Galvanic Deposition of Silver on 80-μm-Cu-fiber for Gas-phase Oxidation of Alcohols

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Microstructured Ag-based catalysts were developed by galvanically depositing Ag onto 80-μm-Cu-fibers for the gas-phase oxidation of alcohols. By taking advantages including large voidage, open porous structure and high heat/mass transfer, as-made catalysts provided a nice combination of high activity/selectivity and enhanced heat transfer. The best catalyst was Ag-10/80-Cu-fiber-400 (Ag-loading: 10 wt%; Cu-fiber pretreated at 400 °C in air), being effective for oxidizing acyclic, benzylic and polynary alcohols. For benzyl alcohol, conversion of 94% was achieved with 99% selectivity to benzaldehyde at 300 °C using a high WHSV of 20 h^{-1}. Computational fluid dynamics (CFD) calculation and experimental result illustrated significant enhancement of the heat transfer. The temperature difference from reactor wall to central line was about 10–20 °C for the Ag-10/80-Cu-fiber-400, much lower than that of 100–110 °C for the Ag-10-Cu-2/Al_2O_3 at equivalent conversion and selectivity. Synergistic interaction between Cu_2O and Ag was discussed, being assignable to the activity improvement. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 1045–1053, 2014
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Introduction

Most present-used catalysts are supported on oxides because of their high surface area as well as thermal and chemical stability.[1] However, some serious problems will emerge when these oxide-supported catalysts are applied in oxidation reactions. Take the gas-phase oxidation of alcohols as an example, which is an important reaction from both academic and industrial points because aldehydes/ketones are widely-used precursors for the synthesis of drugs, vitamins, fragrances, and many other complex syntheses.[2,3] Various oxide-supported catalysts based on coinage metals (Cu, Ag, and Au) have been developed for the gas-phase oxidation of alcohols, including Au-Cu/SiO_2,[4] K-Cu-TiO_2,[5] Cu/MCM-41,[6] (K-Cu)/NaZSM-5,[6] K/Ag/SiO_2,[7] Au/SiO_2,[8] and Au/OMMs.[9] However, their poor heat transfer ability hampered their practical application, because this easily induces hotspots in the catalyst bed where great quantity of reaction heat liberates rapidly and cannot be quickly dissipated.[4,5,8] This is not only a main cause of the catalyst deactivation and selectivity degradation, but also a hidden danger (e.g., bed temperature out of control). For electrolytic silver, it is widely used in the methanol-to-formaldehyde transformation.[10] Nevertheless, it is inactive at temperature of <500 °C, but poorly selective at temperature of >500 °C in the selective oxidation of larger alcohol molecule such as benzyl alcohol.[10]

Hence, it is exigent to render a new kind of catalyst with significantly intensified interlayer heat/mass transfer ability as well as high activity and selectivity for the gas-phase selective oxidation of alcohols. As we know, metal has much higher heat-transfer ability than oxides, and therefore, using metal as support will be logical to fabricate catalysts with desirable heat-transfer ability. To attain this goal, a silver catalyst supported on LTA zeolite film coated on a copper grid (Ag/LTA/Cu-grid) has been developed with acceptable activity and selectivity.[11] Recently, a new class of microfibrous carriers consisting of sinter-locked microfibers has been invented by Tatarchuk.[12,13] More interestingly, such microfibrous structure, with large void volume, entirely open structure, large surface-to-volume ratio, high permeability, high-thermal conductivity and unique form factors, can be made into thin sheets (from sub-millimeter to several millimeters in thickness) of a large area and/or pleated sheet structure to control pressure drop and contacting efficiency in a beneficial manner different from other traditionally employed contacting schemes including packed beds, fluid

Additional Supporting Information may be found in the online version of this article.

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beds, honeycomb monolithes or wovens.[12,13] For applications that entrap small particles within or load active components (e.g., metals) on the microfibrous network, unique combinations of pore size/particle size, thermal conductivity, and large void volume are obtained. Therefore, one can say that such microfibrous structure is a promising carrier technology for the development of high-performance catalysts, especially for the strongly endothermic and exothermic reactions.[14–18] Previous efforts have successfully demonstrated its special beneficial properties in the applications for strongly endothermic NH_3 cracking[14–16] and methanol steam reforming,[17] H_2 fuel cleanup (CO and H_2S removal),[13] and O_3 catalytic decomposition.[18]

For the gas-phase selective oxidation of alcohols, we have developed several catalysts using the sinter-locked metal-microfiber (8 μm in dia.) as supports, such as Ag/Ni-fiber,[10,19,20] Au/Ni-fiber,[21–23] and Au/Cu-fiber[24,25] catalysts. During the long-time test of the oxidation of benzyl alcohol over the Ag/Ni-fiber and Au/Ni-fiber catalysts, carbide of Ni_xC comes into being as poison and deactivates the catalyst activity.[20] In addition, the Au/Cu-fiber catalyst has a high activity with avoiding formation of poisonous carbide, but the 8-μm-Cu-microfiber is so slender that its sinter-connected structure is easily disconnected and powdered during the long-time test because of the oxidation environment.

To avoid the powdering of 8 μm Cu-microfiber support, the copper fiber with large diameter of 80 μm was used to anchor silver particles on its surface via the galvanic exchange reaction between $AgNO_3$ and Cu fiber ($2AgNO_3 + Cu = 2Ag + Cu(NO_3)_2$) due to the electrode potential difference between Cu^{2+}/Cu^0 (0.52 V) and Ag^+/Ag^0 (0.80 V) pairs. The 80-μm-Cu-fiber supported silver catalyst of Ag/80-Cu-fiber exhibited a good activity and selectivity for the gas-phase oxidation of alcohols. Computational fluid dynamics (CFD) calculation combined with experimental measurements was employed to illustrate the significant enhancement of the heat transfer of the catalytic bed at steady working state, benefitted from the high heat conductivity of Ag/80-Cu-fiber catalysts.

