Copper-Fiber-Structured Pd–Au–CuO_x: Preparation and Catalytic Performance in the Vapor-Phase Hydrogenation of Dimethyl Oxalate to Ethylene Glycol

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Cu-fiber-structured ternary Pd–Au–CuO_x catalysts engineered from nano- to macro-scales have been developed for the vapor-phase dimethyl oxalate (DMO) hydrogenation to ethylene glycol (EG), with the aid of galvanic deposition of Pd and Au onto a thin-sheet microfibrous structure using 8 μ m Cu fiber. Effects of Pd and Au loadings and their ratio have been investigated on the catalyst performance as well as the reac-

Introduction

Ethylene glycol (EG) is an important intermediate chemical thanks to its wide applications in polyester manufacture, antifreeze compounds, and solvents.^[1-3] The current commercial production of EG mainly depends on the oxidation of petroleum-derived ethylene. However, with the petroleum dwindling and the ever-increasing demand for EG, the indirect synthesis of EG from syngas attracts extensive attention, in which syngas can be readily derived from biomass, coalbed methane, natural gas, and coal. This indirect process could be realized through a two-step process consisting of the coupling of CO with nitrite esters to form dimethyl oxalate (DMO) and the subsequent hydrogenation of DMO to EG.^[4,5] The first step has been scaled up to commercial production with a capacity of 10000 tons per year in 2010,^[6] and the following DMO hydrogenation process has been considerably investigated in both homogeneous and heterogeneous systems. Ruthenium-based homogeneous catalysts were previously used for liquid-phase DMO hydrogenation with a high EG yield, but greatly suffered from the problems of corrosion and separation.^[7] From an industrial point of view, the vapor-phase hydrogenation process is more attractive because of the convenience of catalyst separation and higher production efficiency especially for the EG production in a bulk form. It has been well established that Cu-based heterogeneous catalysts are highly active and selec-

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tion conditions including reaction temperature and pressure, liquid weight hourly space velocity, and H₂/DMO ratio. The promising 0.1 Pd-0.5 Au-CuO_x/Cu-fiber catalyst is capable of converting 97–99% DMO into EG product at a selectivity of 90–93%. This catalyst is stable for at least 200 h. The Pd-Au-Cu₂O synergistically promotes the hydrogenation activity and stabilizes Cu⁺ sites to suppress deep reduction deactivation.

tive for the vapor-phase hydrogenation of DMO to EG. However, the easy deactivation and inadequate lifespan of Cu-based catalysts severely hinder their practical industrialization. Generally, modification of the catalysts is believed to be an effective method to improve the catalyst stability. CuCr catalyst was reported to be highly active with a long lifetime of 1134 h, however, the toxicity of Cr greatly hampers its application.^[8] Consequently, research efforts have been focused on the development of Cr-free Cu-based catalysts for this reaction. It is reported that the lifetime of Cu/SiO₂ can be dramatically prolonged from only 30 h to 200 h by La_2O_3 modification,^[2] to 300 h by boron modification,^[9] and to 600 h by ZrO₂ modification^[3] under identical reaction conditions. AuCu/SBA-15 has also been reported to be effective for the hydrogenation of DMO to EG, with a prolonged lifetime of 240 h.^[10] More recently, hydroxyapatite-supported Cu catalyst has been fabricated by a facile ammonia-assisted one-pot synthesis method, which owns prolonged lifetime to 120 h because of the stabilizingeffect of the phosphate species on the Cu particles and Cu⁺ species.[11]

Although numerous promising results have been obtained, there are many technical problems to be solved for industrial application. Most of all, the usage of silica support is considered to be problematic because of the severe loss of the silica from the Cu/SiO₂ in the form of tetramethoxysilane if using methanol as solvent.^[12] This silica loss is considered to be a crucial factor promoting copper aggregation, and likely results in low-quality rather than polymerization-grade EG. On the other hand, the DMO hydrogenation to EG is an exothermic reaction $(\Delta H = -58.73 \text{ kJ mol}^{-1})$,^[13] normally generating hotspots that expedites catalyst sintering deactivation. Most current efforts have been devoted to improving the dispersion of Cu species or adding promoters to alleviate the agglomeration has been



paid to the catalyst's heat-transfer ability, although the catalysts usually need to operate in adiabatic packed-bed reactors with high conversion, for which a good heat transfer is mandatory. Hence, from both academic and industrial points of view, it is particularly urgent to develop a novel SiO₂-free catalyst with unique combination of high catalytic activity and selectivity, structural robustness, and excellent thermal conductivity.

Consequently, metal microfibrous-structured materials with much higher heat-transfer ability than oxides have attracted increasing interests as catalyst supports in strongly endothermic and exothermic reactions.^[15] We have demonstrated successful applications of microfibrous matrixes and foams in the development of many structured catalysts for the methanol-to-olefins process,^[16] vapor-phase oxidation of alcohols,^[17] oxidative coupling of methanol to methyl formate,[18] Fischer-Tropsch synthesis to lower olefins,^[19] coalbed methane deoxygenation,^[20] NH₃ cracking,^[21] syngas methanation,^[22] and methanol steam reforming.^[23] In the light of the above success, we aimed to utilize metal fibers with microfibrous structure to prepare a novel SiO₂-free Cu-based catalyst for DMO hydrogenation. We expected that the sintering of the Cu NPs would be relieved because of the higher thermal conductivity of the metal fiber than that of the oxide supports and the SiO₂ leaching encountered for the traditional Cu/SiO₂ during the DMO hydrogenation would be avoided.^[12]

Herein we report on a high-performance monolithic structured Pd-Au-CuO_x/Cu-fiber catalyst by galvanically depositing Pd and Au nanoparticles (NPs) onto the Cu-fiber surfaces. The promising Pd-Au-CuO_x/Cu-fiber catalyst with 0.1 wt% Pd and 0.5 wt% Au could deliver DMO conversion of 97-99% with EG selectivity of 90-93% and could assure activity/selectivity maintenance for at least 200 h at 270 $^\circ\text{C}$ and 2.5 MPa, using a liquid weight hourly space velocity (LWHSV) of 5.3 h^{-1} and a H₂/DMO molar ratio of 180. The synergistic effect of the ternary Pd-Au-CuO_x composite is tentatively discussed. Note that some parts of results concerning this work were previously reported as a short communication,^[24] which focused on the novel microstructured catalyst system rather than the effects of Pd and Au loadings on the catalyst performance as well as the reaction conditions including reaction temperature/pressure, LWHSV, and H₂/DMO ratio.

