



## Metallic short fibers for liquid-phase oxidation reactions<sup>☆</sup>

Achim Stolle<sup>a,\*</sup>, Bernd Ondruschka<sup>a</sup>, Ingrid Morgenthal<sup>b</sup>, Olaf Andersen<sup>b</sup>, Werner Bonrath<sup>c</sup>

<sup>a</sup> Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller University Jena, Lessingstraße 12, D-07743 Jena, Germany

<sup>b</sup> Fraunhofer Institute for Manufacturing and Advanced Materials, Dresden Branch Lab (IFAM-DD), Winterbergstraße 28, D-01277 Dresden, Germany

<sup>c</sup> R&D Chemical Process Technology, DSM Nutritional Products, P.O. Box 2676, CH-4002 Basel, Switzerland

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### ABSTRACT

The application of metallic short fibers (MSF) for the liquid phase oxidation of alcohols and the epoxidation of alkenes has been investigated. Screening of various MSF lead to the conclusion that Cu<sub>3</sub>Sn- and Cu<sub>64</sub>Ni<sub>28</sub>Mn<sub>7</sub>Fe<sub>1</sub>-fibers are the most promising candidates for oxidation reactions. Due to increased decomposition of H<sub>2</sub>O<sub>2</sub> in presence of MSF containing Pt, Pd or Rh, lower yields were obtained with these catalysts. Oxidation reactions with the two above mentioned MSF are characterized by high selectivities for the oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. Reactions are independent from reaction atmosphere and H<sub>2</sub>O<sub>2</sub>-dosage protocol, whereas parameters like solvent, temperature, and oxidant concentration had a significant influence.

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### 1. Introduction

Compared to other chemical reactions oxidations in both gas and liquid phase are in general challenging. Due to the thermodynamics of this reaction type, it is always difficult to prevent the substrates from undergoing over- or even total oxidation [1]. Thus, the application of catalysts is often necessary for selective oxidation processes in liquid phases. For gas phase reactions the application of multi-component metal oxides is beneficial since those materials have a high thermal and chemical resistance. Undesired side reactions can be suppressed by choosing the right catalyst or by variation of the process parameters. However, in the gas phase oxidants with a relative high hazardous potential (O<sub>2</sub>, ozone, NO<sub>x</sub>) are applied requiring high regulatory efforts to prevent (thermal) runaway. Working in liquid phase is advantageous since the solvent can act as heat sink supporting heat and mass transfer and therefore increase the process stability. Additionally, oxidants with a lower hazardous potential like hydrogen peroxide can be applied [2]. Compared to gas phase processes, reactions in liquid phase generally have the disadvantage of lower throughput. Thus, oxidations in liquid phase are often applied in selective oxidations of

functional groups under mild conditions (e.g. in the production of pharmaceuticals).

The employment of catalysts in liquid phase oxidation is advantageous due to the possibility for inherent control of selectivity and conversion, thus making the overall reaction more affordable from economic and ecologic point of view. However, the application of bulk or supported catalysts requires special reactor technology (e.g. fixed-bed). The combination of catalytic activity with material design is therefore interesting, since hierarchical materials/reactors could be designed. Within this topic the application of metallic catalysts is promising due to excellent material properties of metals and the possibility for preparation of various three-dimensional (hierarchical) structures with distinct properties (e.g. wire meshes, networks, metal foams). In line with this concept of catalyst design a bottom-up concept was chosen to investigate the possibilities for use of metal-alloys as oxidation catalysts. In the first stage different alloys and intermetallic phases have been manufactured with similar particle geometry: metallic short fibers (MSF) [3].

Within this paper the application of various MSF in liquid-phase oxidation reactions has been assessed. The formation of ketones from secondary alcohols is used as model reaction and various reaction parameters are varied investigating their influence on the course of reaction. Furthermore, the scope of reactions has been extended by incorporating the selective oxidation of primary alcohols (benzyl alcohol) and the epoxidation of alkenes (styrene, limonene) into this study.

<sup>☆</sup> Supplementary data for this article containing kinetic correlations for variation of solvent, stirring speed, reaction atmosphere, H<sub>2</sub>O<sub>2</sub>-dosage protocol, and H<sub>2</sub>O<sub>2</sub>-concentration are available.

\* Corresponding author. Tel.: +49 3641 948413; fax: +49 3641 948402.

E-mail address: [achim.stolle@uni-jena.de](mailto:achim.stolle@uni-jena.de) (A. Stolle).