Experimental

Catalyst preparation

80-μm copper fibers were first thermally pretreated in air at temperature range of 200–600 °C for 2 h. Sliver particles were then galvanically deposited on copper fiber by incipiently impregnating with aqueous solution containing appointed amount of $AgNO_3$ (Sinopharm Chemical Reagent Co., Ltd., China) at room temperature. The resulting samples was dried overnight at 80 °C and calcined in air at 200–500 °C for 2 h to obtain Ag/Cu-fiber catalysts. The as-made catalysts were labeled as Ag-x/80-Cu-fiber-y, where "x" denotes the Ag loading in wt% metal, "80" the Cu-fiber diameter of 80 μm, and "y" the Cu-fiber pretreatment temperature. For comparison in experimental test and CFD calculation, the Al_2O_3 supported Ag-Cu catalyst, named Ag-10-Cu-2/Al_2O_3, was also prepared by incipiently impregnating with aqueous solution containing appointed amount of $AgNO_3$ and $Cu(NO_3)_2$ at room temperature, followed by calcining at 400 °C for 2 h.

Catalyst characterizations

The catalysts were characterized by scanning electron microscopy (SEM, Hitachi S-4800), X-ray diffraction (XRD, Rigaku Uitima IV diffractometer (Cu Kα)). Specific surface area was determined from N_2 adsorption isotherm at −196 °C using standard Brunauer-Emmett-Teller (BET) theory. Silver loading of the typical sample of Ag-10/80-Cu-fiber-400 was determined to be 9.5 wt% by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a Thermo Scientific iCAP 6300 ICP spectrometer.

Reactivity tests

The gas-phase 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.[20–23] Catalyst (total mass of 0.3 g, including Ag and Cu-fiber support) was packed into the tube reactor and heated to the desired reaction temperature. Alcohol was fed into the reactor continuously using a high-performance liquid pump, in parallel with O_2 and N_2 (diluted gas, constant flow rate of 100 mL/min) feeding using the calibrated mass flow controllers. The organic phase of liquid effluent was collected for analyzing by an HP 5890 gas chromatography-flame ionization detector (GC-FID) with a 60-m HP-5 ms capillary column, and the liquid-phase products included benzene, toluene, benzaldehyde, unconverted benzyl alcohol, and benzoic acid. The gas-phase products such as H_2, CO_x and C1-C3 hydrocarbons were analyzed by an HP-5890 GC with thermal conductivity detector (TCD) and a 30-m AT-plot 300 capillary column. Reaction temperature, alcohol weight hourly space velocity (WHSV) and molar ratio of O_2 to alcoholic hydroxyl (O_2/ol) were varied in range from 280 to 380 °C, 10 to 70 h^{-1}, and 0.4 to 1.2, respectively. Conversion and product selectivity were defined as below, on the basis of C atom. Conversion (%) = {[6/7 × moles of benzene + moles of (toluene + benzaldehyde + benzoic acid) + 1/7 × moles of ($CO + CO_2$)]/[6/7 × moles of benzene + moles of (toluene + benzaldehyde + unreacted benzyl alcohol + benzoic acid) + 1/7 ×moles of ($CO + CO_2$)]} × 100. Selectivity (%) = {moles of benzaldehyde/[6/7 × moles of benzene + moles of (toluene + benzaldehyde + benzoic acid) + 1/7 × moles of ($CO + CO_2$)]} × 100. A carbon mass balance of 98.9–99.6% was achieved.

CFD calculation

The CFD code "FLUENT" was employed to obtain the temperature distribution at steady state inside the catalytic bed. The benzyl alcohol, N_2 and O_2 were preheated at 270 °C, and premixed and then introduced into the tube. The catalytic bed contacting to the isothermal wall was initially at a uniform temperature of 300 °C. The reactant was reheated by the reactor wall when it traveled in the tube before it diffused into the catalyst bed. For CFD simulation for gas-phase oxidation of benzyl alcohol at benzyl alcohol feeding rate of 6 g/h, Ag-10/80-Cu-fiber-400 (Cu fiber: 0.27 g; Ag: 0.03 g; void volume: 89 vol%) catalyst of 0.3 g and was packed in the reactor tube (i.d., 16 mm), and according to the experiments, the conversion of benzyl alcohol was 94% at 300°C. For reference, Ag-10-Cu-2/Al_2O_3 (Al_2O_3: 0.264 g; Ag: 0.03 g; CuO: 0.006 g, void volume: 45 vol%) catalyst of 0.3 g was tested in the reactor tube (i.d., 16 mm), and according to the experiments, the conversion of benzyl alcohol was 92% (close to that for Ag-10/80-Cu-fiber-400) with selectivity of 98% at 300 °C. All the thermophysical properties of the materials (solids and gases) are functions of the local temperature and composition. The modeling and methods were given online in Supporting Information as well as other detailed information.

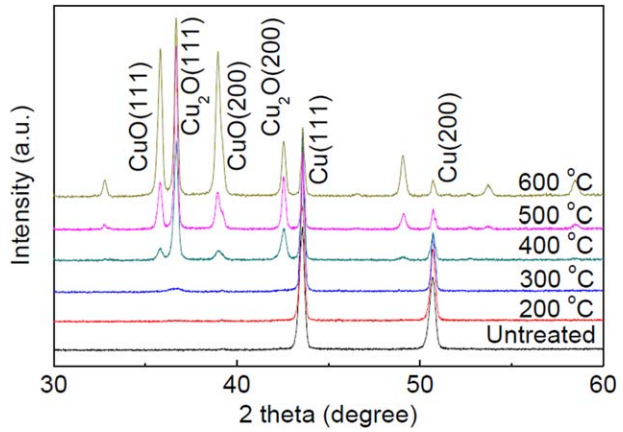


Figure 1. XRD patterns of the Cu-fiber thermally pretreated in air at different temperatures.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Results and Discussion

Ag/80-Cu-fiber catalyst preparation

Thermal Treatment of 80-μm-Cu-fiber Support. The surface area of 80-Cu-fiber is much lower than that of the porous oxides supports such as Al_2O_3. To increase the surface area, Cu-fiber was thermally pretreated in air to make it suitable to load Ag particles. XRD shows the oxidation behavior of the Cu-fibers along with the increase of pretreatment temperature (Figure 1). Clearly, the characteristic peak of the pretreated Cu-fiber is only metallic copper with treatment temperature at or below 200 °C, indicating no clear oxidation of Cu-fiber occurred. Increasing temperature to 300 °C, observable oxidation got started, but only a few Cu_2O was obtained, and up to 400 °C, clear Cu_2O phase with minor CuO formation was obtained. The weight of Cu-fiber was increased by 1.7% after pretreating at 400 °C for 2 h in air, correspondingly indicating that 14% metallic copper was oxidized during such pretreatment by assuming all the copper oxides taken as Cu_2O. According to the related calculations (Table S1, and Supporting Information I), the thickness of the copper oxides (Cu_2O was dominant) was estimated to be 3 μm, 7.5% of the fiber radius. To further increase the surface area and investigate the effect of CuO on the catalyst activity, the Cu-fiber was pretreated at and above 500 °C in air for 2 h. By comparison, along with increasing the pretreating temperature up to 600 °C, the characteristic peak of CuO was increased continuously, while the peaks of metallic copper showed a reverse trend. Along with the increase of pretreating temperature, the characteristic peak of Cu_2O showed a sharp increase at 400 °C and a further slight increase at 500 °C while almost remaining unchanged from 500 to 600 °C.

