, the main precursor of alumina, gives rise to other crystalline phases with raising the annealing temperature. For our support, the ns-AlOOH could remain at boehmite crystalline phase until increasing calcination temperature to 300 °C (Fig. 3A, patterns a,b) and would be totally transformed into ns-γ-Al₂O₃ at a high calcination temperature of 600 °C (Fig. 3A, pattern c). It should be noted that, nevertheless, no Pd XRD peaks were observed for all the catalysts produced from the supports after calcining at various temperatures (Fig. 3A), indicating that the feature of high Pd dispersion was almost independent on the support calcination temperatures studied. In combining this information with the fact of activity decline with the increase of support calcination temperature (Fig. 2B), it was rational to infer that a special surface chemical characteristic rather than the morphology, crystalline phase and Pd dispersion would be existed and be essential to the enhanced activity, which was discussed in posterior Section 3.3.

Fig. 2C shows the effect of catalyst calcination temperature on the performance of

Al-fiber@ns-AlOOH@Pd-0.25 for the CO coupling to DMO reaction process. The catalyst after calcining at 200 °C was not so active and selective as the other catalysts after calcining at 300 °C and above, mostly because of the incomplete decomposition of palladium acetate precursor (decomposition temperature: 242 °C) (Fig. S3). The CO conversion and DMO selectivity were increased to 66.8% and 95.9% with increasing the calcination temperature to 300 °C but were decreased continuously to 61.8% and 94.5% with further increasing the catalyst calcination temperature up to 600 °C (Fig. 2C). Interestingly, no Pd diffraction peaks were observed on the catalysts calcined at 200-300 °C while faint Pd diffraction peaks appeared at $2\theta = 46.9^\circ$ and 68.2° on the catalyst calcined at 450-600 °C (Fig. 3B). On the catalyst calcined at 450-600 °C, γ -Al₂O₃ phase was formed and overlapped the observable Pd peaks (Fig. 3B, pattern c,d). In combining this information with the fact that phase transformation of ns-AlOOH deteriorate the DMO selectivity visibly but almost not the activity (Fig. 2B, Fig. 3A), we reasonably inferred that, at catalyst calcination temperature higher than 300 °C, the aggregation of Pd rather than the ns-AlOOH phase transformation was the main cause for CO conversion decrease.

The effects of catalyst activation conditions were also investigated on the performance of Al-fiber@ns-AlOOH@Pd-0.25 for the CO coupling to DMO reaction, with the results as shown in Fig. 2D. Clearly, a crucial impact on the DMO selectivity rather than the CO conversion was observed, associated with the catalyst activated under the conditions studied. Conversely but more interestingly, the catalyst directly activated in-situ in the reaction stream at 200 °C exhibited the highest DMO selectivity. Such reaction-induced activation effect has also been reported for many other reactions, such as alcohol oxidation [22] and CO oxidation [40]. Neither complete reduction of Pd with H₂ at 200 °C confirmed by TPR (Fig. S4) nor partial reduction of Pd with H₂ at 30 °C or CO

at 200 °C yielded better DMO selectivity. Notably, those partially reduced catalysts, compared to that completely reduced catalyst, delivered relatively higher DMO selectivity. This observation was likely due to a favorable reaction-induced reconstruction of surface Pd of the catalyst in the feed gas of MN and CO, which meant that the active components of the catalyst surface restructured, adapting their geometrical and electronic structure to the reactive environments, possibly caused by adsorbate-induced changes in surface energies and/or by changes in the interfacial energy [41,42]. Thus, the experimental data in the posterior parts were all collected over the catalysts activated in-situ by undergoing the reaction at 200 °C for 2 h.

On the basis of the above results, the best Al-fiber-structured ns-AlOOH@Pd catalyst was the one obtained by placing only 0.25 wt% Pd onto the as-prepared Al-fiber@ns-AlOOH composite support (without any treatment after the endogenous growth of ns-AlOOH on Al-fiber in 120 °C steam) and subsequently calcining at 300 °C in air. This catalyst could be directly activated, only by undergoing the reaction at 200 °C for 2 h, to reach superior CO conversion and DMO selectivity.

3.2.2. Effect of reaction conditions

The effects of reaction conditions (including reaction temperature, CO to MN volume ratio, GHSV and N₂ fraction in feed gas) were investigated on the Al-fiber@ns-AlOOH@Pd-0.25 catalyst for the CO coupling to DMO, with the results as shown in Fig. 4.

Fig. 4A shows the reaction temperature dependence of the CO coupling reaction using a feed of 10 vol% MN and 14 vol% CO in N₂ at a GHSV of 3000 L kg⁻¹ h⁻¹. The CO conversion showed a volcano-type evolution behavior when increasing the reaction temperature from 120 to 170 °C, with the maximum of 66.9% at 150 °C. At temperature higher than 150 °C, the useless decomposition of MN that is a parallel competing reaction in the CO coupling system [16], inevitably occurred and

was boosted with temperature thereby leading to a reduction of the CO conversion. In addition, with the increase of reaction temperature the DMO selectivity gradually decreased from 98.1% to 89.5%, indicating that the elevated reaction temperature was favorable for the formation of byproduct DMC.

Fig. 4B shows the CO conversion and DMO selectivity against the CO to MN volume ratio in the feed gas at 150 °C and a GHSV of 3000 L kg⁻¹ h⁻¹. The DMO selectivity was increased significantly from 88.2% to 95.9% with increasing the CO to MN volume ratio from 1.0 to 1.4 and then was increased slightly to 96.4% with further increasing that ratio up to 2.0. This observation indicated that the excess CO could suppress the side reaction thereby leading to the improvement of the DMO selectivity. Similar result has been revealed by the in-situ FTIR experiments on the CO coupling to DMO reaction, showing that the high coverage of CO on the catalyst surface is favorable to the formation of DMO [14]. It is not surprising that the CO conversion was decreased from 79.4% to 46.7% with the increase of CO to MN volume ratio from 1.0 up to 2.0, because of the excess of CO.