**Table 1**  
Metallic short fibers (MSF) used as catalysts for this study.

Catalyst	Composition (w%)	$l_{\text{fiber}}$ [mm]	$d_{\text{fiber}}$ [ $\mu\text{m}$ ]	$A_{\text{fiber}}$ [ $\text{m}^2 \text{g}^{-1}$ ]
V255	FeAl20Ce10Pt5		86	0.012
V288	FeCrAlPt0.5	11.4	89	0.009 (optical)
V325	FeAl20Ce3Pt1			
V327	FeAl20Pt0.5			
V328 <sup>a</sup>	FeAl30Pt0.5	6.1	59	0.017 (optical)
V420	FeCrAl20.5Pt0.5	4.7	87	0.008
V423	FeCrAl20.5	5.9	62	
V438 <sup>b</sup>	X5Al20Ce3(PtRh)0.5	12.9	105	0.008 (optical)
V441 <sup>a</sup>	Cu68.1Sn31.9 (=Cu3Sn)	5.3	70	0.010 (BET)/0.006 (optical)
V442	Al68.5Cu25.5Fe6	10.3	138	0.042 (BET)/0.010 (optical)
V447	Cu64Ni28Mn7Fe1	10.3	82	0.008 (optical)
V449	Cu88Ni10Mn1Fe1	11.6	98	0.006 (optical)

<sup>a</sup> Intermetallic phase.<sup>b</sup> Alloyed steel.

## 2. Experimental

### 2.1. General remarks

All chemicals were purchased from commercial suppliers (Sigma–Aldrich, Alfa Aesar) and used without further purification. The purity of all substrates was checked prior to use with GC-FID. Metallic short fiber (MSF) catalysts listed in Table 1 have been prepared by crucible melt extraction [3b].

### 2.2. Catalyst characterization

The SEM-images were recorded using a scanning electron microscope DSM 940 (Carl Zeiss). Optical microscopy pictures were taken with a Stemi 2000-C (Carl Zeiss; magnification: 6.5–50 $\times$ ; cold light source KL 1500 LCD) in combination with a digital camera JVC GZ-MC200E (2 mega pixel; 10 $\times$  optical zoom). 6-Point BET measurements were carried out with Autosorb1 (Quantachrome) using N<sub>2</sub> as sorbent gas and a heating temperature of 350 $^{\circ}\text{C}$ .

### 2.3. General reaction procedure for secondary alcohol dehydrogenation

2-Propanol (**1**; 6 mmol) and the catalyst (Table 1; 0.5 g) were suspended in acetonitrile (30 ml). After addition of an appropriate amount of hydrogen peroxide (aqueous, 60 w%), the reaction mixture was heated up to 80 $^{\circ}\text{C}$ . The course of reaction was monitored by samples taken from the reaction mixture and analysis by GC after drying with MgSO<sub>4</sub>. Reactions were performed using a six-place carousel reactor under refluxing conditions. In case of deionized water as solvent extraction with ethyl acetate was performed prior to drying and analysis.

### 2.4. Reaction procedure for the oxidation of benzyl alcohol

Benzyl alcohol (**3**; 6 mmol, 648 mg) and the catalyst (Table 1; 0.5 g) were suspended in water (30 ml). After addition of hydrogen peroxide (4 g aqueous, 60 w%), the reaction mixture was heated up to 80 $^{\circ}\text{C}$ . To avoid any side effects concerning autoxidation of **3**, the reactions have been performed in nitrogen-atmosphere. The course of reaction was monitored by samples taken from the reaction mixture and analysis by GC after drying with MgSO<sub>4</sub> and extraction with ethyl acetate.

### 2.5. Reaction procedure for the epoxidation of styrene and limonene

Styrene (**4**; 6 mmol, 625 mg) or limonene (**5**; 6 mmol, 816 mg) and the catalyst (Table 1; 0.5 g) were suspended in acetonitrile

(30 ml). After addition of hydrogen peroxide (4 g aqueous, 60 w%), the reaction mixture was heated up to 80 $^{\circ}\text{C}$ . The course of reaction was monitored by samples taken from the reaction mixture and analysis by GC after drying with MgSO<sub>4</sub> and extraction with ethyl acetate.

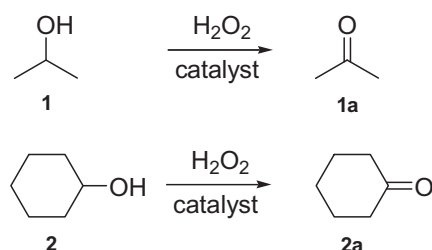
### 2.6. Product analyses

Analyses were carried out with a 6890 Series GC-MSD and a 7890 Series II GC-FID from Agilent Technologies. Products were identified by comparison of their retention times and their mass spectra with those of pure reference compounds. Conditions GC-FID (compound **1**): Poraplot Q, 25 m  $\times$  0.32 mm  $\times$  10  $\mu\text{m}$ , 5 psi H<sub>2</sub>; program: 160 $^{\circ}\text{C}$  (hold 2 min), 10 K min<sup>-1</sup> up to 250 $^{\circ}\text{C}$  (hold 9 min); injector temperature: 250 $^{\circ}\text{C}$ ; detector temperature: 250 $^{\circ}\text{C}$ . Conditions GC-FID (all other compounds): HP 5, 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ , 5 psi H<sub>2</sub>; program: 80 $^{\circ}\text{C}$  (hold 4 min), 20 K min<sup>-1</sup> up to 250 $^{\circ}\text{C}$ ; injector temperature: 250 $^{\circ}\text{C}$ ; detector temperature: 300 $^{\circ}\text{C}$ . Conditions GC-MSD: HP 5-MS, 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ , 9 psi He; program: 50 $^{\circ}\text{C}$  (hold 5 min), 10 K min<sup>-1</sup> up to 250 $^{\circ}\text{C}$  (hold 1 min); injector temperature: 250 $^{\circ}\text{C}$ , detector: electron impact (70 eV).

