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Au/Cu-fiber catalyst with enhanced low-temperature activity and heat transfer for the gas-phase oxidation of alcohols†

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A microfibrous-structured gold catalyst was successfully prepared by gold galvanic deposition on a thin-sheet sinter-locked Cu-fibers. The catalyst has excellent heat transfer ability and enhanced low-temperature activity suitable for gas-phase oxidation of alcohols. The AuCu(alloy)-Cu_2O active composites formed during reaction and their cooperative effect contribute to promoting the low-temperature activity.

Oxidation of alcohols to carbonyl compounds is a pivotal process in chemical industry, but exigently needs a fundamental shift from methods based on toxic and expensive inorganic oxidants to greener and more atom-efficient methods that adopt recyclable catalysts and O_2 as an oxidant.[1–5]

Many supported noble metal catalysts have been explored for the oxidation of alcohols in liquid-phase;[1,6] however, a more effective route for industrial application would be gas-phase oxidation because of the convenience of catalyst separation, solvent-free conditions and higher production efficiency, especially for bulk aldehyde productions such as benzaldehyde.[5] Recently, supported gold nanoparticles (Au NPs) have demonstrated wide versatility and excellent activity in many reactions.[7] Several supported gold-based catalysts have been developed for the gas-phase oxidation of benzyl alcohol, including Au/SiO_2[4a] and $Au–Cu/SiO_2$,[5] as well as copper- and silver-based catalysts.[4b,8] However, the weak thermal conductivity of the oxide-supports can result in partial hot spots because of the strong exothermicity of the oxidation process, which not only causes catalyst degradation but also is very dangerous in industrial applications. In addition, the high reaction temperature (generally over 300 °C) required for these catalysts to achieve a satisfactory product yield is a main cause of catalyst deactivation.[4,5,8] Hence, there is great need, from both an academic and industrial point of view, to develop a new kind of catalyst with a unique combination of excellent low-temperature activity and high heat-transfer ability.

A support with high heat-transfer ability is crucial for this new kind of catalyst. Recently, a new carrier class of thin-sheet sinter-locked metal fibers was developed. This material is characterized with a special three-dimensional network, open structure and especially high thermal conductivity.[9,10] The microfibrous structure is a promising technology for development of high-performance catalysts, especially for strongly endothermic or exothermic reactions.[9,10]

Considering the special property of the sinter-locked metal-fibers and the extraordinary activity of Au NPs, it appeared to us that a novel catalytic material could be created if Au NPs were easily and strongly embedded in a metallic microfibrous structure. We herein, for the first time, demonstrate the preparation of a thin-sheet microfibrous-structured Au/Cu-fiber catalyst by Au galvanic deposition. The deposition can proceed automatically by exposing the Cu-fiber to a $HAuCl_4$ aqueous solution because of the great difference in the potential between Cu^0/Cu^+ (0.19 V) and Au^0/Au^{3+} (1.5 V). The catalyst, with high heat-transfer, showed excellent low-temperature activity for the gas-phase oxidation of alcohols. Preliminary spectroscopic studies suggest that low-temperature activity stems from the synergistic effect between the AuCu alloy and Cu_2O that were formed during the reaction.

A typical microfibrous structure (Figure S1†) consisting of 5 vol% of 8-μm Cu-fiber (95 vol% of voidage) was prepared by regular wet lay-up papermaking with subsequent sintering process.[10] Au NPs were then galvanically formed and firmly embedded into the Cu-fibers after exposing the Cu-microfibrous structure to aqueous $HAuCl_4$ solution at room temperature. The Cu fibers remained mainly in the metallic state with some bulk Cu_2O formed (Fig. 1A). Typically, the best catalyst sample was with a Au-loading of 3 wt% and calcined at 200 °C for 2 h, namely, Au-3/Cu-fiber-200. The catalyst chips for the catalytic bed packaging could be punched out from its large-area thin-sheet, demonstrating a robust thin-sheet structure (Figure S1, Fig. 1B). In addition, the 3D-network structure remained (Fig. 1C) and surface became quite rough (Fig. 1D) compared to pure Cu-fibers (Figure S1), with a slight increase in the surface area from 0.6 to 1.0 $m^2 g^{-1}$ (Figure S2).