As shown in **Fig. 4C**, with increasing the N₂ volume fraction in the feed gas with a CO to MN volume ratio of 1.4, the DMO selectivity was decreased obviously from 95.9% to 90.5% while the CO conversion remained unchanged at 150 °C. Since the external diffusion of CO was more sensitive to volume fraction than that of MN [43], the decline of CO concentration would reduce the CO coverage on the catalyst surface thereby leading the decrease of DMO selectivity.

Fig. 4D shows the CO coupling reaction results as a function of the GHSV at 150 °C, using a feed of 10 vol% MN and 14 vol% CO in N₂. Clearly, the DMO selectivity almost remained constant at ~96% at low GHSV ranged from 1500 to 3000 L kg⁻¹ h⁻¹ and then decreased gradually but slightly to 94.3% with increasing the GHSV up to 60000 L kg⁻¹ h⁻¹. This observation was likely attributed to the thermal effect in the catalyst bed considering that the CO coupling reaction is a strongly

exothermic reaction ($\Delta H_r = -159 \text{ kJ mol}^{-1}$). For example, the temperature rise between the catalyst bed and the external wall of the reactor was increased from 4 to 9 °C when increasing GHSV from 3000 to 9000 $\text{L kg}^{-1} \text{ h}^{-1}$. As shown in Fig. 4A, exactly, the DMO selectivity was very sensitive to the reaction temperature (e.g., 95.9% at 150 °C vs. 93.2% at 160 °C at 3000 $\text{L kg}^{-1} \text{ h}^{-1}$). The similar observation was also observed for other strongly exothermic reactions such as alcohol oxidation [22] and methanation [44], indicating that the temperature rise or hotspots in the catalyst bed deteriorated the target product selectivity. Unlike the DMO selectivity, the CO conversion was decreased continuously with increasing the GHSV from 1500 to 60000 $\text{L kg}^{-1} \text{ h}^{-1}$, mostly because the residence time for the reactants became more and more insufficient with the increase of the GHSV.

3.2.3. Stability

Stability is a significant consideration for the heterogeneous catalysts in their practical applications. Fig. 5A shows the CO conversion and DMO selectivity for the long-term test of CO coupling to DMO over the Al-fiber@ns-AlOOH@Pd-0.25 catalyst. The catalyst provided pleasurable activity/selectivity maintenance, always delivering CO conversion of $65.7 \pm 0.8\%$ and DMO selectivity of $94.3 \pm 0.6\%$ throughout the entire 200 h test. No XRD reflection of Pd phase was observed yet for the catalyst even after 200-h test (Fig. S5), while the Pd dispersion by CO pulse adsorption was decreased slightly from 54% to 41% (corresponding to a slight increase in the Pd nanoparticle size from ~2.1 to ~2.7 nm). The above results indicated the outstanding anti-sintering of the Pd nanoparticles highly dispersed on the ns-AlOOH, being possibly accredited to the interaction of Pd and hydroxyls since abundant hydroxyls can reduce the mobility of Pd nanoparticles confirmed by DFT calculations [45,46]. In comparison with the fresh catalyst, exactly, the honeycomb-like morphology with disorderedly aligned ns-AlOOH (provided abundant hydroxyls) was still preserved

very well for the used catalyst, solidly evidenced by the SEM observation (Fig. 5B,C) and XRD boehmite patterns (Fig. S5).

3.2.4. Structure robustness

As noted previously, the adhesion is the most important property for the structured catalysts [33,34]. The adhesion property of our catalyst was checked using ultrasound test method by immersing the sample into petroleum ether and exposing to ultrasound with power of 200 W for 30 min at room temperature. After that, the sample was dried at 150 °C for 2 h and then its weight loss was measured to estimate the catalyst structure robustness. A very low weight loss of only 0.05 wt% was obtained, indicating the superior mechanical stability of our microfibrinous-structured catalyst. The Al-fiber@ns-AlOOH@Pd-0.25 catalyst after ultrasound test was calcined at 300 °C for 2 h and was examined again in the CO coupling reaction at 150 °C. Not surprisingly, as shown in Fig. S6, the ultrasonic treatment only resulted in a little decrease of the CO conversion but not deteriorated the DMO selectivity: 63.9% conversion with 95.7% selectivity for the catalyst after treatment vs. 66.8% conversion with 95.9% selectivity for the untreated one. A possible explanation was that such ultrasonic treatment reduced the Pd content in the catalyst a little from 0.25 wt% to 0.23 wt% (ICP-AES).

3.3 Synergistic interaction of hydroxyl and Pd

3.3.1. Reactivity comparison: Al-fiber@ns-AlOOH@Pd vs. Pd/ α -Al₂O₃

A Pd/ α -Al₂O₃ catalyst (0.26 wt% Pd, ICP-AES) was also prepared and examined in the CO coupling to DMO for comparison, with the results as shown in Fig. 6. For the Pd/ α -Al₂O₃ catalyst CO conversion also showed a volcano-type curve against the reaction temperature and reached maximum at 140 °C (10 °C lower than that of the Al-fiber@ns-AlOOH@Pd-0.25, Fig. 4A). As

shown in Fig. 4A and Fig. 6, our Al-fiber@ns-AlOOH@Pd-0.25 catalyst delivered CO conversion apparently superior to the counterpart of Pd/ α -Al₂O₃ (e.g., 65.5% vs. 58.6% at 140 °C and 66.8% vs. 55.6% at 150 °C) with higher selectivity to DMO than the Pd/ α -Al₂O₃ (e.g., 97.1% vs. 94.6% at 140 °C and 95.9% vs. 92.9% at 150 °C) at 3000 L kg⁻¹ h⁻¹ using a feed of 10 vol% MN and 14 vol% CO in N₂. Clearly, our Al-fiber@ns-AlOOH@Pd-0.25 catalyst permitted a higher reaction temperature with no penalty paid for the decrease in activity/selectivity, which might be an important feature advantageous over the Pd/ α -Al₂O₃ by considering the strong exothermicity of the titled reaction.