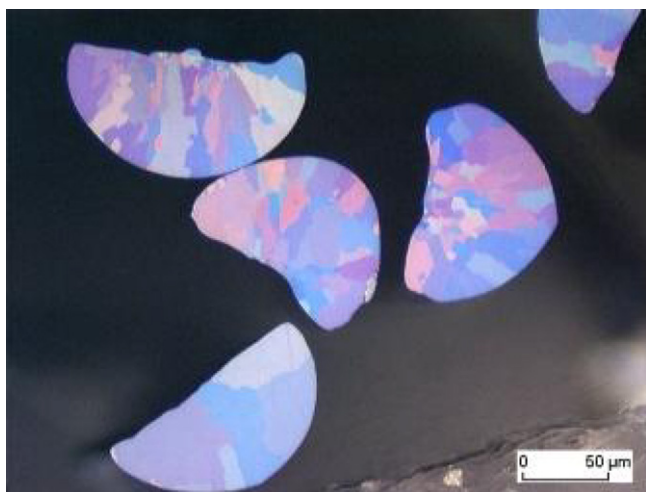
All data reported herein are based on peak-areas and are comparable with the isolated ones. The reported yields were corrected by means of different FID-sensitivity for substrate and product. The data represent values from at least two independent experimental runs.

## 3. Results and discussion

Recently the application of metallic short fibers (MSF) as catalysts for the gas phase oxidative dehydrogenation of propane affording propene and of 2-propanol (**1**) furnishing acetone (**1a**) has been reported (Scheme 1) [4,5]. Comparison with other catalysts revealed that the materials are interesting but the potential applications are limited due to process instabilities and lower conversion and selectivity rates. Thus, the concept of oxidation in presence of MSF has been investigated in liquid phase reactions. As



Scheme 1. Model reactions.



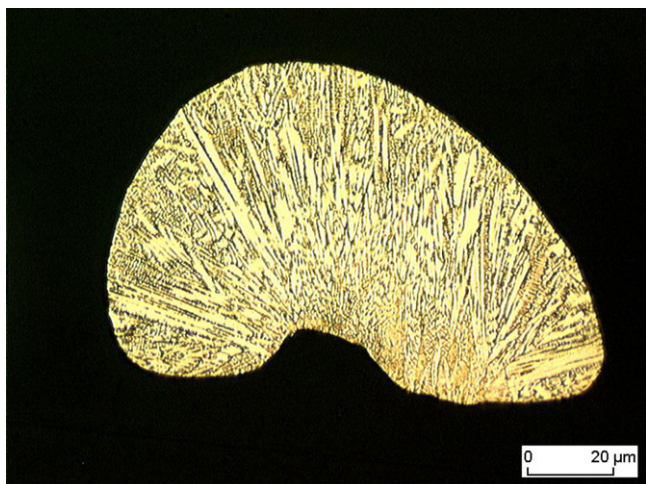
**Fig. 1.** Light microscopy image of the cross section of  $\text{Cu}_3\text{Sn}$ -fibers (V441; crystalline structure visible using polarized light).

model reactions the formation of **1a** and cyclohexanone (**2a**) from **1** and cyclohexanol (**2**), respectively, have been chosen (Scheme 1) [6–9]. Initially a range of MSF (Table 1) has been tested. The most promising candidates are afterwards applied for the investigation of various reaction parameters and also in the oxidation of other substrates.

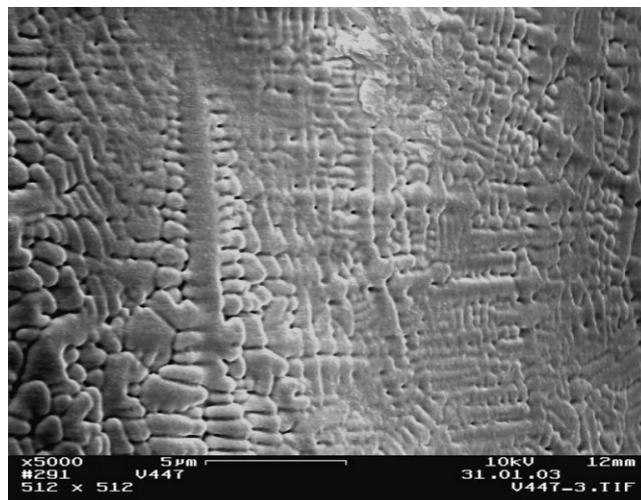
### 3.1. Preparation of metallic short fibers (MSF)