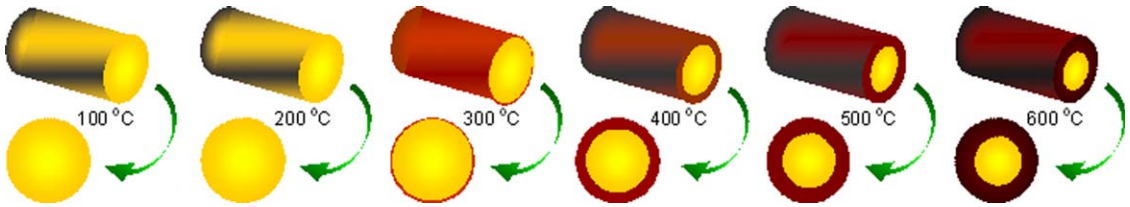
All the pretreated Cu-fiber samples were measured by nitrogen adsorption-desorption and the results were summarized in Table 1 as well as the oxide layer thickness. It is clear that the surface area and pore volume were increased with the oxidative treatment temperature. The surface area of the Cu-fiber samples after pretreating at or below 200 °C in air was very small (<0.1 m^2). Even though at 300 °C, it was only 0.2 m^2/g. The surface area of the Cu-fiber was sharply increased to 2.4 m^2/g after pretreating at 400 °C, and then further increased up to 4.5–6.2 m^2/g along with increasing the pretreating temperature to 500–600 °C. Figure S1 shows the SEM images of the Cu-fiber samples pretreated at 300–500 °C in air. The Cu-fiber pretreated at 300 °C still showed a shining surface (Figure S1A) due to excellent electroconductivity of the sample surface. This indicated no clear oxidation of Cu-fiber occurred at 300 °C, being consistent with the XRD pattern (Figure 1). After pretreating at 400 °C, the original shining and smooth surface became obscure and rough (Figure S1B), indicating coverage by oxides formed on the fiber surface. In addition, the pretreating at 500 °C caused an overoxidation of the Cu-fiber, inducing the huge cracks even with the oxide layer spalling (Figure S1C). Note that the Cu-fiber sample provided a thin oxide layer as thick as 3 μm after pretreating at 400 °C, which not only offers acceptable surface area but also avoids serious degradation of the structure of Cu-fiber. When the Cu-fibers were treated at or above 500 °C, the structure of Cu-fiber was degraded seriously although the surface area could be further increased to 4.5–6.2 m^2/g. Above oxidation evolution behavior was illustrated clearly in Scheme 1 along with the pretreatment temperature.

Galvanic Deposition of Ag Particles on 80-μm-Cu-fiber Support. The aforementioned results show that the pretreating at 400 °C could introduce appropriate amount of oxides onto Cu-fiber. Therefore, the Cu-fiber pretreated at 400 °C was selected first to be used as the support to anchor Ag particles via $AgNO_3$-Cu galvanic exchange reaction. Figure 2 shows the XRD patterns of the untreated Cu fiber, Cu-fiber-400 (pretreated at 400 °C in air for 2 h), and the as-prepared Ag-10/80-Cu-fiber-400 (Ag loading of 10 wt %) catalyst just dried at 80 °C. Clearly, over the catalyst after drying at 80 °C, only metallic Ag XRD patterns were detectable without any ones concerning $AgNO_3$ compound. It is well-known that $AgNO_3$ cannot be decomposed into metallic Ag at 80 °C because $AgNO_3$ decomposition temperature is 418 °C. The formation of metallic Ag, thus, is undoubtedly contributed to the galvanic exchange reaction between the pretreated Cu-fiber surface and $AgNO_3$, because of the electrode potential

Table 1. Phase Composition and Textural Properties of the 80-μm-Cu-Fiber Supports Treated at Different Treatment Temperatures[a]

Treating temp. (°C)	Phase Composition	Oxide layer thickness (μm)[b]	S_{BET} (m^2/g)	D (nm)	V (cm^3/g)
100	Cu^0	0	0.005[c]	–	0
200	Cu^0	0	0.005[c]	–	0
300	Cu^0, Cu_2O	0.04	0.2	–	0
400	Cu_2O, Cu^0, CuO	3	2.4	30	0.01
500	Cu_2O, CuO, Cu^0	13	4.5	25	0.03
600	CuO, Cu_2O, Cu^0	16	6.2	27	0.04

[a]The Cu-fiber was thermal treated in air for 2 h at different temperatures.
[b]The detailed calculation was described in the Supporting Information.
[c]The values was calculated assuming rod shape of 80-μm-Cu-fiber because the real surface area is too low.



Scheme 1. Oxidation evolution behavior of 80-μm-Cu-fiber along with the treatment temperature.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

difference between Cu^{2+}/Cu^0 (0.52 V) or Cu^{2+}/Cu^+ (0.15 V) and Ag^+/Ag^0 (0.8 V) pairs. After calcining at 400 °C, the obtained Ag-10/80-Cu-fiber-400 catalyst showed almost the same metallic Ag XRD patterns as those for just dried sample with a little more copper oxides formed.

To address the effect of copper oxide layer thickness on Ag galvanic deposition, the Cu-fiber supports pretreated at 300, 500, and 600 °C, were also used to prepare silver catalysts. Similar with on the Cu-fiber pretreated at 400 °C, $AgNO_3$ could be galvanically reduced to metallic silver over such pretreated Cu-fibers (Figure S2). For the Cu-fiber pretreated at 300 °C, it is not surprising to observe the galvanic exchange reaction between $AgNO_3$ and copper (Figure S2A), because only few Cu_2O was obtained on this support surface. For the Cu-fiber pretreated at higher temperatures, we wonder whether the galvanic exchange reaction takes place because of the thick copper oxide layers. It is interesting, however, to find that Ag galvanic deposition reaction still proceeded completely (Figure S2B,C). What to be noted is that, over the Cu-fiber pretreated at 500 °C, the characteristic peaks of both metallic copper (Cu^0) and cuprous oxide (Cu_2O) decreased greatly while CuO was formed obviously, suggesting that $AgNO_3$ can be galvanically reduced to metallic Ag by not only Cu^0 but also Cu_2O (Figure S2B,C).