In order to investigate the performance of the catalysts, benzyl alcohol was used as a model substrate in the gas-phase with O_2 as the oxidant. Of special emphasis was the observation that the activity of the catalyst samples could be enhanced significantly

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Table 1 Gas-phase selective oxidation of several alcohols catalyzed by Au/Cu-fiber catalysts[a]

Entry	Catalyst	Substrate	Product	Reaction temp./°C	Conversion (%)	Selectivity (%)[b]
1	Cu-fiber	Benzyl alcohol	Benzaldehyde	220	18.0	98.3
2	Au-1/Cu-fiber-200[c]	Benzyl alcohol	Benzaldehyde	220	69.6	98.2
3	Au-2/Cu-fiber-200	Benzyl alcohol	Benzaldehyde	220	74.7	98.7
4	Au-3/Cu-fiber-200	Benzyl alcohol	Benzaldehyde	220	85.5	98.5
5	Au-4/Cu-fiber-200	Benzyl alcohol	Benzaldehyde	220	76.5	98.8
6	Au-5/Cu-fiber-200	Benzyl alcohol	Benzaldehyde	220	61.6	98.0
7	Au-3/Cu-fiber-100	Benzyl alcohol	Benzaldehyde	220	61.9	98.1
8	Au-3/Cu-fiber-150	Benzyl alcohol	Benzaldehyde	220	76.4	98.6
9	Au-3/Cu-fiber-250	Benzyl alcohol	Benzaldehyde	220	79.0	97.8
10	Au-3/Cu-fiber-300	Benzyl alcohol	Benzaldehyde	220	72.6	98.3
11	Au-3/Cu-fiber-200	Cyclopropylmethanol	Cyclopropylcarboxaldehyde	250	90.6	95.4
12	Au-3/Cu-fiber-200	Cyclohexanol	Cyclohexanone	250	76.0	99.0
13	Au-3/Cu-fiber-200	1-Octanol	Octanal	250	65.0	93.0
14	Au-3/Cu-fiber-200	Crotyl alcohol	Crotonaldehyde	280	85.0	98.5
15	Au-3/Cu-fiber-200	3-Methylbut-2-enol	3-Methylbut-2-enal	280	57.0	88.0

[a] All catalyst samples were pre-activated (*i.e.*, catalysts underwent selective oxidation of benzyl alcohol at 380 °C for 1 h, using O_2/hydroxyl = 0.6 and WHSV = 20 h^{-1}) and then evaluated at the specified temperature. [b] The main by-products were the corresponding acids except for 3-methyl-2-butenol where the main by-products were the cracking products. [c] *Note*: catalysts are labeled as Au-x/Cu-fiber-y, where "x" denotes gold loading and "y" denotes the calcination temperature.
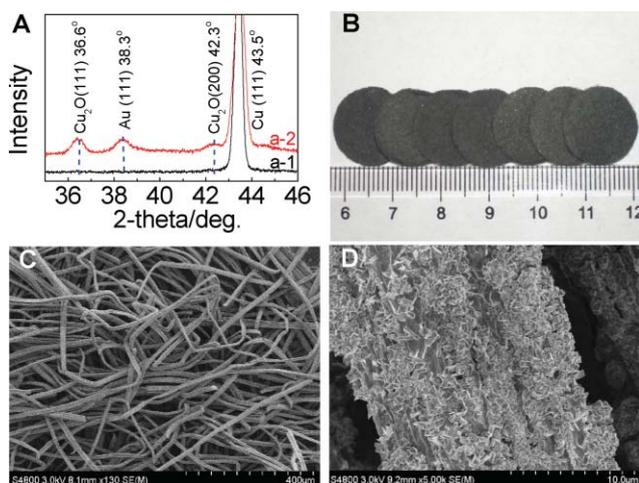