Results and Discussion

Pd and/or Au galvanic deposition, structure, and morphology of the catalyst

Initially, the monolithic sinter-locked microfibrous-structured 8 μ m Cu fibers were prepared by regular wet layup papermaking with a subsequent sintering process,^[25] which were then tailored into desired circular chips (8 mm diameter, 2 mm thickness). Subsequently, 2.5 Au–CuO_x/Cu-fiber, 0.5 Pd–CuO_x/Cu-fiber, and 0.5 Pd–2.5Au–CuO_x/Cu-fiber catalysts were prepared by the galvanic deposition method following by drying at 100 °C overnight and calcination at 300 °C for 2 h in air. As shown in Figure 1A,B, our representative circular chip-like 0.5 Pd–2.5 Au–CuO_x/Cu-fiber sample has a 3D microfibrous net-

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Figure 1. Structural features from nano- to macro-scales for the structured 0.5 Pd-2.5 Au-CuO_x/Cu-fiber catalyst. A) Photograph of the macroscopic sample; B) SEM image, showing its 3 D porous network structure; C) XRD patterns of a) CuO_x/Cu-fiber, b) 0.5 Pd-CuO_x/Cu-fiber, c) 2.5 Au-CuO_x/Cu-fiber, and d) 0.5 Pd-2.5 Au-CuO_x/Cu-fiber catalysts; D) high-magnification SEM image of 0.5 Pd-2.5 Au-CuO_x/Cu-fiber catalyst.

work structure with entirely open but irregular submillimeterscaled macropores. Satisfactorily, Pd and Au were firmly embedded onto the Cu-fiber surface with the aid of galvanic deposition method, and the actual loadings account for about 70% of theoretical ones for all samples (see the inductively coupled plasma atomic-emission spectroscopy, ICP-AES, results in the Supporting Information, Table S1). Such galvanic deposition can proceed spontaneously if wetting the Cu-fiber surface with the aqueous solution containing the appointed amounts of Pd and Au cations, owing to the distinct electrode potential differences between the Cu^{2+}/Cu^{0} (0.34 V; or Cu^{+}/Cu^{0} , 0.52 V) and Au^{3+}/Au^{0} (1.5 V; or Pd^{2+}/Pd^{0} , 0.95 V) pairs. XRD patterns of the fresh catalysts are shown in Figure 1C. Only one XRD peak centered at 36.3° could be clearly detected on the CuO_x/Cufiber and the 0.5 Pd-CuO_x/Cu-fiber catalyst, which was attributed to Cu₂O (JCPDS-77-0199). Except for the Cu₂O diffraction peak, peaks at 35.4° and 38.6° attributed to CuO (JCPDS-80-1916) were also detected on the 2.5 Au-CuO_x/Cu-fiber and 0.5 Pd-2.5Au-CuO_x/Cu-fiber catalysts. Note that no XRD peaks of Au, Pd, or PdO phase could be detected on all samples, indicating high dispersion of the Au and Pd species. Indeed, the TEM images shown in Figure 2 and Supporting Information Figure S1 also confirmed the highly dispersed Au and Pd particles with sizes of approximately 4 nm over all samples. In addition, high magnification SEM image of 0.5 Pd-2.5 Au-CuO_x/Cu fiber revealed the large CuO_x crystalline grains (Figure 1D). The above results indicated that our novel galvanic deposition method was working effectively and efficiently to create such structured 0.5 Pd-CuO_x/Cu-fiber, 2.5 Au-CuO_x/Cu-fiber, and 0.5 Pd-2.5 Au-CuO_x/Cu-fiber catalysts, which were expected to be competent in DMO hydrogenation reaction.

Catalytic performance

The as-prepared $0.5 Pd-CuO_x/Cu$ -fiber, $2.5 Au-CuO_x/Cu$ -fiber, $0.5 Pd-2.5 Au-CuO_x/Cu$ -fiber, and CuO_x/Cu -fiber catalysts were







Figure 2. A) TEM image and B) particle size distribution of 0.5Pd-2.5Au–CuO_x/Cu-fiber catalyst.

tested in the DMO hydrogenation reaction at 270 $^\circ\text{C}$ and 2.5 MPa, using a LWHSV of 5.3 h⁻¹ and H₂/DMO molar ratio of 180, with the results as shown in Table 1. The reference catalyst of CuO_x/Cu-fiber, with Cu₂O phase formation (Figure 1C) that provides the crucial catalytic active sites of Cu⁺ for the hydrogenation of DMO,^[3,9,26-29] showed mere DMO conversion of 40% and poor EG selectivity of only 1%. If Pd or Au was introduced into CuO_x/Cu-fiber, interestingly, either Pd or Au displayed promotion effect, and as a result, the catalytic hydrogenation of DMO was significantly increased. As-obtained 0.5 Pd-CuO_x/Cu-fiber and 2.5 Au-CuO_x/Cu-fiber were capable of converting DMO at conversions of 98% and 94% into EG with selectivities of 87% and 60%, respectively. Analogously, it has been reported that the assistant role of Pd in dissociating molecular H₂ contributes to the enhancement of the hydrogenation performance of Cu-based catalysts in numerous reactions, such as methanol synthesis and alkynes hydrogenation.[30,31]

Table 1. DMO hydrogenation performance over the various catalysts. ^[a]					
Catalyst	DMO conve [%]	ersion EG	Selectivity MG	y [%] Et(ОН
CuO _x /Cu-fiber 0.5 Pd–CuO _x /Cu-fiber 2.5 Au–CuO _x /Cu-fiber 0.5 Pd–CuO _x /Cu-fiber	40 98 94 99	1 87 60 91	96 10 39 5	3 3 1 4	
[a] Reaction conditions:	T=270°C, L	WHSV = 5.3 h^{-1} ,	13 wt%	DMO	in

methanol, $P(H_2) = 2.5$ MPa, $n(H_2)/n(DMO) = 180$. MG = methyl glycolate.