The process of crucible melt extraction allows the production of MSF in almost arbitrary compositions [3b]. A rotating notched wheel is wetted by the molten material. Since the wheel is water-cooled, a high cooling rate is achieved resulting in short fibers with a homogeneous distribution of the metals. Small grain sizes, a high solubility of the constituents and metastable or amorphous phases are possible [3,4]. Due to continuous development of the melt extraction process at Fraunhofer IFAM, the production of fibers with an average equivalence diameter of 50–150  $\mu\text{m}$  is possible. The length of the fibers can be varied from 3 to 12 mm. For this study, different types of fibers were produced and characterized (Table 1).

The melt extracted fibers typically possess a kidney shaped cross section (see Figs. 1 and 2). The crystalline structure is visible by light



**Fig. 2.** Light microscopy image of the cross section of a  $\text{Cu}_{64}\text{Ni}_{28}\text{Mn}_7\text{Fe}_1$ -fiber (V447).

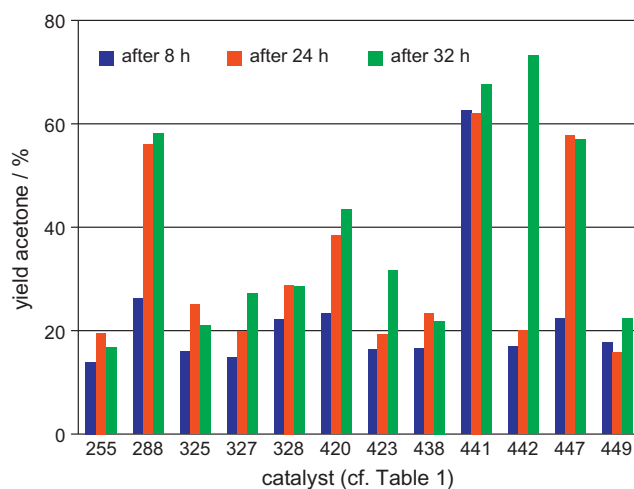


**Fig. 3.** Scanning electron microscopy image of a  $\text{Cu}_{64}\text{Ni}_{28}\text{Mn}_7\text{Fe}_1$ -fiber surface (V447).

microscopy or scanning electron microscopic (SEM) characterization (see Figs. 1–3). The SEM surface image of a  $\text{Cu}_{64}\text{Ni}_{28}\text{Mn}_7\text{Fe}_1$  fiber (V447) reveals fine surface structures, e.g. roughness. Such a rough surface structure was also found on  $\text{AlCuFe}$  fibers (V442). This explains the difference between measured values of the specific surface area (BET or optical). By means of the BET-method the morphology of the fiber surface is detected and, therefore, the measured values are higher (see Table 1).

### 3.2. Catalyst screening

Results of screening experiments for oxidation of 2-propanol (**1**) to acetone (**1a**) using aqueous  $\text{H}_2\text{O}_2$  under refluxing conditions in acetonitrile are described in Fig. 4. In all cases **1a** was identified as the only oxidation product. Blank reactions without the catalyst afforded **1a** in minor amounts (<5% after 24 h). Except for catalysts V288, V420, V441, V442, and V447 the content of 20% was reached within 8 h. The increase in yield of oxidation product after 24 or 32 h is usually not higher than 5%. In case of V288 and V420 the MSF contains Pt as well as Cr but no Ce, which seems to be beneficial for the reaction. Employment of the Ni-containing MSF V447 results in significantly higher yields of **1a** within longer reaction



**Fig. 4.** Results of oxidation of 2-propanol (**1**; 6 mmol) to acetone (**1a**) using hydrogen peroxide (2 g; 60 w%; aqueous) in 30 ml acetonitrile using catalysts listed in Table 1 (0.5 g;  $T=80^\circ\text{C}$ ).



**Table 2**  
Solvent influence on the oxidation of cyclohexanol (**2**) to cyclohexanone (**2a**)<sup>a,b</sup>.

Catalyst <sup>c</sup>	Solvent	Y <sub>cyclohexanone</sub> [%]
V441	Ethyl acetate	8
	Acetonitrile	23
	Deionized water	14
V447	Ethyl acetate	3
	Acetonitrile	40
	Deionized water	53

<sup>a</sup> Substrate: 6 mmol **2**, oxidant: aqueous H<sub>2</sub>O<sub>2</sub> (60 w%, 4 g), solvent: 30 ml, *t* = 5 h, *T* = 80 °C.

<sup>b</sup> For complete dependency from reaction time cf. *SD-I*.