Reaction performance of Ag/80-Cu-fiber catalysts

The effects of catalyst preparation parameters were studied on the catalyst performance for the gas-phase oxidation of benzyl alcohol, with the results as shown in Figure 3. Obviously, the pretreatment of Cu-fiber played a key role in improving the catalyst activity (Figure 3A). As predicted, the Cu-fiber calcining at 400 °C was the best support compared to the ones calcining at low (i.e., 200 and 300 °C) or high temperatures (i.e., 500 and 600 °C). Whereas Cu-fiber supports pretreated at 500 and 600 °C both had larger surface area than the one at 400 °C, their corresponding catalysts delivered lower benzyl alcohol conversion. This is maybe due to the mass formation of CuO that likely showed negative effect on the catalyst activity.[5]

It is clear from Figures 3B and 3C that the catalyst activity was strongly dependent on the Ag loading and catalyst calcination temperature. The benzyl alcohol conversion was promoted from 4 to 94% along with increasing the Ag-loading from 0 to 10 wt% but was decreased dramatically to 45% with further increasing the Ag-loading to 20 wt% (Figure 3B). For the Ag-10/80-Cu-fiber catalysts, increasing the catalyst calcination temperature from 100 to 400 °C promoted the benzyl alcohol conversion from 85 to 94% while further increasing the calcination temperature up to 500 °C decreased the conversion down to 86% (Figure 3C). Note that the selectivity was not sensitive to either the Ag-loading or the catalyst calcination temperature. We can say that the best catalyst was the Ag-10/80-Cu-fiber-400 (Cu-fiber support: thermally pretreated at 400 °C for 2 h in air in advance; Ag loading of 10 wt%; catalyst calcined at 400 °C for 2 h in air), delivering 94% conversion with 99% selectivity in the gas-phase oxidation of benzyl alcohol at 300 °C and WHSV of 20 h^{-1}. The detectable byproducts included benzene, toluene, benzoic acid and CO_x, whose total selectivity was about 1–2%. For reference, the neat Cu-fibers calcined at different temperatures ranging from 200 to 600 °C delivered a low benzyl alcohol conversion of only 4% with selectivity of 99% under identical reaction conditions. The aforementioned results definitely indicate that Ag embedment modification of Cu-fiber promoted the catalyst activity remarkably.

Effects of reaction conditions

The effects of reaction conditions on the performance of Ag-10/80-Cu-fiber-400 catalyst for the gas-phase selective oxidation of benzyl alcohol were carefully investigated, with the results as shown in Figure 4.

Figure 4A shows the benzyl alcohol conversion and benzaldehyde selectivity as a function of reaction temperature over the Ag-10/80-Cu-fiber-400 catalyst, using a WHSV of 20 h^{-1} and an O_2/ol ratio of 0.6. At 280 °C, a low benzyl alcohol conversion was obtained of only 65%. Along with the increase of reaction temperature, the conversion was sharply promoted to 93% at 300 °C, slightly to 95% at 320 °C, and then retained almost constant at ~98% at up to 380 °C. Notably, the selectivity to benzaldehyde decreased progressively from 99 to 96% in the whole temperature range from 280 to 380 °C.

At 300 °C under a WHSV of 20 h^{-1}, the benzyl alcohol conversion is 72% with O_2/ol ratio of 0.4 (Figure 4B; stoichiomatric O_2/ol ratio is 0.5), slightly lower than the theoretically attainable conversion of 80% at 99% selectivity to benzaldehyde, indicating that the catalyst Ag-10/80-Cu-fiber-400 showed a high O_2 utilization efficiency (90%). With increasing O_2/ol from 0.4 to 0.6 and then up to 1.2, the benzyl alcohol conversion was increased to 94% and then slowly decreased down to 89% while the selectivity to benzaldehyde remained almost unchanged. Similarly with the previously reported catalysts of Au/Ni-fiber[21–23] and Au/Cu-fiber,[24,25] the Ag-10/80-Cu-fiber-400 catalyst showed an excellent ability of selective oxidation rather than deep oxidation even in an O_2-rich atmosphere. On the balance between benzyl alcohol conversion and O_2 utilization efficiency, the optimal O_2/ol ratio was set as 0.6.

Along with the increase of WHSV from 10 to 30 h^{-1}, conversion of benzyl alcohol was smoothly increased from 89 to 96% while the selectivity to benzaldehyde decreased from 99 to 98%, using O_2/ol of 0.6 at 300 °C (Figure 4C). This observation was likely due to the visible increase of real bed temperature (Figure S3 and Supporting Information II; ΔT (temperature difference between catalyst bed and reactor external wall): 5 °C for WHSV of 10 h^{-1}; 14 °C for

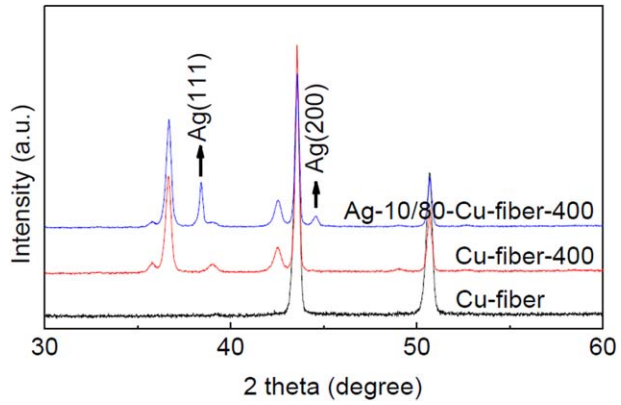


Figure 2. XRD patterns of the Cu-fiber, Cu-fiber-400 (thermally pretreated at 400 °C in air for 2 h) and as-prepared Ag-10/80-Cu-fiber-400 catalyst.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

WHSV of 30 h^{-1}). Further increasing WHSV from 30 to 70 h^{-1} decreased the benzyl alcohol conversion to 52% and the selectivity from 98 to 85%, and meanwhile, the ΔT was slightly increased only from 14 to 26 °C. We, thus, believed that, along with WHSV from 30 to 70 h^{-1}, the resistance time became not long enough for more reactant and product molecules to react with O_2, thereby leading to the decrease of conversion but a slight increase of selectivity (Figure S3 and Supporting Information II). Considering a balance between good product yield at high selectivity and small ΔT, it was optimal to operate the reaction at 300 °C using O_2/ol of 0.6 and WHSV of 20 h^{-1}.