Moreover, Wang and co-workers have reported that Au-modified 6Cu1.9Au/SBA-15 catalyst exhibits remarkable enhanced catalytic performance for the hydrogenation of DMO to EG compared with 6Cu/SBA-15, as indicated by the increased turnover frequency (TOF from 23 to 121 h⁻¹.^[10] Excitingly, the 0.1Pd-0.5Au-CuO_x/Cu-fiber catalyst with co-introduction of Pd and Au in this study could further enhance the catalytic performance, delivering the highest DMO conversion of 99% and the optimal selectivity of 91% toward EG. Clearly, the above results suggested the existence of a synergistic promotion effect of Pd and Au on the catalyst activity, which will be further discussed below.

Effects of Pd/Au ratio and Pd (Au) loadings

It has been reported that the composition of Pd-Au bimetallic catalysts has a significant effect on their catalytic performances, such as Pd (Au) loadings and Pd/Au ratio.[32] Herein, the effect of Pd/Au weight ratio on the Pd-Au-CuO_x/Cu-fiber catalysts for the DMO hydrogenation was investigated at a fixed Pd loading of 0.5 wt% and a fixed Au loading of 0.5 wt%, with the results displayed in Figure 3 A,B. The actual loadings of Au and Pd measured by ICP-AES are listed in Table S1. As shown in Figure 3A, at a fixed Pd loading of 0.5 wt%, the DMO conversion and EG selectivity slightly increased and 99% and 91%, respectively, along with the increase of the Au loading to a Pd/ Au weight ratio up to 1:1 (corresponding to 0.5 wt% Pd and 0.5 wt% Au), but it showed a gradual decline with further increasing the Pd/Au weight ratio. Similar evolution behavior of the conversion/selectivity against the Pd/Au weight ratio was observed also for keeping the Au loading constant at 0.5 wt%. As shown in Figure 3B, the 0.1Pd-0.5Au-CuO_x/Cu-fiber catalyst with the Pd/Au weight ratio of 1:5 delivered the highest activity and selectivity (99% DMO conversion and 93% EG selectivity). Consequently, the Pd/Au weight ratio of 1:5 was considered to be optimal for our Pd-Au-CuO_x/Cu-fiber catalyst for the DMO hydrogenation and the 0.1 Pd-0.5 Au-CuO_x/Cu fiber was the most promising catalyst with combination of high-performance and acceptably low precious metal usage. At a fixed Pd/Au weight ratio of 1:5, Pd-Au-CuO_x/Cu-fiber catalysts with further lowering the loadings of Au and Pd were prepared and tested in the DMO hydrogenation, but no conversion and se-



Figure 3. Effect of the Pd/Au ratio on the DMO hydrogenation performance of Pd–Au–CuO_x/Cu-fiber catalysts with A) fixed Pd loading of 0.5 wt % and B) fixed Au loading of 0.5 wt %; C) Effects of Pd and Au loadings on the DMO hydrogenation performance of Pd–Au–CuO_x/Cu-fiber catalysts with fixed Pd/Au weight ratio of 1:5. Reaction conditions: T = 270 °C, LWHSV = 5.3 h⁻¹, 13 wt % DMO in methanol, $P(H_3) = 2.5$ MPa, $n(H_3)/n(DMO) = 180$. MG = methyl glycolate.

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lectivity comparable to those for the 0.1 Pd-0.5 Au-CuO_x/Cufiber catalyst could be yielded (Figure 3C). For example, the 0.02 Pd-0.1 Au-CuO_x/Cu-fiber with 0.02 wt% Pd and 0.1 wt% Au loadings showed a DMO conversion of 89% with a relatively low EG selectivity of only 43% under identical reaction conditions.

Effects of reaction conditions

It is known that DMO hydrogenation comprises several continuous reactions (Scheme 1), including DMO hydrogenation to methyl glycolate (MG), MG hydrogenation to EG, and deep hydrogenation of EG to ethanol. The catalyst performance for the DMO hydrogenation is distinctly influenced by the reaction conditions including temperature, pressure, LWHSV, and molar ratio of H₂/DMO. Thus the effects of the reaction conditions on the catalytic performance of our 0.1 Pd–0.5 Au–CuO_x/Cu-fiber catalyst for the DMO hydrogenation were investigated, with the results shown in Figure 4A–D.

In Figure 4A, the temperature-dependent conversion and selectivities for the DMO hydrogenation using $0.1 Pd-0.5 Au-CuO_x/Cu$ -fiber catalyst are displayed, at 2.5 MPa using a H₂/DMO ratio of 180 and LWHSV of 5.3 h⁻¹. With the increase of the reaction temperature from 210 to 270 °C, the DMO conver-

Ö						
C-OCH ₃	+2H.	CH ₂ OH	+2H	CH ₂ OH	+H.	CH ₂ OH
.	\rightarrow		$\xrightarrow{+211_2}$	1 .	• 112	→ [°]
C-OCH ₃	-CH ₃ OH	C-OCH ₃	-CH ₃ OH	CH_2OH	$-H_2O$	CH_3
Ö		Ö				

Scheme 1. Hydrogenation of DMO to MG, EG, and ethanol.