TOF was determined based on CO pulse adsorption and TEM images, and similar TOF results were obtained by the two methods (Table 2). Interestingly, the Al-fiber@ns-AlOOH@Pd-0.25 catalyst exhibited a TOF (calculated with the CO conversion below 10% based on the amount of surface Pd atoms determined by TEM images in Fig. S2) of 20.4 min⁻¹, 2-fold larger than that (6.2 min⁻¹) of the Pd/ α -Al₂O₃ (Table 2), indicating that the Al-fiber@ns-AlOOH@Pd-0.25 catalyst possessed much higher intrinsic activity for the CO coupling reaction. In view of the similar Pd particle size distribution and Pd oxidation state and equivalent Pd content (Fig. S2, Fig. S7 and Table 2), it was thus assured that the enhanced intrinsic activity was initially accredited to the different properties of ns-AlOOH and α -alumina. One of the most differential characteristics between ns-AlOOH and α -alumina is that the former possesses much more hydroxyls than the latter. By combining this information with the fact that our Al-fiber@ns-AlOOH@Pd-0.25 was more active and selective than the Pd/ α -Al₂O₃, we believe that the hydroxyl might be essential to such activity/selectivity enhancement via hydroxyl-Pd synergistic interaction. As clearly shown in Fig. 2B,C, indeed, the CO conversion of the Al-fiber@ns-AlOOH@Pd-0.25 catalysts showed decline trend with the increase of the calcination temperature of them and their support of

Al-fiber@ns-AlOOH. This further confirmed that hydroxyl groups likely played a key role in promoting the Pd activity for the Al-fiber@ns-AlOOH@Pd-0.25 catalyst in the CO oxidative coupling reaction.

3.3.2. Pd-hydroxyl synergistic interaction

To clearly verify such proposed Pd-hydroxyl synergistic interaction, intrinsic activity (i.e., TOF) of the Pd catalysts supported on the Al-fiber@ns-AlOOH after calcined at different temperatures was firstly measured as well as the Pd/ α -Al₂O₃ for reference and the results were collected also in Table 2. For convenience, CAT-1, CAT-2 and CAT-3 were used to denominate the catalysts using the Al-fiber@ns-AlOOH support without calcination treatment (as-prepared), after calcining at 300 °C and at 600 °C, respectively. By doing so, impacts of calcination temperature on other catalyst parameters such as Pd dispersion would be excluded. As shown in Table 2, the intrinsic activity (TOF, calculated with the CO conversion below 10% based on the amount of surface Pd atoms determined by TEM images in Fig. S2) of these three catalysts decreased progressively from 20.4 to 9.4 min⁻¹ with increasing the support calcination temperature of Al-fiber@ns-AlOOH supports. Note that the Pd/ α -Al₂O₃ delivered the lowest TOF of 6.2 min⁻¹. As well known, AlOOH possesses plentiful surface hydroxyls and will dehydroxylate at elevated calcination temperatures to form γ -Al₂O₃ and even α -Al₂O₃ [47,48]. In addition, all these four catalyst samples provided almost identical Pd content, similar Pd particle size distribution and Pd oxidation state (Table 2, Fig. S2 and Fig. S7). Thus, we believed that surface hydroxyls were exclusively responsible for the intrinsic activity improvement. To further confirm this claim, TPD experiments on these four catalysts were carried out and their hydroxyl amount were determined on the basis of TPD peak areas accordingly, showing that the hydroxyl amount indeed decreased gradually from CAT-1 to Pd/ α -Al₂O₃ (Fig. 7A). Moreover,

the TOFs (namely intrinsic activity) of these catalysts were correlated with their hydroxyl amount, and not surprisingly, a nearly linear relationship was shown for TOF against catalyst hydroxyl amount (Fig. 7B). Furthermore, either hydroxyl-deficient α -Al₂O₃ or as-made hydroxyl-abundant Al-fiber@ns-AlOOH supports alone delivered very low CO conversion of below 2% at 150 °C with GHSV of 3000 L kg⁻¹ h⁻¹ (Fig. S8), revealing that the supports themselves were inactive for the CO coupling reaction. The above results solidly evidenced that hydroxyl showed critical role in the catalytic activity improvement via hydroxyl-Pd synergistic effect.

3.3.3. Insight into the hydroxyl-Pd synergistic effect: enhancement of adsorption of bridged CO

In view of the Langmuir-Hinshelwood (L-H) mechanism of CO coupling reaction [14,15,49], the effects of hydroxyl-Pd synergistic interaction on the CO adsorption, MN adsorption and CO/MN reaction were investigated. Initially, the DRIFTS technique was employed to probe the adsorption of reactant CH₃ONO (MN) on the CAT-1, -2, -3 and Pd/ α -Al₂O₃ catalysts. Fig. 8 shows the background-subtracted DRIFTS spectra of these four catalysts exposed to MN at 35 °C and at 150 °C. The bands at about 2942 and 2836 cm⁻¹ were assigned to CH₃ asymmetric and symmetric stretching vibrations and band at about 1028 cm⁻¹ corresponds to stretching vibration of C-O, which indicated that the CH₃O- species was acquired through the adsorption of MN (Fig. 8A) [14]. However, neither gaseous NO during the adsorption of MN nor Pd-NO (1753 cm⁻¹) [14] after the adsorption was observed (Fig. 8A). Conversely but more interestingly, the bands observed at about 1630 cm⁻¹ and at about 1420 and 1330 cm⁻¹ were attributed to the formation of coordinated alumina bound nitrates and nitrites, respectively [50,51]. The NO species originated from MN dissociation may transfer from Pd to alumina, which generated nitrates and nitrites. These revealed that the active MN could even dissociate at 35 °C generating CH₃O- species due to the very weak CH₃O-NO band (about 42 kcal