<sup>c</sup> 0.5 g; cf. *Table 1*.

times than 8 h, indicating an induction period for the catalyst. With V288 and V447 yields of 40–60% can be achieved. Performing reactions with Cu-containing MSF V441 and V442, the conversion of **1** can reach 70%, whereby the latter shows a significant induction period of almost 24 h [10,11].

Besides oxidation with hydrogen peroxide, experiments have been conducted employing gaseous oxygen as the oxidant in PTFE-shielded stainless-steel autoclaves (*p*<sub>O<sub>2</sub></sub> = 0.8 MPa). The reactions afforded **1a** as the only reaction product [7]. In contrast to results summarized in *Fig. 4* Pt-containing MSF lead to the highest conversions (*Table 1*). However, yields were restricted by the external oxygen pressure. Due to this fact, the decreased hazardous potential for application of H<sub>2</sub>O<sub>2</sub> instead of O<sub>2</sub>, and the improved mass transport (two-phase instead of three-phase reaction) further experiments have been carried out in the presence of aqueous H<sub>2</sub>O<sub>2</sub> as the oxidant.

### 3.3. Influence of reaction parameters

As with other chemical transformations, oxidations with aqueous hydrogen peroxide are processes with many (un-)constrained variables and parameters. The most obvious ones: are solvent, reaction temperature, reaction-atmosphere, and oxidant concentration, as well as the type of substrate [6]. Experimental investigation of the influence of the parameters on the product yield was performed with two model reactions: (i) oxidation of 2-propanol (**1**) to acetone (**2**) and (ii) formation of cyclohexanone (**2a**) from cyclohexanol (**2**; *Scheme 1*). Due to lower solubility of **2** with aqueous H<sub>2</sub>O<sub>2</sub> solvent effects are more pronounced in comparison to the application of **1** as substrate. The use of water or polar organic solvents with a high hydrophilicity (acetonitrile) afforded higher yields compared to the reaction in ethyl acetate (*Table 2*). The unfavorable solvent properties of ethyl acetate resulted in low conversions due to the poor mixing between organic and aqueous phases containing the substrate and oxidant, respectively. However, the solvent effect is more pronounced in case of catalyst V447. The kinetics of the oxidation in water or acetonitrile is similar for both catalysts (cf. *Supplementary Data: SD-I*). Unfavorable mass transport due to the low solubility of **2** in water may hinder the reaction. Uniform dispersion of oxidant, catalyst, and substrate is necessary for high yields and can be realized by more intensive stirring. However, variation of the stirring frequency between 100 and 600 rpm revealed identical kinetic reaction profiles for both catalysts (*SD-II*).

The application of H<sub>2</sub>O<sub>2</sub> as terminal oxidant is problematic, since the oxidizing agent may undergo self-decomposition initiated either by higher temperature *T*, light, the presence of acids and bases or by contact with metal-surfaces [2b,c]. Titration experiments during the conversion of **1** and **2** revealed that the decomposition of H<sub>2</sub>O<sub>2</sub> is not as significant as thought. However, variation of *T* from 50 to 100 °C afforded a tremendous change in reactivity and activity of the catalysts (*Fig. 5*) [12]. For both model

**Table 3**  
Oxidation of 2-propanol (**1**) and cyclohexanol (**2**) under various reaction atmospheres<sup>a,b</sup>.

Reaction atmosphere	Y <sub>acetone</sub> [%] for MSF <sup>c,d</sup>		Y <sub>cyclohexanone</sub> [%] for MSF <sup>c,e</sup>	
	V441	V447	V441	V447
Air	63	89	32	38
N <sub>2</sub>	65	87	29	37
Ar	61	63	34	35
CO <sub>2</sub>	57	33	9	38
O <sub>2</sub>	62	62	27	35

<sup>a</sup> Substrate: 6 mmol, oxidant: aqueous H<sub>2</sub>O<sub>2</sub> (60 w%, 4 g), solvent: 30 ml deionized water, *t* = 6 h, *T* = 80 °C.

<sup>b</sup> For complete dependency from reaction time cf. *SD-III*.

<sup>c</sup> Catalyst: 0.5 g MSF; cf. *Table 1*.

<sup>d</sup> Substrate: **1**.

<sup>e</sup> Substrate: **2**.

catalysts it can be concluded that elevated *T* is advantageous for the reaction of **2** to **2a**. In case of the Cu–Sn-alloy V441 (*Fig. 5, left*), variation of *T* effected the kinetics of the reaction resulting in a higher production rate at higher *T*. At 50 °C the reaction rate was almost zero. In contrast, *T* influences the reaction kinetics only at the beginning of the reaction in presence of the Cu88Ni10Mn1Fe1-fiber (V447; *Fig. 5, right*) reaching a plateau of approximately 50% yield (*T* = 80–100 °C). Within the applied reaction time this plateau cannot be reached for oxidation at 70 °C. Similar to the behavior of catalyst V441, the reaction rates are significantly lower at *T* = 50 °C.