Fig. 1 (A) XRD patterns of pure 8-μm Cu-fibers (a-1) and Au-3/Cu-fiber (a-2) just after Au galvanic deposition without drying; (B) optical photograph of Au-3/Cu-fiber-200 chips for reactor packaging; (C) SEM images of sinter-locked structure; (D) surface morphology of Au-3/Cu-fiber-200.

after first undergoing a 1 h oxidation of benzyl alcohol at 380 °C (called pre-activation, Table S1†). Therefore, all the subsequent catalysts prepared with different gold loadings and calcination temperatures were investigated after pre-activation. For all samples with or without pre-activation, the selectivity remained high at >98.5% at 220 °C and the conversion could be tuned by adjusting the Au loading and calcination temperature (Table 1, entries 1–10, Table S1). It is worth noting that higher Au loadings (>4 wt%) and higher calcination temperatures (>300 °C) in air would lead to a loss of catalytic activity. At 220 °C (boiling point for benzyl alcohol = 203 °C), the Au-3/Cu-fiber-200 catalyst delivered the highest conversion of 85.5% (Table 1, entry 4, Table S1). Benzyl alcohol conversion of >92% could be obtained with a 97.2% selectivity at a higher temperature of 250 °C using the Au-3/Cu-fiber-200 catalyst (Table S2). Our previously reported Ag/Ni-fiber catalysts could yield comparable conversions and

selectivities but only at or above 300 °C.[10d,e] The Au-3/Cu-fiber-200 catalyst also showed promising stability and good reactivity within a 50 h test at 220 °C (Figure S3), due to the excellent coking resistance compared with those Ag/Ni-fiber systems.[10d,e] For reference, the Cu-fibers after calcining at 200 °C for 2 h in air were also tested and resulted in a conversion of only 18.0% with benzaldehyde selectivity of 98.3% at 220 °C, indicating that gold embedment led to a remarkable promotion of the low-temperature activity.

We then extended the tests using several larger volatile alcohols over the Au-3/Cu-fiber-200 catalyst at various reaction temperatures and the results show the catalyst was effective for these substrates (Table 1, entries 11 to 15; Table S3†). Cyclopropylmethanol could be efficiently transformed to cyclopropylcarboxaldehyde (important synthetic building block and a new kind bactericide), with a conversion of 90.6% and a selectivity of 95.4% at 250 °C. At 250 °C, the conversion of 1-octanol was 65% with a selectivity for octanal of 93%. Cyclohexanol could be oxidized to cyclohexanone with a conversion of 76% and very high selectivity of 99%. Interestingly, oxidation of evaporable unsaturated alcohols of crotyl alcohol and 3-methylbut-2-enol could also proceed highly selectively with good conversions at 280 °C.

Another advantage of the Au/Cu-fiber catalyst is that its excellent heat conductivity helps to rapidly dissipate great quantities of reaction heat liberated from such strongly exothermic selective oxidation processes. For example, the catalytic bed packed with Au-3/Cu-fiber-200 delivered a very low ΔT between the bed and reactor external wall of 7 °C in the oxidation of benzyl alcohol at 220 °C, or 11 °C even at 280 °C, with a high weight hourly space velocity (WHSV) of 20 h^{-1} (Table S2†). In contrast, very severe heat transfer limitations existed over the oxide-support-produced catalysts due to their poor thermal conductivity;[4,8] for instance a ΔT of ~53 °C for AuCu/SiO$_2$[5] using WHSV of 10 h^{-1} and a ΔT of ~17 °C for KCuTi[4b] even using an extremely low WHSV of only 0.6 h^{-1} were observed previously in the oxidation of benzyl alcohol. At equivalent alcohol conversion (>95%) and product selectivity (>97%), it should be pointed out that the heat liberation rates and the

product yielding rates in the cases of AuCu/SiO$_2$[5] and KCuTi[4b] are 50% and only 3% of our example using a WHSV of 20 h^{-1}.