mol⁻¹) [52]. At 150 °C, the bands at 2942 and 2836 cm⁻¹ disappeared since the CH₃O- species were decomposed to CH₃OH and CH₃OCOH (Fig. 8B) [16]. The bands at 1310-1710 cm⁻¹ were assigned to different bridged and bidentate nitrates resulted from the decomposition of nitrites (Fig. 8B) [50,51]. Moreover, the catalytic decomposition of MN was examined on CAT-1, -2, -3 and Pd/α-Al₂O₃ catalysts at 150 °C and an ultra-high GHSV of 52000 L kg⁻¹ h⁻¹. These four catalysts all showed comparable high activities for the catalytic dissociation of MN, delivering MN conversions above 96% (Fig. S9). It is thus reasonable to infer from such hydroxyl-independent MN dissociation activity that the surface hydroxyl shows ability to tune the CO adsorption on the Pd nanoparticles thereby facilitating the catalytic performance of the CO coupling reaction. In addition, the DRIFTS spectra of CO adsorption on the above four catalysts in range from 35 °C to 150 °C were collected and shown in Fig. 9. For the Pd/α-Al₂O₃ in Fig. 9A, the bands could be assigned to linear CO (2084 cm⁻¹) adsorbed on low coordination sites (e.g., corners and edges), bridged CO (1973 cm⁻¹) adsorbed on Pd (110) or Pd (100) and bridged CO (~1940 and ~1890 cm⁻¹) adsorbed on Pd (111) [53-55]. In comparison with the Pd/α-Al₂O₃, the CAT-1, -2, and -3 catalysts exhibited an obvious redshift and decrease of the intensity for linear CO (~2060 cm⁻¹). Additionally, the bridged CO (~1973, ~1940 and ~1890 cm⁻¹) was all observable over these four catalysts but with ~1940 cm⁻¹ as main band on CAT-1, -2, and -3 catalysts instead of ~1973 cm⁻¹ on Pd/α-Al₂O₃, and the intensities of bridged CO (~1940 cm⁻¹) progressively declined from CAT-1, -2, -3 to Pd/α-Al₂O₃ (Fig. 9A). These differences were likely accredited to the presence of abundant surface hydroxyls around Pd nanoparticles, as detailed below: the hydroxyls could produce a decorating effect and tune the types of Pd surface sites, which induced a bathochromic shift of linear CO, weakened the intensity of linear CO and effected the adsorption of bridged CO [53,56,57]; moreover, the hydroxyls, which were reported to be

electron donors, would improve the electron density of Pd surface sites and thus the CO-Pd bonding was enhanced because of the metal back-donation contribution to the bonding of CO to the Pd surface [58,59]. As shown in Table 3 upon the quantitative analysis of DRIFTS results, moreover, the band area ratio of the bridged CO to the linear CO increased with the order of Pd/ α -Al₂O₃ < CAT-3 < CAT-2 < CAT-1 in range from 35 °C to 100 °C, keeping in line with their hydroxyl amount (Fig. 7A). It is worth noting that in Table 3 both linear CO and bridged CO areas of the Pd/ α -Al₂O₃ at 35 °C were larger than those of the other three catalysts, most likely due to their difference in the refractive index and packing density [60]. Moreover, the areas of bridged CO and the linear CO decreased with the increase of temperature and the linear CO was even not observable at 150 °C on all these four catalysts, while the bridged CO on the Pd/ α -Al₂O₃ declined apparently faster than the counterparts on the other three catalysts when elevating the temperature from 35 to 150 °C, which indicated that the hydroxyl-Pd synergistic interaction could enhance the adsorption of bridged CO (Fig. 9, Table 3).

The apparent activation energies for CO coupling to DMO were calculated from the kinetic studies with the results as shown in Fig. 10. Clearly, CAT-1, -2, -3 and Pd/ α -Al₂O₃ all provided almost identical apparent activation energies of 94, 89, 86 and 87 kJ mol⁻¹ (Supporting Information for the calculation details in Fig. S10 and Fig. S11), respectively. This suggested that the hydroxyl-Pd synergistic interaction seemed to have little impact on the reaction pathways and/or the rate-controlled step [61,62]. Furthermore, *in situ* DRIFTS spectra obtained from a time-dependence study of the CO coupling reaction after CO pre-adsorption were performed on these four catalysts at 150 °C (Fig. S12). Before the CO/MN reaction attained steady state (i.e., the bridged CO (2005-1800 cm⁻¹) was abundant on the catalyst surface after CO pre-adsorption), the bands attributed to DMO gradually increased with the increase of gaseous MN bands and the bridged CO progressively

declined along with the formation of DMO, which indicated that the bridged CO participated in the reaction (Fig. S12). Meanwhile, the pulse reactions of *in situ* DRIFTS were performed over CAT-1 and Pd/ α -Al₂O₃ at 100 °C and 150 °C, respectively (Fig. 11). Typically, the reduced catalyst was exposed to CO, purged in N₂ thoroughly and then the MN gas was pulsed into the DRIFTS reaction cell. Not surprisingly, the bands of bridged CO (2005-1800 cm⁻¹) declined with the pulse number and a nearly inverse proportional relationship was shown for band area of bridged CO against pulse number on both CAT-1 and Pd/ α -Al₂O₃ at 100 °C and 150 °C, which indicated that the CO coupling reaction rather than the competitive adsorption occurred between bridged CO and MN pulse (Fig. 11) [63,64]. Since the band area of linear CO was much smaller than the counterpart of bridged CO at 100 °C and even almost zero at 150 °C on both CAT-1 and Pd/ α -Al₂O₃ (Fig. 9, Fig. 11) while the CO coupling reaction followed the L-H mechanism as previously stated [14,15,49], linear CO would make little contribution to the target reaction at the optimal reaction temperature of 150 °C based on the fundamental L-H kinetics [65]. This was consistent with the well-investigated results of that, actually, linear CO was a spectator and only the bridged CO was a participant for the CO coupling reaction [14]. We thus believed that the Pd-hydroxyl interaction was 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. Despite of above achievement, in-depth understanding of the mechanism of CO coupling reaction in case of existing Pd-hydroxyl interaction is still particularly desirable.

4. Conclusions

Our results tentatively established a promising thin-sheet microfibrinous-structured Al-fiber@ns-AlOOH@Pd catalyst system for the gas-phase CO coupling to dimethyl oxalate. Such

structured catalysts engineered from micro- to macro-scale are obtained by highly dispersing Pd nanoparticles via incipient wetness impregnation method with a toluene solution of palladium acetate, onto the boehmite nanosheets (ns-AlOOH) endogenously grown on a 3D network using 60- μm Al-fiber through oxidation reaction between Al metal and H_2O ($2\text{Al} + 4\text{H}_2\text{O} \rightarrow 2\text{AlOOH} + 3\text{H}_2$). Our microfibrinous-structured ns-AlOOH@Pd catalysts provide unique combination of high activity/selectivity and good stability with high permeability and high thermal conductivity. Over a representative catalyst with very low Pd-loading of only 0.25 wt%, a high CO conversion of $\sim 66\%$ is achieved with a high DMO selectivity of $\sim 94\%$ 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 is maintained almost unchanged for at least 200 h. Our Al-fiber@ns-AlOOH@Pd catalyst demonstrates two times higher intrinsic activity (expressed by TOF) compared to a traditional Pd/ $\alpha\text{-Al}_2\text{O}_3$. It is found that the intrinsic activity is intimately related to the hydroxyl amount on the catalyst surface, indicating the existence of Pd-hydroxyl synergistic interaction which is paramount to the enhanced catalytic performance for the CO coupling reaction. By nature, the presence of hydroxyls facilitates the adsorption of bridged CO on the Pd surface, which is the only reactive adsorbed CO species for the CO coupling reaction [14].