The influence of reaction atmosphere on the oxidation of both **1** and **2** to the corresponding ketones was investigated by purging different gases through the reaction mixtures (*Table 3*). Either inert gases (N<sub>2</sub>, Ar) or reactive gases (air, CO<sub>2</sub>, O<sub>2</sub>) have been applied for the investigations. The pressure was kept constant in all cases at 0.11 MPa and a flow rate of 1 ml min<sup>-1</sup> was maintained. Comparison of the results of reactions in air with those reported previously (no purging but air-atmosphere) revealed similar results for both catalysts and substrates after 6 h of reaction time. The product yields are independent from the gas purged through the reaction mixtures, since the levels of yields are similar. Although the kinetic profiles revealed differences (especially in the presence of CO<sub>2</sub>), the terminal selectivity and yield are comparable for the oxidation of **1** and **2** in presence of either V441 or V447 (*SD-III*). Thus, further reactions have been performed under standard air-atmosphere without purging.

Generally, lower local oxidant concentrations are assumed to afford higher yields since over-oxidation is suppressed as well as the effectiveness of oxidant consumption increases due to suppression of H<sub>2</sub>O<sub>2</sub> decomposition. Thus, different dosage-protocols for the oxidant have been applied in presence of catalysts V441 or V447 (*Table 4*). The overall mass of 60 w% aqueous H<sub>2</sub>O<sub>2</sub> added to the reaction mixture was 4 g (≈2.4 g = 72 mmol H<sub>2</sub>O<sub>2</sub>). The amount was either added in one portion at the beginning of the reaction

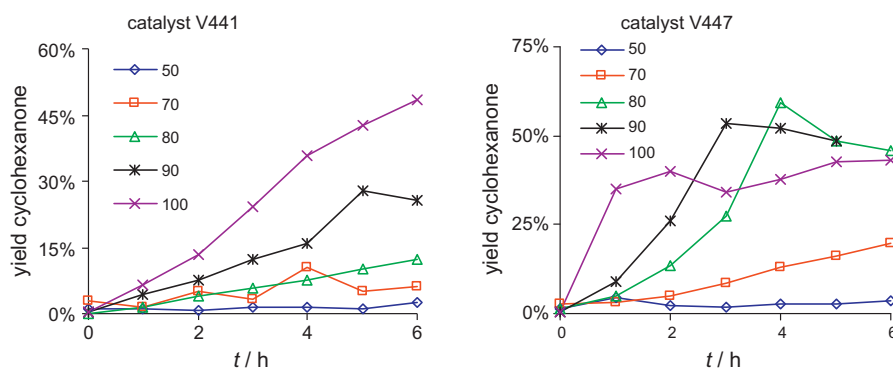
**Table 4**  
Variation of the H<sub>2</sub>O<sub>2</sub>-dosage protocol for the oxidation of cyclohexanol (**2**)<sup>a,b</sup>.

Dosage protocol	Addition of aqueous H <sub>2</sub> O <sub>2</sub> [g] after ...				Y <sub>cyclohexanone</sub> [%] for MSF <sup>c</sup>	
	0 h	1 h	2 h	3 h	V441	V447
A	4				14	53
B	2	2			12	44
C	2		2		12	58
D	1	1	1	1	12	41

<sup>a</sup> Substrate: 6 mmol **2**, oxidant: aqueous H<sub>2</sub>O<sub>2</sub> (60 w%, Σ*m* = 4 g; *n*(H<sub>2</sub>O<sub>2</sub>) = 72 mmol), solvent: 30 ml deionized water, *t* = 5 h, *T* = 80 °C.

<sup>b</sup> For complete dependency from reaction time cf. *SD-IV*.

<sup>c</sup> Catalyst: 0.5 g MSF; cf. *Table 1*.



**Fig. 5.** Influence of reaction temperature  $T$  on the oxidation of cyclohexanol (**2**; 6 mmol) to cyclohexanone (**2a**) using hydrogen peroxide (4 g; 60 w% aqueous) in 30 ml deionized water in presence of MSF V441 and V447 (0.5 g, cf. Table 1).

or addition in smaller portions at different time periods during the reaction. Apparently, the final product yields are independent from the employed catalysts and the reaction protocol. It might be expected, that the dosage protocol does not influence the terminal results but reaction kinetics. However, time dependency of product yield for the conditions shown in Table 4 revealed no significant invariance as provided in SD-IV. Furthermore, the selectivities are >99% and also the reaction plateau typical for catalyst V447 (compare Fig. 5, right) is reproduced. For further reactions the oxidant is added in one portion at the beginning of the reactions.

Another important reaction parameter influencing the course of reaction is the substrate-to-oxidant ratio, which can be varied in different ways: (i) variation of  $n_{\text{oxidant}}$  ( $n_{\text{substrate}} = \text{constant}$ ), (ii) variation of the oxidant concentration ( $n_{\text{oxidant}}$  and  $n_{\text{substrate}} = \text{constant}$ ), and (iii) variation of  $n_{\text{substrate}}$  ( $n_{\text{oxidant}} = \text{constant}$ ).