Figure 4. Effects of certain reaction parameters on DMO hydrogenation performance of 0.1 Pd–0.5 Au–CuO_x/Cu-fiber: A) reaction temperature, at reaction conditions: LWHSV = 5.3 h⁻¹, 13 wt% DMO in methanol, *P*=2.5 MPa, $n(H_2):n(DMO) = 180$; B) pressure, at reaction conditions: 270 °C, LWHSV = 5.3 h⁻¹, 13 wt% DMO in methanol, $n(H_2):n(DMO) = 180$; C) LWHSV, at reaction conditions: 270 °C, 13 wt% DMO in methanol, *P*=2.5 MPa, $n(H_2):n(DMO) = 180$; (D) molar ratio of H₂/DMO, at reaction conditions: 270 °C, LWHSV = 5.3 h⁻¹, 13 wt% DMO in methanol, *P*=2.5 MPa, $n(H_2):n(DMO) = 180$; (D) molar ratio of H₂/DMO, at reaction conditions: 270 °C, LWHSV = 5.3 h⁻¹, 13 wt% DMO in methanol, *P*=2.5 MPa.

sion increased from 45% to 99% and the EG selectivity increased from 12% to 93%. With further increasing temperature to 280 °C, the DMO conversion remained at 99%, however, the EG selectivity decreased to 91% while the ethanol selectivity increased from 3% at 270 °C to 6%. Clearly, relatively high reaction temperature was favorable for our Au–Pd–CuO_x/Cu-fiber catalyst for hydrogenation of DMO into EG. However, excessive hydrogenation would proceed to form ethanol at too high temperature thereby leading to a decline of EG selectivity.

In Figure 4B, the DMO conversion and product selectivities for the DMO hydrogenation using 0.1 Pd-0.5Au-CuO_x/Cu-fiber catalyst are plotted against the reaction pressure at 270 °C using a H_2 /DMO ratio of 180 and a LWHSV of 5.3 h⁻¹. Clearly, catalytic activity and products distribution were sensitive to reaction pressure. DMO conversion and EG selectivity showed volcano evolution behavior with increasing the reaction pressure from 0.5 to 3.0 MPa. The DMO conversion increased from 24% to 99% and the EG selectivity increased from 23% to 93% with increasing the H₂ pressure from 0.5 to 2.5 MPa, which is a common promotion effect in hydrogenation reactions.^[33] If further increasing the H₂ pressure up to 3.0 MPa, the DMO conversion still remained unchanged at 99%, however, the EG selectivity fell down to 90% associated with an increase of ethanol selectivity from 3% (2.5 MPa) to 6% as a result of the excessive hydrogenation.

In Figure 4C, the DMO conversion and EG selectivity for the DMO hydrogenation using 0.1 Pd-0.5 Au-CuO_x/Cu-fiber catalyst is displayed as a function of the LWHSV at 270 $^\circ\text{C}$ and 2.5 MPa using a H₂/DMO of 180. Clearly, the DMO conversion was retained at 99% or above with the increase of the LWHSV up to 5.3 h⁻¹ and gradually declined from 99% to 85% with the LWHSV from 5.3 to 14.2 h⁻¹ as a result of inadequate residential time that was unfavorable to the DMO hydrogenation. Regarding the EG selectivity, it exhibited a volcano-shaped distribution within the LWHSV range studied. The EG selectivity mounted from 38% to 93% with the LWHSV from 2.7 to 5.3 h⁻¹ and then continuously declined from the climax to 52% with further increase of the LWHSV up to 14.2 h^{-1} . It is logical that a proper residential time might exist for DMO hydrogenation to EG, because much longer residential time led to excessive hydrogenation of EG into ethanol while quite shorter residential time was not enough for intermediate product MG hydrogenation to EG.

The plot in Figure 4D shows a volcano-shaped curve for the DMO conversion and EG selectivity against the H₂/DMO molar ratio ranging from 60 to 240. At 270 °C, 2.5 MPa and 5.3 h⁻¹, the DMO conversion and EG selectivity both reached a climax at the H₂/DMO molar ratio of 180. The use of low H₂/DMO molar ratio of < 180 made the 0.1 Pd–0.5 Au–CuO_x/Cu-fiber catalyst not active and selective enough, while the high H₂/DMO molar ratio of 240 impaired the EG selectivity likely because the MG residence time was not long enough to be hydrogenated into EG.

On the basis of the above results, the optimal reaction conditions were: reaction temperature of 270 °C, H₂ pressure of 2.5 MPa, total LWHSV of 5.3 h^{-1} and H₂/DMO molar ratio of 180, for the DMO hydrogenation over the 0.1 Pd–0.5 Au–CuO_x/



Cu-fiber catalyst using a feed of 13 wt % DMO in methanol. As a result, a high DMO conversion of > 99% was achievable with a high EG selectivity of 93%.

Stability

It is well-known that the durability of Cu-based catalysts is the tightest bottleneck that restricts its industrial applications. A long-term test of the $0.1 Pd-0.5 Au-CuO_x/Cu$ -fiber catalyst was performed under the optimal reaction conditions, with the results as shown in Figure 5. For comparison, stability testing of



Figure 5. Conversion and product selectivity for the 200 h test of DMO hydrogenation over 0.1 Pd–0.5 Au–CuO_x/Cu-fiber. Reaction conditions: T = 270 °C, LWHSV = 5.3 h⁻¹, 13 wt% DMO in methanol, $P(H_2) = 2.5$ MPa, $n(H_2)/n(DMO) = 180$.

the CuO_x/Cu-fiber, 0.1 Pd-CuO_x/Cu-fiber and 0.5 Au-CuO_x/Cufiber catalysts were also performed, with the results shown in Figure S2A-C. Clearly, the CuO_x/Cu-fiber catalyst showed a poor stability with a DMO conversion decline from 40% to 12% within only 27 h (Figure S2A). Whereas the $0.1 Pd-CuO_x/$ Cu-fiber catalyst delivered a high initial DMO conversion of 98% and EG selectivity of 90%, the poor stability was its technique shortcoming, showing a fast decline of DMO conversion from 98% to 42% within 45 h (Figure S2B). Notably, the 0.5 Au-CuO_x/Cu-fiber catalyst exhibited significantly enhanced stability with a good maintenance of the DMO conversion of 90-92% throughout entire 80 h test but suffered from a low EG selectivity of only 13-58% (Figure S2C). Very interestingly, the 0.1 Pd-0.5 Au-CuO_x/Cu-fiber catalyst provided a unique combination of high activity/selectivity of the Pd-CuOx/Cu fiber and promising stability for the Au-CuO_x/Cu fiber; such catalyst not only delivered a very high initial conversion of 99% but also significantly prolonged the catalyst lifetime at such high conversion to at least 200 h without any signs of deactivation (Figure 5). A possible explanation is that synergistic interaction among ternary Au-Pd-CuO_x composite was generated, which was paramount to the activity-promoting and stability-enhancing effects.