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References

- [1] H. Yue, X. Ma, J. Gong, *Acc. Chem. Res.* 47 (2014) 1483.

- [2] H. Yue, Y. Zhao, X. Ma, J. Gong, Chem. Soc. Rev. 41 (2012) 4218.
- [3] Y. Zhu, X. Kong, S. Zhu, F. Dong, H. Zheng, Y. Zhu, Y. Li, Appl. Catal. B 166-167 (2015) 551.
- [4] J. Bedard, H. Chiang, A. Bhan, J. Catal. 290 (2012) 210.
- [5] X. Gao, Y. Zhao, S. Wang, Y. Yin, B. Wang, X. Ma, Chem. Eng. Sci. 66 (2011) 3513.
- [6] D. M. Fenton, P. J. Steinwand, J. Org. Chem. 39 (1974) 701.
- [7] S. Peng, Z. Xu, Q. Chen, Y. Chen, J. Sun, Z. Wang, M. Wang, G. Guo, Chem. Commun. 49 (2013) 5718.
- [8] Z. Xu, J. Sun, C. Lin, X. Jiang, Q. Chen, S. Peng, M. Wang, G. Guo, ACS Catal. 3 (2013) 118.
- [9] L. Zhang, L. Han, G. Zhao, R. Chai, Q. Zhang, Y. Liu, Y. Lu, Chem. Commun. 51 (2015) 10547.
- [10] S. Zhao, H. Yue, Y. Zhao, B. Wang, Y. Geng, J. Lv, S. Wang, J. Gong, X. Ma, J. Catal. 297 (2013) 142.
- [11] Y. Huang, H. Ariga, X. Zheng, X. Duan, S. Takakusagi, K. Asakura, Y. Yuan, J. Catal. 307 (2013) 74.
- [12] S. Uchiumi, K. Ataka, T. Matsuzaki, J. Organomet. Chem. 576 (1999) 279.
- [13] T. Zhao, D. Chen, Y. Dai, W. Yuan, A. Holmen, Ind. Eng. Chem. Res. 43 (2004) 4595.
- [14] Y. Ji, G. Liu, W. Li, W. Xiao, J. Mol. Catal. A: Chem. 314 (2009) 63.
- [15] X. Zhao, Q. Lin, W. Xiao, Appl. Catal. A 284 (2005) 253.
- [16] Z. Gao, Z. Liu, F. He, G. Xu, J. Mol. Catal. A: Chem. 235 (2005) 143.
- [17] S. Peng, Z. Xu, Q. Chen, Z. Wang, Y. Chen, D. Lv, G. Lu, G. Guo, Catal. Sci. Technol. 4 (2014) 1925.

- [18] G. Zhao, Y. Li, Q. Zhang, M. Deng, F. Cao, Y. Lu, *AIChE J.* 60 (2014) 1045.
- [19] X. Wang, M. Wen, C. Wang, J. Ding, Y. Sun, Y. Liu, Y. Lu, *Chem. Commun.* 50 (2014) 6343.
- [20] M. Altomare, O. Pfoch, A. Tighineanu, R. Kirchgeorg, K. Lee, E. Selli, P. Schmuki, *J. Am. Chem. Soc.* 137 (2015) 5646.
- [21] Z. Ren, V. Botu, S. Wang, Y. Meng, W. Song, Y. Guo, R. Ramprasad, S. L. Suib, P. Gao, *Angew. Chem. Int. Ed.* 53 (2014) 7223.
- [22] G. Zhao, M. Deng, Y. Jiang, H. Hu, J. Huang, Y. Lu, *J. Catal.* 301 (2013) 46.
- [23] G. Zhao, H. Hu, M. Deng, Y. Lu, *Chem. Commun.* 47 (2011) 9642.
- [24] W. Chen, G. Zhao, Q. Xue, L. Chen, Y. Lu, *Appl. Catal. B* 136-137 (2013) 260.
- [25] X. Du, D. Zhang, L. Shi, R. Gao, J. Zhang, *Nanoscale* 5 (2013) 2659.
- [26] Q. Zhang, Y. Li, L. Zhang, L. Chen, Y. Liu, Y. Lu, *J. Catal.* 317 (2014) 54.
- [27] Y. Guo, Z. Ren, W. Xiao, C. Liu, H. Sharma, H. Gao, A. Mhadeshwar, P. Gao, *Nano Energy* 2 (2013) 873.
- [28] F. M. Dautzenberg, *Catal. Rev.* 46 (2004) 335.
- [29] F. M. Dautzenberg, M. Mukherjee, *Chem. Eng. Sci.* 56 (2001) 251.
- [30] R. R. Kalluri, D. R. Cahela, B. J. Tatarchuk, *Appl. Catal. B* 90 (2009) 507.
- [31] J. Gascon, J. R. van Ommen, J. A. Moulijn, F. Kapteijn, *Catal. Sci. Technol.* 5 (2015) 807.
- [32] S. Wang, X. Zhang, Y. Zhao, Y. Ge, J. Lv, B. Wang, X. Ma, *Front. Chem. Sci. Eng.* 6 (2012) 259.
- [33] S. Wahid, D. R. Cahela, B. J. Tatarchuk, *AIChE J.* 60 (2014) 3814.
- [34] A. Montebelli, C. G. Visconti, G. Groppi, E. Tronconi, C. Cristiani, C. Ferreira, S. Kohler, *Catal. Sci. Technol.* 4 (2014) 2846.