The origin of the low-temperature activity remains a very important question. It has been shown that Cu$_2$O is a key factor in determining the catalytic activity of the copper-based catalysts for the selective oxidation of alcohols.[4b,11] XRD results showed that the Cu$_2$O phase was observed clearly on both the Cu-fibers and Au-3/Cu-fiber-200 after pre-activation. Subsequently, more Cu$_2$O with smaller particle size (21 nm as estimated by Scherrer equation) was formed on Cu-fibers rather than on Au-3/Cu-fiber-200 (Cu$_2$O size: 30 nm) during the reaction (Fig. 2A). This observation is clearly the reverse of the conversion trend on both samples (Table 1, 18.0% for Cu-fibers, entry 1, and 85.5% for Au-3/Cu-fiber-200, entry 4).
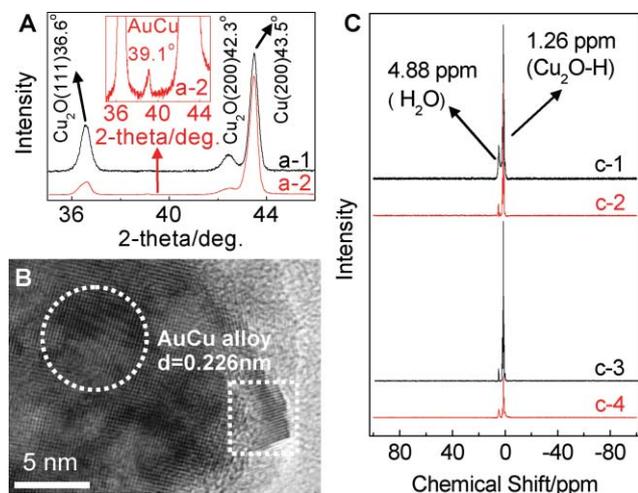

Fig. 2 (A) XRD patterns of the sinter-locked Cu-fibers (a-1) and the Au-3/Cu-fiber-200 (a-2) after pre-activation (see Note *a* of Table 1); (B) TEM image of the same sample a-2 as in Fig. 2A; (C) solid-state ^{1}H-NMR spectra of the pre-activated Cu-fibers (c-1, c-2) and Au-3/Cu-fiber-200 catalyst (c-3, c-4). Samples (c-1) and (c-3) are the ones reacted with benzyl alcohol in the absence of O$_2$ for 1 h at 220 °C using a WHSV of 20 h^{-1}. Samples (c-2) and (c-4) are the samples (c-1) and (c-3) followed by a 10-minute exposure to a O$_2$/N$_2$ (10%) mixture gas flow (110 ml min^{-1}) at 220 °C.

Along with the pre-activation, the characteristic peak of Au(111) surprisingly presented an obvious 2θ shift from 38.3° to 39.1° thereby leading to a reduction of the $d_{(111)}$ spacing from 0.231 to 0.226 nm (Fig. 2A, and Figures S4, S5†). This observed Au(111) XRD peak shift can be accounted for only if homo-AuCu-alloy was formed. TEM tests at high resolution clearly identified highly crystalline metal particles with lattice fringes of 0.226 nm (Fig. 2B) from the Cu$_2$O particles with (111) and (200) lattice fringes of 0.243 and 0.209 nm (Figure S6). This number agrees very well with the $d_{(111)}$ spacing (0.226 nm) deduced from the XRD data, further confirming the formation of AuCu alloy. It should be pointed out that the formation of AuCu alloy did not proceed when directly running the reaction over the fresh catalyst sample at lower temperature (*e.g.*, 250 °C; benzyl alcohol conversion: only 18%) even for a longer time period (*e.g.*, 6 h), as evidenced by no shift of the Au(111) XRD peak at 2θ of 38.3°.