Heat transfer promotion

Experimental Aspect. In comparison with the reported oxide-support-produced catalysts for the gas-phase oxidation of alcohols,[4,5] the Ag/80-Cu-fiber catalyst showed high-heat conductivity, which helped in rapidly dissipating the great quantity of reaction heat liberated from such strongly exothermic processes. For example, the catalyst bed packed with Ag-10/80-Cu-fiber-400 delivered a low ΔT (the temperature difference between catalyst bed and reactor external wall) of 10 °C at 300 °C and of 15 °C at 360 °C using a high WHSV of 20 h^{-1}, which was much lower than that on the oxide-supported catalysts (Figure 5). In contrast, a ΔT of 120–150 °C over Ag-10-Cu-2/Al_2O_3 was observed in the gas-phase selective oxidation of benzyl alcohol with WHSV of 20 h^{-1}. In addition, a ΔT of 56 °C over AuCu/SiO_2 catalyst[4] existed in this reaction, using a low WHSV of 10 h^{-1}

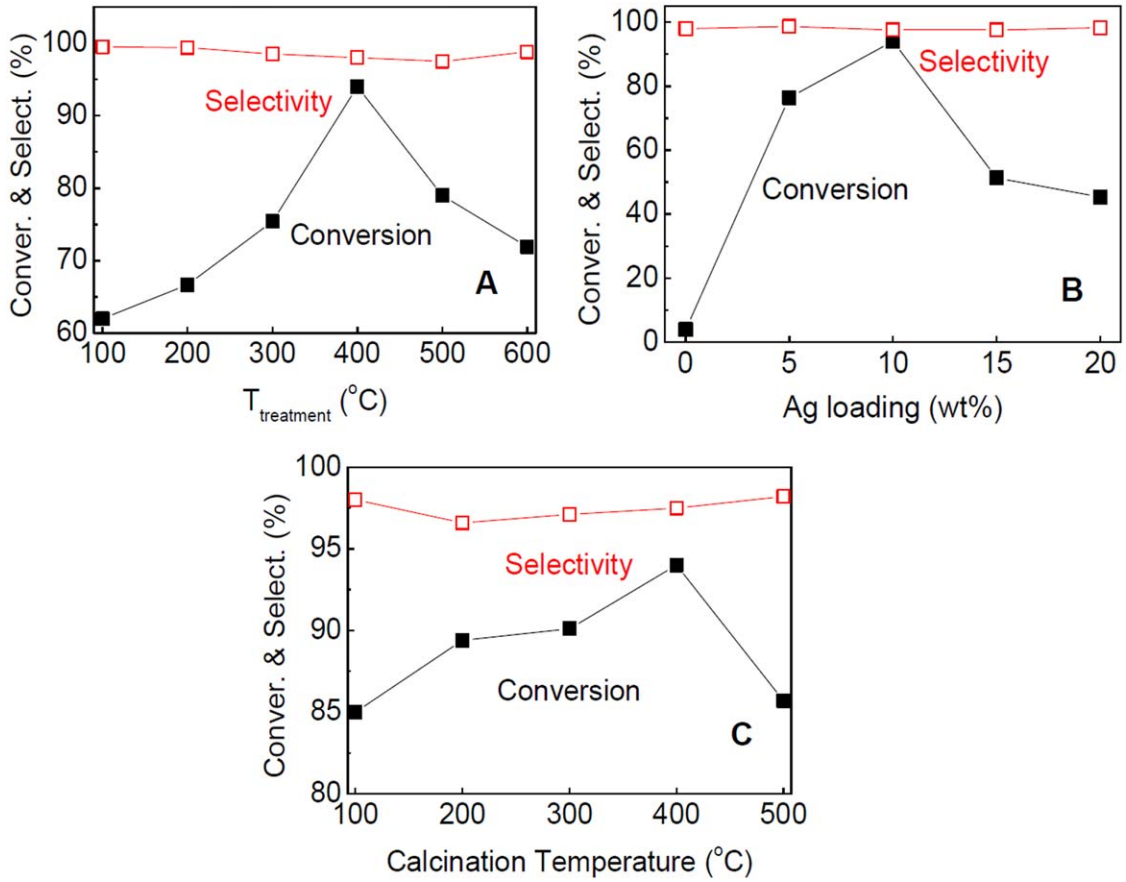


Figure 3. Effects of the catalyst preparation parameters on the performance of Ag/80-Cu-fiber for the gas-phase oxidation of benzyl alcohol using O_2/ol of 0.6 and WHSV of 20 h^{-1}.

(A) Effect of thermal treatment temperature of Cu-fiber support (catalyst: Ag loading 10 wt%, calcination temperature 400 °C; reaction temperature: 300 °C, (B) effect of Ag loading (thermal treatment temperature of Cu-fiber support: 400 °C; catalyst calcination temperature: 400 °C; reaction temperature: 300 °C), and (C) effect of catalyst calcination temperature (thermal treatment temperature of Cu-fiber support: 400 °C; Ag loading: 10 wt%; reaction temperature: 300 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