- [35] D. Wu, S. Kong, H. Zhang, Y. Li, *AIChE J.* 60 (2014) 2765.
- [36] C. Wang, L. Han, Q. Zhang, Y. Li, G. Zhao, Y. Liu, Y. Lu, *Green Chem.* 17 (2015) 3762.
- [37] N. Mahata, V. Vishwanathan, *J. Catal.* 196 (2000) 262.
- [38] Z. Li, X. Hu, L. Zhang, S. Liu, G. Lu, *Appl. Catal. A* 417-418 (2012) 281.
- [39] J. H. Holles, R. J. Davis, T. M. Murray, J. M. Howe, *J. Catal.* 195 (2000) 193.
- [40] M. Kurnatowska, L. Kepinski, W. Mista, *Appl. Catal. B* 117-118 (2012) 135.
- [41] P. L. Hansen, J. B. Wagner, S. Helveg, J. R. Rostrup-Nielsen, B. S. Clausen, H. Topsøe, *Science* 295 (2002) 2053.
- [42] F. Tao, M. Salmeron, *Science* 331 (2011) 171.
- [43] B. Wang, X. Ma, G. Xu, L. Mao, *Comput. Chem. Eng.* 24 (2000) 1337.
- [44] Y. Li, Q. Zhang, R. Chai, G. Zhao, Y. Liu, Y. Lu, *ChemCatChem* 7 (2015) 1427.
- [45] R. Addou, T. P. Senftle, N. O'Connor, M. J. Janik, A. C. T. van Duin, M. Batzill, *ACS Nano* 8 (2014) 6321.
- [46] M. C. Valero, P. Raybaud, P. Sautet, *J. Phys. Chem. B* 110 (2006) 1759.
- [47] J. Huang, Y. Wang, J. Zheng, W. Dai, K. Fan, *Appl. Catal. B* 103 (2011) 343.
- [48] T. He, L. Xiang, S. Zhu, *CrystEngComm* 11 (2009) 1338.
- [49] Q. Li, Z. Zhou, R. Chen, B. Sun, L. Qiao, Y. Yao, K. Wu, *Phys. Chem. Chem. Phys.* 17 (2015) 9126.
- [50] W. S. Kijlstra, D. S. Brands, E. K. Poels, A. Blik, *J. Catal.* 171 (1997) 208.
- [51] S. Parres-Esclapez, I. Such-Basañez, M. J. Illán-Gómez, C. Salinas-Martínez de Lecea, A. Bueno-López, *J. Catal.* 276 (2010) 390.
- [52] C. J. Cassady, B. S. Freiser, *J. Am. Chem. Soc.* 107 (1985) 1566.

- [53] L. F. Liotta, G. A. Martin, G. Deganello, *J. Catal.* 164 (1996) 322.
- [54] J. Goetz, M. A. Volpe, A. M. Sica, C. E. Gigola, R. Touroude, *J. Catal.* 167 (1997) 314.
- [55] O. Dulaurent, K. Chandes, C. Bouly, D. Bianchi, *J. Catal.* 188 (1999) 237.
- [56] Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A. U. Nilekar, G. Peng, J. A. Herron, D. C. Bell, H. Saltsburg, M. Mavrikakis, M. Flytzani-Stephanopoulos, *Science* 329 (2010) 1633.
- [57] J. Yu, D. Mao, L. Han, Q. Guo, G. Lu, *J. Mol. Catal. A: Chem.* 367 (2013) 38.
- [58] Y. Fujimori, W. E. Kaden, M. A. Brown, B. Roldan Cuenya, M. Sterrer, H. Freund, *J. Phys. Chem. C* 118 (2014) 17717.
- [59] N. Bârsan, U. Weimar, *J. Phys.: Condens. Matter* 15 (2003) R813.
- [60] P. Larkin, *Infrared and Raman Spectroscopy*, Elsevier, Oxford, 2011, p. 41.
- [61] J. Bagg, *J. Catal.* 13 (1969) 271.
- [62] H. Guan, J. Lin, L. Li, X. Wang, T. Zhang, *Appl. Catal. B* 184 (2016) 299.
- [63] A. J. Renouprez, J. F. Trillat, G. Bergeret, P. Delichère, J. L. Rousset, J. Massardier, D. Loffreda, D. Simon, F. Delbecq, P. Sautet, *J. Catal.* 198 (2001) 243.
- [64] C. Chen, W. Cheng, *Catal. Lett.* 83 (2002) 121.
- [65] G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, *Handbook of Heterogeneous Catalysis*, second ed., Wiley-VCH, Weinheim, 2008, 1696.

Table and Figure Captions

Table 1. Effect of Pd loading on the Pd dispersion and particle size for Al-fiber@ns-AlOOH@Pd catalysts.

Table 2. Catalyst characteristics and TOF for the CO coupling to DMO.

Table 3. Band areas of bridged CO and linear CO and the band area ratio from DRIFTS spectra.

Fig. 1. All-in-one for the Al-fiber@ns-AlOOH and Al-fiber@ns-AlOOH@Pd (0.25 wt% Pd, ICP-AES). (A) The schematic illustration for top-down preparation (A-1, stream-only oxidation at 120 °C for 6 h; A-2, impregnation with Pd precursor and calcination at 300 °C for 2 h in air). Optical photograph of mother Al-fiber (B) and Al-fiber@ns-AlOOH@Pd (C). SEM images of the mother Al-fiber (D) and Al-fiber@ns-AlOOH (E, insert: core(Al-fiber)@shell(ns-AlOOH) structure). (F) XRD patterns of mother Al-fiber (a), Al-fiber@ns-AlOOH (b) and Al-fiber@ns-AlOOH@Pd (c). N₂ adsorption-desorption isothermal (G, insert: Barrett-Jovner-Halenda (BJH) mesopore size distribution), SEM image (H) and TEM image (I, insert: Pd particle size distribution) of Al-fiber@ns-AlOOH@Pd.