In order to investigate the influence by variation according to case (i), the oxidation of 6 mmol **2** in presence of catalyst V447 was performed by variation of  $n(\text{H}_2\text{O}_2)$  from 18 to 72 mmol. Thus, the oxidant-to-substrate ratio ranges from 3 to 12, respectively (Table 5). Comparison of the yields after 2 and 6 h revealed a direct proportionality between oxidant-to-substrate ratio and product yield, thus assuming that these parameters are constrained variables [13]. The slopes of the linear regression functions are 0.0477 and 0.0480 and the cubic proximity levels  $R^2$  are 0.9939 and 0.9912 for the results after 2 and 6 h of reaction time, respectively (compare SD-VI).

The assessment of results from the variation of experiments with different oxidant concentrations ( $n_{\text{oxidant}}$  and  $n_{\text{substrate}} = \text{constant}$ ) is more difficult. The concentration of aqueous  $\text{H}_2\text{O}_2$ , indicated as  $w(\text{H}_2\text{O}_2, \text{aq})$ , has been varied between 30 and 60 w%. The overall amount of oxidizing agent is constant (72 mmol), thus an oxidant-to-substrate ratio of 12 has been employed for the reactions of **1** and **2** in the presence of catalysts V441 and V447 (Table 6). Similar to the variation of reaction atmosphere (cf. Table 3) the yields after 6 h reaction time are independent from

**Table 5**  
Influence of the oxidant-to-substrate ratio for the oxidation of cyclohexanol (**2**)<sup>a</sup>.

$m(\text{H}_2\text{O}_2, \text{aq})$ [g]	$n(\text{H}_2\text{O}_2)$ [mmol]	$n(\text{H}_2\text{O}_2)/$ $n(\text{substrate})$	$X_{\text{cyclohexanone}} [\%]$ after:	
			$t = 2 \text{ h}$	$t = 6 \text{ h}$
2.1	18	3	18	15
4.1	36	6	35	32
6.1	54	9	49	47
8.0	72	12	61	58

<sup>a</sup> Substrate: 6 mmol **2**, oxidant: aqueous  $\text{H}_2\text{O}_2$  (30 w%), solvent: 30 ml acetonitrile, catalyst: 0.5 g V447 (cf. Table 1;  $T = 80^\circ\text{C}$ ).

$w(\text{H}_2\text{O}_2, \text{aq})$ , thus assuming that dilution of the oxidant by water has no influence on the chemical transformations shown in Scheme 1. Even the typical yield plateau in case of fiber V447 is independent from the substrate and  $w(\text{H}_2\text{O}_2, \text{aq})$ , indicated by kinetic reaction profiles (SD-V). The higher rates of conversions reported for the oxidation of **1** compared to the reaction of **2** (Tables 3 and 6) is attributed to the higher molecular flexibility of **1** leading to a higher reactivity of this substrate.

Kinetic reaction profiles for the oxidation of **2** furnishing **2a** with variation of  $n_{\text{substrate}}$  from 2 to 12 mmol are reported in Fig. 6. Independent from reaction time and catalyst the highest yields are afforded in case of 3 mmol **2** (oxidant-to-substrate ratio = 24). However, plotting of the absolute product yields in dependence of reaction time reveals strong similarities for different  $n_{\text{substrate}}$ . Thus, the oxidant-to-substrate ratio shows no visible influence on the absolute substrate conversion, when keeping  $n_{\text{oxidant}}$  constant [14,15]. Comparing the results with those reported in Table 5 for variation of  $n_{\text{oxidant}}$  revealed significant differences. Whereas in the former case a linear time-independent relationship was found, variation of  $n_{\text{substrate}}$  strongly influences the reaction kinetics (Fig. 6). Notwithstanding those differences, the functional correlation between oxidant-to-substrate ratio and yield of **2a** for both modes of variation is linear as indicated by linear regression functions (SD-VI). Concluding that the reaction rates are of zero- and first-order with respect to the substrate and oxidant, respectively.

### 3.4. Substrate screening

For all tested substrates blank reactions in absence of the metallic short fibers have been conducted resulted in either inferior yields (<3%; secondary alcohols) or conversion rates below 3% (**3–5**) after 6 h of reaction time. In addition to the oxidation of primary (**3**)

**Table 6**  
Influence of  $\text{H}_2\text{O}_2$ -concentration on the oxidation of 2-propanol (**1**) and cyclohexanol (**2**)<sup>a,b</sup>.