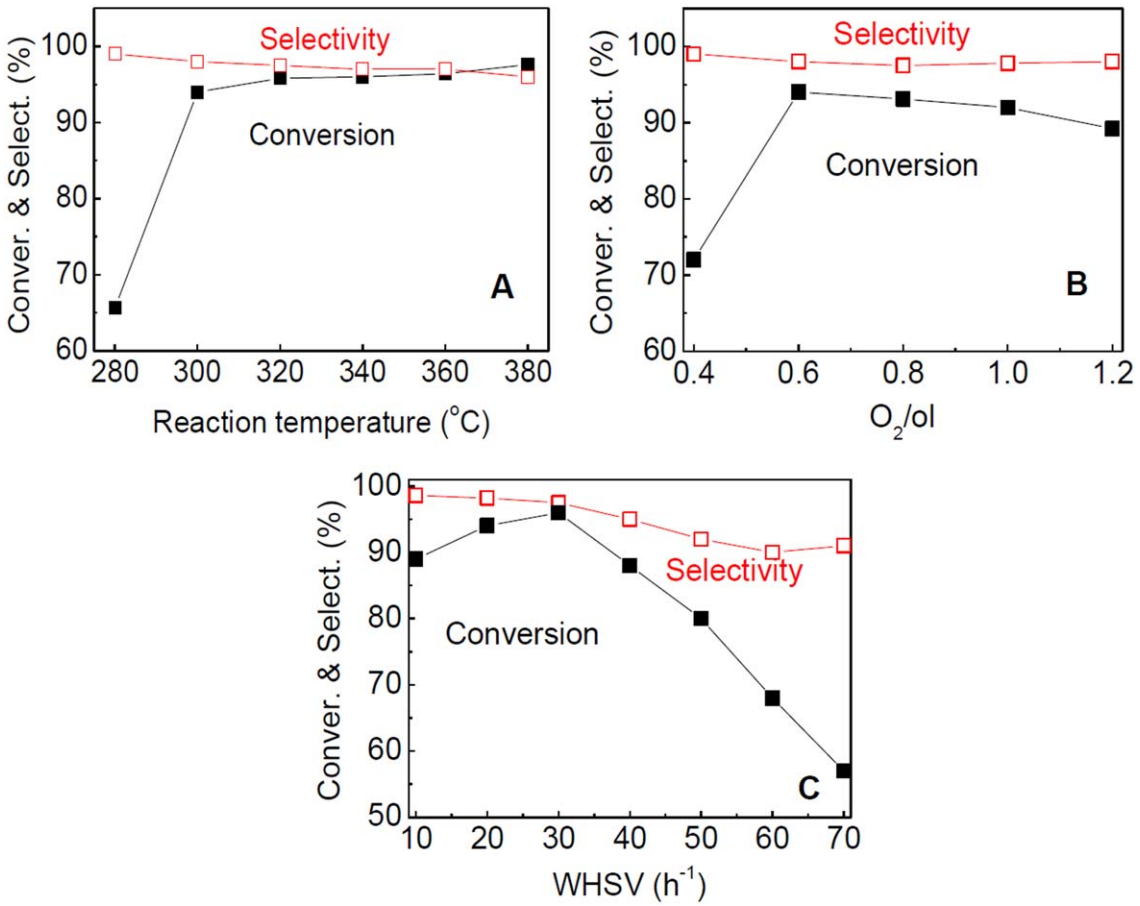


Figure 4. Effects of reaction conditions on the catalytic performance of Ag-10/80-Cu-fiber-400 for the gas-phase oxidation of benzyl alcohol.

(A) Effect of reaction temperature with WHSV = 20 h^{-1} and O_2/ol = 0.6, (B) effect of O_2/ol ratio with WHSV = 20 h^{-1} and reaction temperature = 300 °C, and (C) Effect of WHSV with O_2/ol = 0.6 and reaction temperature = 300 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and ~17 °C on K-Cu-TiO_2 catalyst[5] even under an extremely low WHSV of 0.6 h^{-1}, due to their poor thermal conductivity. Notably, at equivalent conversion (>95%) and selectivity (>97%), the heat-liberating rates over AuCu/SiO_2 and K-Cu-TiO_2 could be estimated to be 50% (WHSV of 10 h^{-1}), and only 3% (WHSV of 0.6 h^{-1}) of that over the Ag-10/Cu-fiber-400 catalyst with WHSV of 20 h^{-1}.

CFD Calculation Aspect. The CFD calculation was used to illustrate the heat-transfer enhancement of the catalyst stemming from the metallic support of copper fiber. The modeling (Figure S4) and methods are described in Supporting Information III. For CFD simulation, the Ag-10/80-Cu-fiber-400 catalyst of 0.3 g was packed in the reactor tube (i.d., 16 mm), and according to the experiments, benzyl alcohol conversion was 94% with benzaldehyde selectivity of 98% at 300 °C. The reference catalyst (0.3 g) of Ag-10-Cu-2/Al_2O_3 was packed without dilution in the same reactor tube and the benzyl alcohol conversion of 92% was obtained with the selectivity of 98% at 300 °C. Figure 6 details the steady-state temperature distribution within the two catalyst beds. For both of them, the hot spot appeared in the upwind-side of the catalyst bed where the reaction took place intensively. Whereas the alcohol oxidation released an equivalent amount of heat on the catalyst surfaces in both catalyst beds, our Ag-10/80-Cu-fiber-400 catalyst bed provided a hot point with temperature increment much smaller than that of the Ag-10-Cu-2/Al_2O_3. The temperature difference from reactor wall to central line was about 10–20 °C for the Ag-10/80-Cu-fiber-400 but 100–110 °C for the Ag-10-Cu-2/Al_2O_3. The CFD results for the bed temperature distribution are

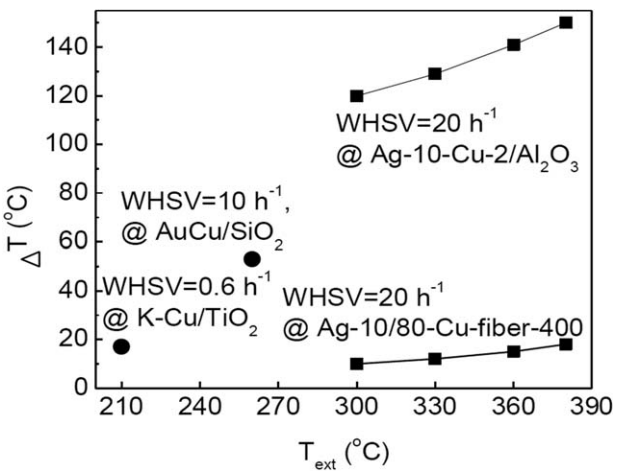


Figure 5. Temperature difference (ΔT) between the setup temperature (T_{ext}) and the catalyst-bed temperature (T_{bed}) in the gas-phase oxidation of benzyl alcohol over the Ag-10/80-Cu-fiber-400, Ag-10-Cu-2/Al_2O_3, Au-Cu/SiO_2 [4] and K-Cu-TiO_2.[5]

Reaction conditions: WHSV = 20 h^{-1}, O_2/ol = 0.6.