Fig. 2. Effects of preparation parameters on the catalytic performance of Al-fiber@ns-AlOOH@Pd catalysts for the CO coupling to DMO at 150 °C. (A) Pd loading; (B) calcination temperature of support; (C) calcination temperature of catalyst and (D) activation conditions with different atmospheres and temperatures (the as-prepared catalyst is activated in pure H₂ at 200 °C, pure H₂ at 30 °C, pure CO at 200 °C and feed gas at 200 °C, respectively). Other conditions: 0.80 g catalyst, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 3. XRD patterns of the used Al-fiber@ns-AlOOH@Pd-0.25 catalysts with different support calcination temperatures (A, a: no calcination, b: 300 °C and c: 600 °C) and catalyst calcination

temperatures (B, a: 200 °C, b: 300 °C, c: 450 °C and d: 600 °C).

Fig. 4. Effects of reaction conditions on the catalytic performance of Al-fiber@ns-AlOOH@Pd-0.25 catalyst for the CO coupling to DMO at 0.1 MPa. (A) GHSV of 3000 L kg⁻¹ h⁻¹ and CO to MN volume ratio of 1.4; (B) GHSV of 3000 L kg⁻¹ h⁻¹ at 150 °C; (C) CO to MN volume ratio of 1.4 at 150 °C and (D) CO to MN volume ratio of 1.4 at 150 °C. The catalyst is 0.08 g and 0.80 g for low GHSV (from 1500 to 9000 L kg⁻¹ h⁻¹) and high GHSV (from 30000 to 60000 L kg⁻¹ h⁻¹), respectively.

Fig. 5. Lifetime test (A) of the Al-fiber@ns-AlOOH@Pd-0.25 catalyst and SEM images of the catalyst before (B) and after (C) 200 h on steam. Reaction conditions: 0.80 g catalyst, 150 °C, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 6. CO conversion and DMO selectivity for Pd/ α -Al₂O₃ catalyst as a function of reaction temperature. Other conditions: 0.80 g catalyst, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 7. (A) The TPD profiles of dehydroxylation (the data are the peak areas from 150 °C to 580 °C); (B) the relationship between the hydroxyl amount (TPD peak areas) and TOFs as well as the linear fit. CAT-1, CAT-2 and CAT-3 were used to denominate the catalysts using the Al-fiber@ns-AlOOH support without calcination treatment (as-prepared), after calcining at 300 °C and at 600 °C for 2 h, respectively. Other conditions: 0.08 g catalyst, 110 °C, GHSV of 60000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa, TOF ([The detailed calculations in Supporting Information](#)) based on DMO yield and the amount of surface Pd atoms, calculated by reducing the CO conversion to below 10% with ultra-high GHSV and low reaction temperature. Note: the surface Pd atoms were obtained on the basis of Pd particle size (d) determined by TEM images in [Fig. S2](#) and Pd dispersion (D) calculated by the equation ($d = 1.12 / D$ [\[37\]](#)).

Fig. 8. DRIFTS spectra of MN adsorbed on CAT-1, -2, -3 and Pd/ α -Al₂O₃ at 35 °C (A) and 150 °C (B). The sample was prereduced in H₂ at 150 °C for 2 h, purged in N₂ at 200 °C for 1 h, cooled down to 35 °C, exposed to 11.6 % MN in N₂ for 30 min and subsequently flushed in N₂ for 1 h. After that, the spectra were recorded in range from 35 °C to 150 °C.

Fig. 9. DRIFTS spectra of CO adsorbed on CAT-1, -2, -3 and Pd/ α -Al₂O₃ at 35 °C (A), 50 °C (B), 100 °C (C) and 150 °C (D). The sample was prereduced in H₂ at 150 °C for 2 h, purged in N₂ at 200 °C for 1 h, cooled down to 35 °C, exposed to pure CO for 30 min and subsequently flushed in N₂ for 1 h. After that, the spectra were recorded in range from 35 °C to 150 °C.

Fig. 10. Arrhenius plot for CO coupling to DMO over CAT-1, -2, -3 and Pd/ α -Al₂O₃ (**Supporting Information for the calculation details in Fig. S10 and Fig. S11**).

Fig. 11. Dynamic changes of DRIFTS spectra on CAT-1 and Pd/ α -Al₂O₃ catalysts after CO pre-adsorption at 100 °C and 150 °C as a function of MN pulse number (0, 1, 3, 5, 9, 13, 17 and 25) and the relationship between band area of bridged CO (2005-1800 cm⁻¹) and pulse number as well as the fit.

Table 1. Effect of Pd loading on the Pd dispersion and particle size for Al-fiber@ns-AlOOH@Pd catalysts.

Theoretical Pd loading (wt%)	0.06	0.1	0.3	0.5	1.0
Pd dispersion (%) ^a	67	62	54	42	32
Pd particle size (nm) ^b	1.7	1.8	2.1	2.7	3.5

^a Pd dispersion (D) measured by CO pulse adsorption assuming a CO/Pd ratio of 1 on account of the systematic errors. ^b Pd particle size (d) calculated by the equation: $d = 1.12 / D$ [37].

Table 2. Catalyst characteristics and TOF for the CO coupling to DMO^a.

Catalyst	Pd (wt%) ^c	d (nm) ^d	D (%) ^d		Conv. (%) ^e	Sel. (%) ^e	TOF (min ⁻¹) ^f	
			D-1 ^d	D-2 ^d			TOF-1 ^f	TOF-2 ^f
CAT-1 ^b	0.25	1.8	62	54	9.0	98.0	20.4	23.4
CAT-2 ^b	0.24	1.9	59	57	5.6	97.9	13.7	14.2
CAT-3 ^b	0.26	1.8	62	56	4.3	97.7	9.4	10.4
Pd/ α -Al ₂ O ₃	0.26	2.0	56	60	2.7	98.2	6.2	5.8

^a Reaction conditions: 0.08 g catalyst, 110 °C, GHSV of 60000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa. ^b CAT-1, CAT-2 and CAT-3 were used to denominate the catalysts using the Al-fiber@ns-AlOOH support without calcination treatment (as-prepared), after calcining at 300 °C and at 600 °C for 2 h, respectively. ^c Pd loading determined by ICP-AES. ^d Pd particle size (*d*) determined by TEM images in Fig. S2 and Pd dispersion (*D-1*) calculated by the equation ($d = 1.12 / D-1$ [37]) and Pd dispersion (*D-2*) measured by CO pulse adsorption assuming a CO/Pd ratio of 1 on account of the systematic errors. ^e Conversion of CO and selectivity of DMO. ^f TOF (The detailed calculations in Supporting Information) based on DMO yield and the amount of surface Pd atoms (*TOF-1* vs. *D-1*, *TOF-2* vs. *D-2*), calculated by reducing the CO conversion to below 10% with ultra-high GHSV and low reaction temperature.