O$_2$-temperature programmed desorption (O$_2$-TPD) was carried out on Au-3/Cu-fibers and Cu-fibers after pre-

activation, followed by oxidation of benzyl alcohol for 1 h at 220 °C, and similar TPD curves were obtained. No O$_2$ desorption could be identified on the Au-3/Cu-fiber-200 sample as compared to the Cu-fibers sample (Figure S7†). This result ruled out the feasibility of the summarized direct oxidation-dehydrogenation route,[3] where the hydrogen of the hydroxyl was abstracted by the adsorbed active oxygen species on *gold*.

In general, the selective oxidation of alcohols by O$_2$ over copper-based catalysts proceeds as follows.[4b,11] Copper(I) oxide catalyzed alcohol dehydrogenation takes place first to form surface Cu$_2$O–H hydride species and alcoholates, which are subsequently decomposed into aldehydes, then the oxygen accepts the hydrogen of the hybrid by releasing the free active Cu$_2$O sites. Indeed, we observed over Au-3/Cu-fiber-200 that the benzyl alcohol conversion decreased from 85.5% to ~7% within a few minutes after switching off O$_2$ gas and could remain at ~7% with continuous hydrogen formation through the entire 6 h test at 220 °C (Figure S8†). Furthermore, it was also observed in the absence of O$_2$ that the pre-activated Cu-fibers with a great amount of Cu$_2$O could deliver a benzyl alcohol conversion of ~5% with continuously detectable hydrogen formation through the entire 4 h test at 220 °C (Figure S9, conversion with O$_2$ added: only 18.0% at 220 °C (Table 1)). The data indicated: (1) both Au-3/Cu-fiber-200 and Cu-fiber samples showed comparable catalytic dehydrogenation ability, due to Cu$_2$O sites[4b,11] rather than the AuCu alloy; (2) their ability to catalyze the oxidization of surface Cu$_2$O–H hydride species by O$_2$ might be quite different thereby leading to a significant differences in low-temperature activity.

Solid-state nuclear magnetic resonance (NMR) experiments were carried out to identify the Cu$_2$O–H hydride species on both the pre-activated Au-3/Cu-fiber-200 and Cu-fiber samples after reacting with benzyl alcohol alone. Strong ^{1}H NMR peaks are observed at a chemical shift (δ_H: 400 MHz) of 1.26 ppm on both samples after 1 h reaction with benzyl alcohol at 220 °C, and are assignable to the Cu$_2$O–H hydride species (solid-state ^{1}H NMR data analysis in SI-1†). Note that such ^{1}H NMR peaks for Cu$_2$O–H hydride species have comparable intensity for both samples (Fig. 2C, c-1 & c-3), being in good agreement with their similarity in their catalytic dehydrogenation ability. In order to detect the reactivity of the formed Cu$_2$O–H hybrid species with O$_2$ molecules, the samples reacted with benzyl alcohol for 1 h at 220 °C were exposed to a O$_2$/N$_2$ (10%) mixed gas flow (110 ml min^{-1}) for 10 min at the same temperature point and then were analyzed by solid-state NMR. As expected, the ^{1}H NMR peaks for Cu$_2$O–H hydride species had decreased dramatically (peak area ratio $A_{c-4}/A_{c-3} = 0.28$) on the Au-3/Cu-fiber-200 sample but only slightly decreased ($A_{c-2}/A_{c-1} = 0.81$) on the Cu-fiber sample (Fig. 2C, c-1 & c-2). Very similar results were also obtained on both samples after undergoing gas-phase oxidation of benzyl alcohol at 220 °C (not shown). Such observations correlate very well with the fact that benzyl alcohol conversion was promoted sharply from ~7% to 85.5% with O$_2$ addition for Au-3/Cu-fiber-200 at 220 °C but from ~5% to only 18.0% for Cu-fibers. Hence, the AuCu alloy was very active for aerobically oxidizing the surface hydride species formed in the Cu$_2$O-catalyzed dehydrogenation step thus driving the reaction towards completion (Scheme S1).