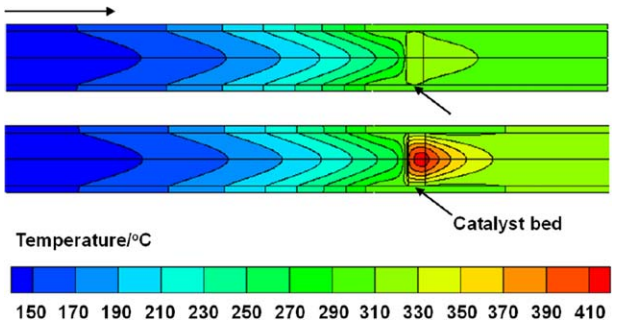


Figure 6. Temperature distribution at steady-state inside reaction bed: Ag-10/80-Cu-fiber-400 (upper); Ag-10-Cu-2/Al_2O_3 (lower).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

consistent with the experimental observation and are in well agreement with the reported results.[26–28]

Reaction of other alcohols

The Ag-10/80-Cu-fiber-400 catalyst was also tested with a range of acyclic, benzylic, and polynary alcohols, and the results showed that the catalytic performance was influenced by the structure of alcohol substrates (Tables 2 and S2). The faster oxidation of conjugated aromatic alcohols to the corresponding conjugated aldehydes or ketones was observed compared to the oxidation of aliphatic alcohols. For 1-phenylethanol, the conversion could reach 97% with a selectivity of 98% at 320 °C. In contrast, the conversion of 2-phenylethanol was much lower than that of 1-phenylethanol, which reached only 48% at 360 °C. For octanol, the primary linear aliphatic alcohol (1-ol) showed a higher activity and selectivity than the secondary counterparts (2-ol). The conversion of 1-octanol was 58% with a selectivity of 92% at 340 °C, but the conversion of 2-octanol was only 27% with a selectivity of 65% even at 380 °C. Interestingly, cyclohexanol could be selectively oxidized to cyclohexanone (a key raw material in the synthesis of many useful chemicals, such as caprolactam fornylon 6 and adipic acid for nylon 66) with a good conversion of 69% and a high selectivity of 95%. In the case of cyclopropyl carbinol, the conversion of 85% was obtained at 320 °C with 94% selectivity to cycloprogyl dehyde that is an important synthetic building block and a new-type bactericide. Furthermore, alcohols containing two hydroxyl groups, such as 1,2-propylene glycol which is favorable to form hydroxylketone rather than methyl glyoxal, could also be oxidized to the target product with the selectivity of 67% at the conversion of 93%.

Stability

The catalyst stability is an important consideration for its practical application. Figure 7 shows the reaction results against the time on stream over the Ag-10/80-Cu-fiber-400 catalyst at 300 °C using O_2/ol ratio of 0.6 and a WHSV of 20 h^{-1}. Obviously, temporary deactivation occurred during this longer-term test. The initial benzyl alcohol conversion was 94% and then declined to ~78% within first 50 h, while no degradation of the target product selectivity (>96%) was observed. The regeneration on the spent catalyst after 50-h test was carried out by quitting alcohol feeding, heating the catalyst bed to 400 °C for 2 h in the O_2/N_2 (12.4/100 (mol/mol)) mixture flow (112.4 mL/min). Afterward, the catalytic bed temperature was reduced to 300 °C, and meanwhile the alcohol feeding was restarted. The regenerated catalyst delivered the conversion of 93% with the target product selectivity of >97% and underwent a reaction evolution similar to the first 50-h reaction again. Obviously, the spent catalyst can recover completely to its fresh conversion/selectivity level only through a simple oxidation treatment. In addition, no any deterioration in activity/selectivity of Ag-10/80-Cu-fiber-400 catalyst was observed after two reaction-regeneration cycles, indicating a good regenerability of this catalyst.

Comparison

Several silver-based catalysts have been reported for the gas-phase oxidation of benzyl alcohol, such as K/Ag/SiO_2,[7] Ag/LTA/Cu-grid,[11] electrolytic silver,[10] Ag/Ni-fiber[10] and Ag/Ni-fiber-M.[20] The benzyl alcohol conversion over electrolytic silver is very low, only 55%, even at high temperature of 500 °C, and the selectivity to benzaldehyde is 80% due to the over-oxidation at high reaction temperature.[10] Such low conversion may be caused by the weak catalytic activity of large Ag crystals of electrolytic silver. Supporting Ag on SiO_2 greatly increases benzyl alcohol conversion to 80% at a relative low reaction temperature of 300 °C.[7] To enhance the heat conductivity of catalyst, a silver catalyst supported on LTA zeolite film, which was then coated on a copper grid (Ag/LTA/Cu-grid), has been developed with lower activity and selectivity (benzyl alcohol conversion of 5% selectivity to benzaldehyde of 90%, at 320 °C).[11] Recently, a microfibrous-structured silver catalyst of Ag/Ni-fiber-M was developed, which delivers a much better benzyl alcohol conversion of 90% and benzaldehyde selectivity of 97% at 300 °C.[20] Our developed Ag-10/80-Cu-fiber-400 catalyst delivers an identical activity with that of Ag/Ni-fiber-M, but much better than other Ag-based catalysts mentioned previously. In addition, the AuCu/SiO_2 catalyst is reported to deliver a high benzyl alcohol conversion of 98% with benzaldehyde selectivity of 99% at a setup temperature of 260 °C;[4] however, the real catalyst bed temperature is 316 °C,[4] which is almost similar with the real temperature of our fibrous catalyst bed (310–320 °C, Figures 5 and 6). The benzyl alcohol conversion was 94% over our Ag-10/80-Cu-fiber-400 catalyst, slightly lower than that over the AuCu/SiO_2 catalyst; but it should be noted that the WHSV used in our case was much higher than that for the AuCu/SiO_2 catalyst (20 *vs* 8 h^{-1}). In accordance, we can say that our Ag-10/80-Cu-fiber-400 catalyst indicates the comparable activity to the AuCu/SiO_2 catalyst.