Insight into the synergistic interaction of Au-Pd-CuO_x

Pd–Au copromoted CuO_x/Cu-fiber catalyst performed better in the catalytic hydrogenation of DMO to EG than Pd or Au indi-

vidually promoted ones. To reveal the synergistic promotion nature of Pd–Au, TOF (the number of converted DMO molecules per surface Cu⁺ site per hour) measurements on the 0.1 Pd–0.5 Au–CuO_x/Cu-fiber, 0.1 Pd–CuO_x/Cu-fiber, 0.5 Au–CuO_x/Cu-fiber as well as CuO_x/Cu-fiber were firstly conducted at 210 °C and at controlled DMO conversion below 30%, with the results shown in Table 2. The CuO_x/Cu-fiber delivered a low

Table 2. DMO hydrogenation conversion and the corresponding TOF over the various catalysts.			
Catalyst	DMO conversion	Cu ⁺ sites	TOF
	[%] ^[a]	[molg _{cat} ⁻¹] ^[b]	$[h^{-1}]^{[c]}$
0.1 Pd-0.5Au-CuO _x /Cu-fiber	32.0	1.80×10^{-6}	612
CuO _x /Cu-fiber	4.2	8.46×10^{-6}	17
0.1 Pd-CuO _x /Cu-fiber	6.4	2.73×10^{-6}	80
0.5 Au-CuO _x /Cu-fiber	18.3	3.60×10^{-6}	174
[a] To obtain the intrinsic activity of all the catalysts, DMO conversion was kept below 30% under the following reaction conditions: catalyst 0.5 g, 210 °C, LWHSV of total liquid feed of 9 h ⁻¹ with 13 wt% DMO dissolved in methanol, H ₂ pressure of 2.5 MPa, molar ratio of H ₂ to DMO of 180. [b] The calculation of Cu ⁺ site is exemplified for 0.1Pd–0.5 Au–CuO _x /Cu-fiber catalyst: Cu ⁺ sites=surface area of 0.1Pd–0.5 Au–CuO _x /Cu-fiber (0.48 m ² g ⁻¹)/area occupied by one Cu ⁺ site (0.444 nm ² , see the equation in TOF calculations) = $1.08 \times 10^{18} = 1.80 \times 10^{-6}$ mol/g. [c] The TOF was calculated as TOF = converting DMO rate/Cu ⁺ sites, for the detailed calculation method see the Experimental Section.			

TOF of 17 h⁻¹, but the TOF was increased to 80 or 174 h⁻¹ with Pd or Au adding (i.e., 0.1 Pd–CuO_x/Cu-fiber, or 0.5 Au–CuO_x/Cu-fiber). This observation clearly confirmed the activity-promoting effect of Pd or Au alone on the CuO_x/Cu-fiber. Most notably, co-adding Pd and Au provided an activity-promoting effect much higher than the Pd or Au adding solely, and the corresponding 0.1 Pd-0.5 Au–CuO_x/Cu-fiber catalyst delivered a high TOF of 612 h⁻¹. The above results clearly revealed the existence of synergistic interaction among ternary Au–Pd–CuO_x composite, which was responsible for the significantly enhanced intrinsic reactivity.

H₂ temperature-programmed reduction (TPR), a very useful tool for revealing metal-metal and metal-support strong interactions, was used to study the interaction of the ternary Au-Pd-CuO_x composite as well as the binary Pd-CuO_x and Au-CuO_x, with the results shown in Figure 6. As shown in Figure 6 A, the CuO_x/Cu-fiber catalyst provided a single-peak H_2 TPR profile with a peak temperature of 365 °C, assigned to Cu₂O (by XRD in Figure 1C) reduction. The 0.1Pd-CuO_x/Cufiber catalyst also provided a single-peak H₂-TPR profile but the peak temperature shifted down to 240 °C. This observation indicated that the reduction of Cu₂O in this catalyst (by XRD in Figure 1C) was catalyzed by Pd, probably with the H₂ spillover of Pd that promoted the Cu₂O reduction. Logically, the promoted activity of 0.1 Pd-CuO_x/Cu-fiber was attributed to the assistant dissociation of H₂ on Pd sites with spillover of active H species onto the neighboring Cu⁺ sites at which DMO hydrogenation took place. However, such H₂-assistant role of Pd could simultaneously facilitate the reduction of Cu⁺ species, the crucial catalytic active sites for the hydrogenation of



Figure 6. TPR profiles of A) the different catalysts and B) the Pd-Au-CuO_x/Cu-fiber catalysts with Pd loading of 0.5 wt% but varied Au/Pd weight ratio.