In summary, a novel microfibrous-structured gold catalyst was successfully obtained by gold galvanic deposition on a paper-like microfibrous structure of 8 µm Cu-fibers. The catalyst showed excellent heat conductivity and demonstrated remarkable low-temperature activity in the gas-phase selective oxidation of several typical alcohols. The selective oxidation proceeds *via* alcohol dehydrogenation at the Cu_2O sites and sequential O_2 reduction on Au/Cu-fiber catalyst. The AuCu alloy formed during the reaction can significantly accelerate the reaction by catalyzing the oxidation of surface hybrid species formed in the dehydrogenation step to release free active Cu_2O sites.

Experimental section

Catalyst preparation

Sinter-locked 3D microfibrous networks consisting of 5 vol% 8 µm Cu (IntraMicron Inc., USA) fibers and 95 vol% void volume were built up by the regular papermaking/sintering processes.[10] 5 g of Cu-fibers and 1.5 g of cellulose fibers were added into water (1 L) and stirred vigorously to produce a uniform suspension. The resulting suspension was transferred into the head box of a 159 mm dia. circular sheet former (ZCX-159A, made in China) and a 159 mm circular preform was then formed by draining and drying in air. The as-made preform paper was oxidized in air at 300 °C to remove the cellulosic binders and subsequently sintered in hydrogen at 900 °C to create the three-dimensional sinter-locked networks. Au was then galvanically deposited on this sinter-locked Cu-fiber by incipiently impregnating with aqueous solution containing an appointed amount of $HAuCl_4$ at room temperature. The resulting samples was dried overnight at 80 °C and calcined in air at temperature range between 100 and 300 °C for 2 h to obtain Au/Cu-fiber catalysts.

Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD, a Rigaku Uitima IV diffractometer (Cu-Kα)), scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscope (TEM, JEOL-JEM-2010 instrument at 200 kV), UV-visible diffuse reflectance spectroscopy (UV-vis DRS, Shimadzu UV-2400PC) and solid-state nuclear magnetic resonance (MAS-NMR, 400 MHz, Varian VNMR-SYS-400WB, rotation frequency ~ 4.5 kHz). The catalysts were also studied by temperature programmed desorption (TPD) on a Quantachrome ChemBET 3000 chemisorption apparatus with a TCD. Au loading of the Au-3/Cu-fiber-200 was determined to be 2.8 wt% by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo Scientific iCAP 6300 ICP spectrometer.

Reactivity tests

The gas-phase selective oxidation of alcohols on these catalysts with molecular oxygen was carried out on a fixed-bed quartz tube reactor (i.d., 16 mm) under atmospheric pressure as described previously.[10d,e] Circular chips (16.1 mm diameter) of the microfibrous-structured Au/Cu-fiber catalysts were punched down from their large sheet sample and packed layer-up-layer into the tube reactor. Note that the diameter of 0.1 mm, larger than the i.d. of the tubular reactor, was retained deliberately to avoid the appearance of the gap between the reactor wall and the edges of the catalyst chips thereby preventing the gas bypassing. Alcohols were fed continuously using a high-performance liquid pump, in parallel with an O_2 (oxidant) and N_2 (diluted gas) feed using the calibrated mass flow controllers, into the reactor heated to the desired reaction temperature. The effluent was cooled using an ice-salt bath (−15 °C) to liquefy the condensable vapors for analyzing by an HP 5890 gas chromatography-flame ionization detector (GC-FID) with a 60 m HP-5 ms capillary column. The gas-phase products such as H_2, CO_x and C1-C3 hydrocarbons were analyzed by an HP-5890 GC with a thermal conductivity detector (TCD) and a 30 m AT-plot 300 capillary column.

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