Table 3. Band areas of bridged CO and linear CO and the band area ratio from DRIFTS spectra^a.

Temperature (°C)	Catalyst	A _{bridged CO} ^b	A _{linear CO} ^b	A _{bridged CO} : A _{linear CO}
35	CAT-1	3.25	0.26	12.5
	CAT-2	3.28	0.36	9.1
	CAT-3	3.19	0.45	7.1
	Pd/ α -Al ₂ O ₃	3.59	0.95	3.8
50	CAT-1	3.18	0.21	15.1
	CAT-2	3.15	0.35	9.0
	CAT-3	2.99	0.41	7.3
	Pd/ α -Al ₂ O ₃	3.45	0.70	4.9
100	CAT-1	2.29	0.08	28.6
	CAT-2	2.41	0.14	17.2
	CAT-3	2.62	0.19	13.8
	Pd/ α -Al ₂ O ₃	2.26	0.23	9.8
150	CAT-1	2.16	~0	—
	CAT-2	2.07	~0	—
	CAT-3	1.91	~0	—
	Pd/ α -Al ₂ O ₃	0.90	~0	—

^a The DRIFTS spectra of CO adsorbed on CAT-1, -2, -3 and Pd/ α -Al₂O₃ at 35, 50, 100 and 150 °C. ^b Areas of bridged CO band (2005-1800 cm⁻¹) and linear CO band (2120-2005 cm⁻¹) based on the DRIFTS spectra.

Fig. 1. All-in-one for the Al-fiber@ns-AlOOH and Al-fiber@ns-AlOOH@Pd (0.25 wt% Pd, ICP-AES). (A) The schematic illustration for top-down preparation (A-1, stream-only oxidation at 120 °C for 6 h; A-2, impregnation with Pd precursor and calcination at 300 °C for 2 h in air). Optical photograph of mother Al-fiber (B) and Al-fiber@ns-AlOOH@Pd (C). SEM images of the mother Al-fiber (D) and Al-fiber@ns-AlOOH (E, insert: core(Al-fiber)@shell(ns-AlOOH) structure). (F) XRD patterns of mother Al-fiber (a), Al-fiber@ns-AlOOH (b) and Al-fiber@ns-AlOOH@Pd (c). N₂ adsorption-desorption isothermal (G, insert: Barrett-Jovner-Halenda (BJH) mesopore size distribution), SEM image (H) and TEM image (I, insert: Pd particle size distribution) of Al-fiber@ns-AlOOH@Pd.

Fig. 2. Effects of preparation parameters on the catalytic performance of Al-fiber@ns-AlOOH@Pd catalysts for the CO coupling to DMO at 150 °C. (A) Pd loading; (B) calcination temperature of support; (C) calcination temperature of catalyst and (D) activation conditions with different atmospheres and temperatures (the as-prepared catalyst is activated in pure H₂ at 200 °C, pure H₂ at 30 °C, pure CO at 200 °C and feed gas at 200 °C, respectively). Other conditions: 0.80 g catalyst, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 3. XRD patterns of the used Al-fiber@ns-AlOOH@Pd-0.25 catalysts with different support calcination temperatures (A, a: no calcination, b: 300 °C and c: 600 °C) and catalyst calcination temperatures (B, a: 200 °C, b: 300 °C, c: 450 °C and d: 600 °C).

Fig. 4. Effects of reaction conditions on the catalytic performance of Al-fiber@ns-AlOOH@Pd-0.25 catalyst for the CO coupling to DMO at 0.1 MPa. (A) GHSV of 3000 L kg⁻¹ h⁻¹ and CO to MN volume ratio of 1.4; (B) GHSV of 3000 L kg⁻¹ h⁻¹ at 150 °C; (C) CO to MN volume ratio of 1.4 at 150 °C and (D) CO to MN volume ratio of 1.4 at 150 °C. The catalyst is 0.08 g and 0.80 g for low GHSV (from 1500 to 9000 L kg⁻¹ h⁻¹) and high GHSV (from 30000 to 60000 L kg⁻¹ h⁻¹), respectively.

Fig. 5. Lifetime test (A) of the Al-fiber@ns-AlOOH@Pd-0.25 catalyst and SEM images of the catalyst before (B) and after (C) 200 h on steam. Reaction conditions: 0.80 g catalyst, 150 °C, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 6. CO conversion and DMO selectivity for Pd/ α -Al₂O₃ catalyst as a function of reaction temperature. Other conditions: 0.80 g catalyst, GHSV of 3000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa.

Fig. 7. (A) The TPD profiles of dehydroxylation (the data are the peak areas from 150 °C to 580 °C); (B) the relationship between the hydroxyl amount (TPD peak areas) and TOFs as well as the linear fit. CAT-1, CAT-2 and CAT-3 were used to denominate the catalysts using the Al-fiber@ns-AlOOH support without calcination treatment (as-prepared), after calcining at 300 °C and at 600 °C for 2 h, respectively. Other conditions: 0.08 g catalyst, 110 °C, GHSV of 60000 L kg⁻¹ h⁻¹, CO to MN volume ratio of 1.4, 0.1 MPa, TOF ([The detailed calculations in Supporting Information](#)) based on DMO yield and the amount of surface Pd atoms, calculated by reducing the CO conversion to below 10% with ultra-high GHSV and low reaction temperature. Note: the surface Pd atoms were obtained on the basis of Pd particle size (d) determined by TEM images in [Fig. S2](#) and Pd dispersion (D) calculated by the equation ($d = 1.12 / D$ [[37](#)]).

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Fig. 10. Arrhenius plot for CO coupling to DMO over CAT-1, -2, -3 and $\text{Pd}/\alpha\text{-Al}_2\text{O}_3$ (Supporting Information for the calculation details in Fig. S10 and Fig. S11).

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