DMO,^[3,9,26-29] thereby leading to a very short lifetime (Figure S2B). Interestingly, for the 0.5 Au-CuO_x/Cu-fiber catalyst the reduction peak of Cu₂O-CuO (by XRD in Figure 1C) became broadened and asymmetric while the reduction temperature was shifted to 495°C, which is much higher than that for either the 0.1 Pd-CuO_x/Cu-fiber or the CuO_x/Cu-fiber. The retarded reduction of cationic Cu in the 0.5 Au-CuOx/Cu-fiber could be attributed to the stabilizing-effect of Au on cationic Cu.^[10,34] Accordingly, Au adding was believed to be helpful for tuning the Cu⁺/Cu⁰ proportion to a proper level and assuring its maintenance, which not only improved the catalyst activi $ty^{[10]}$ but also enhanced the catalyst stability (Figure S2C) in comparison with the CuO_x/Cu-fiber base catalyst. For the 0.1 Pd-0.5Au-CuO_x/Cu-fiber, interestingly, Pd-catalyzed reduction of the Cu₂O-CuO (by XRD in Figure 1C) was not observed along with the Pd adding into the 0.5 Au-CuO_x/Cu-fiber, solidly evidenced by broad asymmetric hydrogen consumption peak with a high reduction temperature of 535 °C. Clearly, adding Pd would not counteract the stabilizing effect of Au on the cationic Cu, and consequently, the 0.1 Pd-0.5 Au-CuO_x/Cu-fiber showed good stability for at least 200 h (Figure 5). On the other hand, the 0.1 Pd-0.5 Au-CuOx/Cu-fiber delivered the EG selectivity comparable to the initial EG selectivity (at 5 h) for the 0.1 Pd-CuO_x/Cu-fiber but higher than that (at 5 h) for the 0.5 Au-CuO_x/Cu-fiber (Figure 5 and Figure S2B and C), indicating that such catalyst effectively and efficiently integrated high activity/selectivity of the 0.1Pd-CuO_x/Cu-fiber with the good stability of the 0.5Au–CuO_x/Cu-fiber.

Furthermore, the H₂ TPR measurements for the Pd–Au–CuO_x/Cu-fiber catalysts with more Pd loading of 0.5 wt% at varying Au/Pd weight ratio were also performed, with the results as shown in Figure 6B. Clearly, the reduction temperature of the cationic Cu could be shifted to 460°C even adding 0.1 wt% Au into the 0.5 Pd–CuO_x/Cu-fiber, and progressively to 575°C along with increasing the Au loading up to 2.5 wt% (corresponding to Au/Pd ratio of 5:1). Such results further confirmed the strong stabilizing effect of Au on the cationic Cu in the catalyst.

To further reveal the nature of synergistic interaction among ternary $Au-Pd-CuO_x$ composite, the valence states of surface Cu species over every sample at different stages during the stability testing were characterized by X-ray photoelectron spectroscopy (XPS). As shown in Figure 7, all the samples, no



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Figure 7. Cu 2p XPS spectra of the samples after different reaction times. a) CuO_x/Cu-fiber after 10 h; b) CuO_x/Cu-fiber after 30 h; c) 0.1 Pd–CuO_x/Cu-fiber after 10 h; d) 0.1 Pd–CuO_x/Cu-fiber after 50 h; e) 0.5 Au–CuO_x/Cu-fiber after 10 h; f) 0.5Au–CuO_x/Cu-fiber after 60 h; g) 0.1 Pd–0.5 Au–CuO_x/Cu-fiber after 10 h; h) 0.1 Pd–0.5 Au–CuO_x/Cu-fiber after 60 h.

matter if in active or deactivated state, show XPS peaks at binding energies of 932.7 and 952.5 eV, which are the characteristic peaks of $Cu 2p_{3/2}$ and $Cu 2p_{1/2}$ for Cu^+ or Cu^0 species. In addition, no shakeup satellite peaks of Cu²⁺ at 942.3 eV could be detected, which indicates that most of the Cu²⁺ species were reduced to Cu⁰ and/or Cu⁺ under the reaction condition. As the XPS Cu 2p_{3/2} peaks cannot differentiate between Cu⁺ and Cu⁰, Cu LMM Auger spectra were recorded to distinguish Cu⁺ and Cu⁰ by their different binding energies in the Cu LMM spectra: Cu⁺ at 570.0 eV and Cu⁰ at 567.7 eV.^[35-37] As shown in Figure 8 A, B, asymmetric Auger binding-energy peaks could be detected over all samples, demonstrating the simultaneous existence of Cu⁰ and Cu⁺ on the surface of the catalysts, and the molar percentage of Cu^+ to the total $Cu^0 + Cu^+$ content after deconvolution are listed in Table 3. The Cu⁺ fraction of the CuO_x/Cu-fiber catalyst decreased from 74.3% (10 h running on stream) to 43.0% (30 h running on stream) with DMO conversion decreasing from 40% to 12% (Figure 8A, Table 3, and Figure S2 A). For the $0.1 Pd-CuO_x/Cu$ -fiber catalyst, the Cu⁺ fraction decreased from 54.8% (10 h running on stream) to 34.0% (50 h running on stream) and DMO conversion decreased from 98% to 42% (Figure 8A, Table 3, and Figure S2B). Combined with the results of H₂ TPR, it is further confirmed that the introduction of Pd could not only promote the catalytic activity $(TOF = 80 h^{-1} \text{ for } 0.1 Pd - CuO_y/Cu-fiber vs. 17 h^{-1} \text{ for } CuO_y/Cu$ fiber, in Table 2) but also catalyze the reduction of Cu⁺ species,



Figure 8. Cu LMM Auger spectra of the samples after different reaction time. A1) CuO_x/Cu-fiber after 10 h; A2) CuO_x/Cu-fiber after 30 h; A3) 0.1 Pd–CuO_x/Cu-fiber after 10 h; A4) 0.1 Pd–CuO_x/Cu-fiber after 50 h; B1) 0.5 Au–CuO_x/Cu-fiber after 10 h; B2) 0.5 Au–CuO_x/Cu-fiber after 60 h; B3) 0.1 Pd–0.5 Au–CuO_x/Cu-fiber after 10 h; B4) 0.1 Pd–0.5 Au–CuO_x/Cu-fiber after 60 h.