As for the lifetime, the Au/SiO_2 catalyst is estimated at 315 °C with a lifetime just for 70 h, as well as selectivity around 90–100% and conversion in a wider range of 50–75%.[4] The decay of the catalytic behavior is probably ascribed to the formation of a pitch-dark deposited on the catalyst surface, because of the weak heat transfer ability. Although the Ag/Ni-fiber-M catalyst exhibits a better stability than that of Au/SiO_2,[4,20] the benzyl alcohol conversion remains at 94–97% only within the first 23 h and then declined dramatically to 70–77%. Whereas the K-Cu-TiO_2 shows a very high conversion of 99% at 210 °C (bed temperature: 227 °C) using a very low WHSV of 0.6 h^{-1}, its lifetime is only 50 h and its throughput is extremely low.[5] The previously reported Au/Cu-fiber catalyst is highly active but its longer-term stability is only 50 h with the benzyl alcohol

conversion of 85% at 220 °C, and cannot be regenerated effectively, which will limit its practical application.[24] Our previously reported Ag/Ni-fiber-M catalyst shows a lifetime of 120 h after twice regenerations. In this work, the Ag-10/80-Cu-fiber-400 showed marked stability improvement with a longer lifetime of 170 h after twice regenerations.

Tentative insight into the synergistic effect of Ag and Cu_2O

As previously noted on the Au/Cu-fiber catalyst,[24,25] the AuCu(alloy)-Cu_2O active composites are formed during the alcohol oxidation reaction and provide a synergistic effect, thereby leading to a dramatic improvement in the catalytic activity. For the Ag-10/80-Cu-fiber-400 catalyst, is there a similar synergistic interaction between Ag and Cu_2O? On the working Ag-10/80-Cu-fiber-400 catalyst, only Cu_2O and Ag XRD phases were presented on Cu-fiber with completely disappearance of the weak CuO phase that was observable on the fresh Ag-10/80-Cu-fiber-400 catalyst sample (Figure S4A). In addition, no shift of XRD peak 2θ value for Ag phase was observed on the used catalyst sample, ruling out the formation of AgCu alloy (Figure S4A), and the Ag surface was composited of metallic Ag (Figure S4B).[29] By combining this information with the reaction results, we postulated that there has a synergistic interaction between Cu_2O and Ag, which dramatically improves the activity for the gas-phase alcohol oxidation.

To gain insight into this speculative synergistic effect, the contrastive catalysts, Ag/CuO and Ag/Cu_2O, were prepared by impregnating CuO and Cu_2O oxides with $AgNO_3$ solution, followed by calcining at 300 °C in air. The as-prepared Ag/CuO and Ag/Cu_2O catalysts were tested in the gas-phase benzyl alcohol oxidation reaction under the identical conditions. The results showed that the Ag/Cu_2O catalyst delivered a much higher benzyl alcohol conversion than the Ag/CuO catalyst (Table S3). The Cu_2O and CuO were also tested under identical conditions and yielded very low conversions: 23 and 17%. As shown in Figures 2 and S2, the Ag-10/80-Cu-fiber-400 had much lower content of CuO than the Ag-10/80-Cu-fiber-600 catalyst while the former catalyst was much more active for the alcohol oxidation than the latter one (Figure 3A). This is in good agreement with the observation over the Ag/Cu_2O and Ag/CuO catalyst samples. The above results indicated that Cu_2O is exactly more effective than CuO to synergistically work with Ag to significantly promote the catalyst activity. As previously reported on K-Cu-Ti catalyst, Cu^{2+} showed negative effect on the catalytic activity.[5] Despite of above advance, in-depth understanding of the synergistic effect of Ag-Cu_2O is particularly desirable, which is useful for high-performance catalyst design.

Table 2. Oxidation of Various Alcohols Catalyzed by Ag-10/80-Cu-fiber-400 using WHSV of 20 h^{-1}

Substrate	O_2/ol ratio (mol/mol)	$T_{Reaction}$ (°C)	Conversion (%)	Selectivity (%)
1-phenylethanol	0.7	320	97	98
2-phenylethanol	0.7	360	48	96
1-octanol	0.6	340	58	92
2-octanol	0.6	380	27	65
Cyclohexanol	0.6	340	69	95
Cyclopropyl carbinol	0.6	320	85	94
1,2-propanediol	1.4	380	93	67

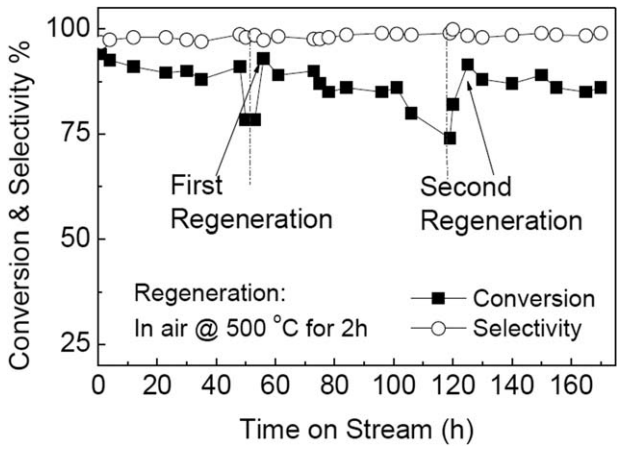


Figure 7. Lifetime test of the Ag-10/80-Cu-fiber-400 catalyst.

Reaction conditions: O_2/ol = 0.6, WHSV = 20 h^{-1}, T = 300 °C.

Conclusion

A promising 80-μm-Cu-fiber structured Ag catalyst Ag/80-Cu-fiber, which showed a unique combination of high activity and selectivity, good stability and high heat transfer ability, was successfully prepared for the gas-phase selective oxidation of alcohols. The Ag/80-Cu-fiber catalysts were obtained by galvanic deposition of Ag onto a thermally treated Cu-fiber. The best catalyst was Ag-10/80-Cu-fiber-400 (Ag-loading: 10 wt%; Cu-fiber pretreated at 400 °C in air), which was effective for acyclic, benzylic and polynary alcohols using a high WHSV of 20 h^{-1}. For benzyl alcohol, the conversion of 94% was achievable with >99% selectivity to benzaldehyde at 300 °C. In addition, a low ΔT of 10 °C between the catalyst bed and reactor external wall was observed in the selective oxidation of benzyl alcohol. Such semi-isothermal operation was contributed to the enhanced heat-transfer ability that permits to rapidly dissipate large quantities of reaction heat, which is clearly demonstrated by the CFD calculation. As a result, the Ag-10/80-Cu-fiber-400 catalyst showed a prolonged stability with good regenerability by heating in air. Cu_2O is found synergistically work with Ag to significantly promote the catalyst activity. Despite these interesting results, in-depth investigation on the catalytic nature and deactivation mechanism of the catalyst is particularly desirable.

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