Table 3. Molar ratio of Cu^+ to $Cu^0 + Cu^+$ on the catalyst surfaces after DMO hydrogenation.	er

	$Cu^{+}/(Cu^{\circ}+Cu^{+})$ [%]		
Catalyst	Stage A ^[a]	Stage B ^[b]	Stage C ^[c]
CuO _x /Cu-fiber	74.3	43.0	n.d. ^[d]
0.1 Pd–CuO _x /Cu-fiber	54.8	34.0	n.d.
0.5 Au–CuO _x /Cu-fiber	64.0	n.d.	66.6
0.1 Pd-0.5Au–CuO _x /Cu-fiber	62.7	n.d.	62.5

[a] All the catalysts after the reaction for 10 h. [b] The CuO_x/Cu-fiber after the reaction for 30 h and the deactivated 0.1 Pd–CuO_x/Cu-fiber after the reaction for 50 h. [c] The catalysts after the reaction for 60 h. [d] Not detected (n.d.). Reaction conditions: T=270 °C, LWHSV=5.3 h⁻¹, 13 wt% DMO in methanol, $P(H_3)=2.5$ MPa, $n(H_3)/n(DMO)=180$.

leading to a short lifetime. However, the Cu⁺ fraction of the 0.5 Au-CuO_x/Cu-fiber catalyst remained at 64-67% in 60 h running on-stream with a steady DMO conversion of 90-92% (Figure 8B, Table 3, and Figure S2C), which further evidenced that Au not only provided an activity-promoting effect (TOF = 174 h^{-1} for 0.5 Au–CuO_x/Cu-fiber vs. 17 h^{-1} for CuO_x/Cu-fiber), but also a stabilizing-effect of Au on the cationic Cu. Interestingly, the Cu⁺ fraction of the 0.1 Pd-0.5Au–CuO_x/Cu-fiber catalyst also remained at approximately 62-63% after the 60 h running (Figure 8B and Table 3). Clearly, with the addition of Pd into $0.5 \text{Au}-\text{CuO}_{x}/\text{Cu}$ -fiber, the catalyst activity (TOF = 612 h⁻¹ for 0.1 Pd-0.5Au-CuO_x/Cu-fiber vs. 174 h⁻¹ for 0.5 Au-CuO_x/Cufiber, in Table 2) is further significantly improved but the catalyst stability is not impaired. These results convincingly indicated the specific synergistic effect between Pd and Au that significantly improved the activity of Cu⁺ but not attenuated the ability of Au for stabilizing Cu⁺ sites.

One question is not answered yet: why the Pd-catalyzed reduction of the cationic Cu was suppressed in the presence of Au? We believe that the existence of a Pd–Au electron interaction is paramount to the enhanced activity and prolonged stability. To check this speculation, we firstly probed the nanostructure of Au and Pd in the Au–Pd–CuO_x composite. The 0.1 Pd-0.5Au–CuO_x/Cu-fiber catalyst after 10 h running on stream was characterized by the elemental maps of high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM). As shown in Figure 9, Pd was distributed ho-



Figure 9. A,B) HAADF–STEM images and C,D) the corresponding elemental maps of $0.1 Pd-0.5 Au-CuO_x/Cu$ -fiber after reaction for 10 h.

mogeneously with Au in the mapped part (Figure 9C,D), indicating the formation of Au-Pd alloy. It has been reported that strong electron interaction could occur over Au-Pd alloy as well as in the Au@Pd core-shell structures.[38-40] Therefore, the electron interaction for Au and Pd in the Au–Pd–CuO_x composite was further investigated by XPS. The spectra in Figure 10 clearly reveal the evolution of $Pd3d_{3/2}$ and $Au4f_{7/2}$ binding energies for 0.1 Pd-0.5 Au/Cu-fiber compared to 0.1 Pd-CuOx/Cufiber and 0.5 Au-CuO_x/Cu-fiber (10 h running on stream): the metallic Pd3d_{3/2} binding energy showed a clear upshifting from 335.0 eV for 0.1 Pd-CuOx/Cu-fiber to 335.6 eV for 0.1 Pd-0.5Au–CuO_x/Cu-fiber (Figure 10 A), while the metallic Au $4f_{7/2}$ binding energies showed a slight downshifting from 84.2 eV for 0.5 Au-CuO_x/Cu-fiber to 84.0 eV for 0.1 Pd-0.5 Au-CuO_x/Cufiber, likely resulting from the low Pd/Au weight ratio of only 1:5 (Figure 10B). The results indeed confirmed the strong Pd-Au electron interaction, in which Pd species for the 0.1 Pd-0.5Au-CuO_x/Cu-fiber was electron-deficient to some extent because of the Au electron-drawing effect. Such electron interaction between Pd and Au contributed to the improvement of catalytic performance, which has been evidenced for another important reaction of the direct synthesis of H₂O₂ from H₂ and $\mathsf{O}_2.^{^{[38-40]}}$ As previous reported, much higher H_2 conversion was obtained on an Au@Pd core-shell composite and Au-Pd alloy than either Pd or Au because of the improved ability for H₂ activation to generate more active hydrogen species.[38-40] It thus

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Figure 10. A) XPS spectra of Pd3d of 0.1Pd–CuO_x/Cu-fiber and 0.1Pd–0.5Au–CuO_x/Cu-fiber after 10 h run; (B) XPS spectra of Au4f of 0.5 Au–CuO_x/Cu-fiber and 0.1Pd–0.5Au–CuO_x/Cu-fiber after 10 h run;

can be inferred that the significant improvement of the DMO hydrogenation activity for the 0.1 Pd–0.5 Au–CuO_x/Cu-fiber catalyst benefited from the Pd–Au electron interaction in Au–Pd alloy, in analogy with Au@Pd core–shell composite and Au–Pd alloy for direct H_2O_2 synthesis.^[38–40] Furthermore, such electron interaction among Au–Pd alloy also played a significant role possibly in suppressing Pd-catalyzed reduction of the cationic Cu species thereby leading to the improved catalyst stability.

Conclusions

We have established a promising Cu-fiber-structured ternary Pd-Au-CuO_x catalysts engineered from nano- to macro-scales for the vapor-phase dimethyl oxalate (DMO) hydrogenation to ethylene glycol, with the aid of galvanic deposition of Pd and Au onto a thin-sheet microfibrous structure using 8 µm Cu fiber. Effects of Pd and Au loadings and their ratio have been investigated on the catalyst performance as well as the reaction conditions including reaction temperature and pressure, liquid weight hourly space velocity, and H₂/DMO ratio. The optimized 0.1 Pd-0.5 Au-CuO_x/Cu-fiber catalyst is capable of 97-99% DMO conversion with ethylene glycol selectivity of 90-93% and stable for at least 200 h. The Pd-Au-Cu₂O synergistically promotes the hydrogenation activity and stabilizes Cu⁺ sites to suppress deep reduction deactivation. It is believed that our finding opens up a new path to develop a highly efficient microstructured catalyst for DMO hydrogenation, which exhibits great potential for industrial applications.

Experimental Section

Catalyst preparation

The thin-sheet sinter-locked microfibrous structure consisting of 15 vol% 8 μ m Cu fibers and 85 vol% voidage, with entirely open 3D porous network, were prepared through wet layup paper making/sintering processes^[25] to use as substrates. The Pd, Au, and Pd–Au were then galvanically deposited onto the Cu-fiber surface of the microfibrous structure by incipiently wetting the substrates using an aqueous solution containing the appointed amounts of palladium acetate, chloroauric acid, and both of them (Sinopharm Chemical Reagent Co., Ltd., China) at RT. The as-prepared samples were dried overnight at 100 °C and calcined in air at 300 °C for 2 h

to obtain the catalyst products, referred as to $nPd-CuO_x/Cu$ -fiber, $mAu-CuO_x/Cu$ -fiber, and $nPd-mAu-CuO_x/Cu$ -fiber (n and m are the theoretical loadings of Pd and Au, respectively). For reference, the pure Cu-fiber substrate directly calcined in air at 300 °C for 2 h was also prepared, denoted as CuO_x/Cu -fiber.

Catalyst characterization

The catalysts were characterized by SEM (Hitachi S-4800, Japan), XRD (Rigaku Uitima IV with Cu_{Ka} radiation at 35 kV and 25 mA, Japan), ICP–AES (Thermo Scientific iCAP 6300, USA). Specific surface area was calculated using the standard BET theory based on the N₂ adsorption isotherm obtained on a Quantachrome apparatus (Autosorb-3B, USA) at -196 °C. H₂ TPR was performed on a Quantachrome chemisorption apparatus (ChemBET 3000, USA) with a thermal conductivity detector and an online Mass Spectrometer (Proline Dycor, AMETEK Process Instrument, USA). The XPS and Auger electron spectroscopy were recorded on an Escalab 250xi spectrometer, using a standard Al_{ka} 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.

Reactivity tests

The hydrogenation of DMO to EG was performed in a fixed-bed stainless-steel reactor with 8 mm inner diameter. Firstly the catalyst (0.5 g) was loaded into the reactor and heated to 270 °C, and then pure hydrogen was introduced to the reactor until the pressure was raised to 2.5 MPa, and DMO methanol solution (13 wt%) was simultaneously introduced to the reactor. The DMO methanol solution was pumped with a high-pressure advection pump and the liquid products were collected and analyzed by using a Shimadzu 2014C gas chromatography-flame ionization detector with a HP-IN-NOWax column. The DMO conversion and product selectivity were calculated as follows:

DMO conversion (%) = $(1 - A_{DMO} f_{DMO} / \Sigma A_i f_i) \times 100$ (1)

Si
$$(\%) = (A_i f_i / \Sigma A_i f_i) \times 100$$
 (2)

where A_i is the peak area of the individual component *i* and f_i is the molar correction factor of the individual component *i*. The turnover frequency (TOF) of all the catalysts was defined as the number of DMO converted per Cu⁺ site per time, and was calculated based on the following equation:



$$TOF = \frac{DMO \text{ converting rate } (mol g_{cat}^{-1} h^{-1})}{numbers \text{ of } Cu^+ \text{ sites } (mol g_{cat}^{-1})}$$
(3)

The number of surface Cu^+ sites was calculated based on the following equation:

$$n(Cu^{+})\sum \left(\frac{Xi}{X_{Cu^{+}}}\pi r_{i}^{2}\right)=S_{BET} \tag{4}$$

where $n(Cu^+)$ is the number of Cu^+ sites, X_i is the molar fraction of individual atom *i* analyzed by XPS (*i* contains Cu^0 , Cu^+ , Au, Pd, C, and O), S_{BET} is the specific surface area of catalysts. To obtain the intrinsic activity of catalysts, the DMO conversion was kept below 30% at 210 °C and high LWHSV of 9 h⁻¹.

The X_i (*i* contains Cu⁰ and Cu⁺, Au, Pd, C and O) was calculated on the basis of XPS spectra. As exemplified for the 0.1 Pd–0.5Au– CuO_x/Cu-fiber catalyst, the surface molar ratio of Cu:Au:Pd:C:O is provided from the XPS survey spectra. Firstly, the surface molar ratio of Cu:Au: Pd:C:O is supposed to be $X_{Cu}:X_{Au}:X_{Pd}:X_C:X_0$ ($X_{Cu} + X_{Au} + X_{Pd} + X_C + X_0 = 1$). As Cu2p_{3/2} XPS spectra cannot differentiate between Cu⁺ and Cu⁰, Cu LMM Auger spectra were used to differentiate Cu⁺ and Cu⁰. Considering the extremely low Cu²⁺ percentage in all the Cu states, Cu²⁺ was omitted from the total Cu states to calculate the " X_i ". Subsequently, the Cu⁺/Cu⁰ molar ratio could be determined using Cu LMM Auger spectra and was supposed to be $\chi_{Cu+}:\chi_{Cu0}$ ($\chi_{Cu+} + \chi_{Cu0} = 1$). Finally, the surface molar ratio of Cu⁰/ Cu⁺/Au/Pd/C/O could be determined to be ($X_{Cu} \times \chi_{Cu0}$):($X_{Cu} \times \chi_{Cu+}$): $X_{Au}:X_{Pd}:X_C:X_0$.

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