$w(\text{H}_2\text{O}_2, \text{aq})$ [w%]	$m(\text{H}_2\text{O}_2, \text{aq})$ [g]	$Y_{\text{acetone}} [\%]$ for MSF <sup>c,d</sup>		$Y_{\text{cyclohexanone}} [\%]$ for MSF <sup>c,e</sup>	
		V441	V447	V441	V447
30	8.0	65	58	29	37
40	6.0	68	51	29	43
50	4.8	66	65	32	35
60	4.0	64	61	32	38

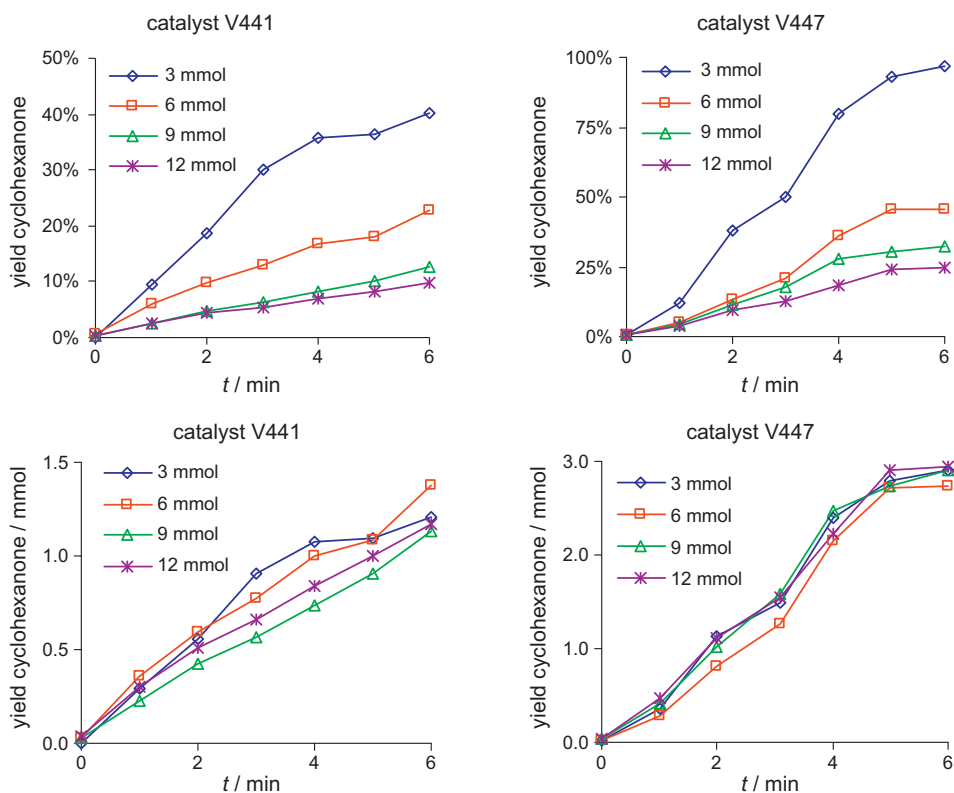
<sup>a</sup> Substrate: 6 mmol, oxidant: aqueous  $\text{H}_2\text{O}_2$  ( $n = 72 \text{ mmol}$ ,  $m(\text{H}_2\text{O}_2) = 2.4 \text{ g}$ ), solvent: 30 ml acetonitrile,  $t = 6 \text{ h}$ ,  $T = 80^\circ\text{C}$ .

<sup>b</sup> For complete dependency from reaction time cf. SD-V.

<sup>c</sup> Catalyst: 0.5 g MSF; cf. Table 1.

<sup>d</sup> Substrate: **1**.

<sup>e</sup> Substrate: **2**.



**Fig. 6.** Influence of substrate concentration on the oxidation of cyclohexanol (**2**; 3–12 mmol) to cyclohexanone (**2a**) using hydrogen peroxide (4 g,  $n(\text{H}_2\text{O}_2) = 36$  mmol; 30 w% aqueous) in 30 ml deionized water in presence of MSF V441 and V447 (0.5 g, cf. Table 1;  $T = 80^\circ\text{C}$ ). The top diagrams display relative yields and the bottom ones absolute yields.

and secondary alcohols, the epoxidation of alkenes (**4**, **5**) has been investigated.

Table 7 summarizes the results for the oxidation of secondary alcohols in presence of two different fiber catalysts: V441 and V447. In almost all cases the reaction furnishes the corresponding ketones with excellent selectivity (>99%). The yields strongly depend on the nature and reactivity of the substrate. Lower acyclic alcohols (< $\text{C}_6$ ) lead to higher conversions compared to longer-chain educts. In contrast to the lower homologues, 2-decanol afforded side reaction products also (nonanoic acid) decreasing the selectivity for 2-decanone to 46 and 67% for oxidation in presence of V441 and V447, respectively. The comparison of the reaction rates of **1** with **2** and 3-pentanol is interesting, because the latter contains **1** as substructure flanked by methyl groups or fixated in a cyclohex-

**Table 7**

Oxidation of secondary alcohols in the presence of 0.5 g metallic short fibers (cf. Table 1).<sup>a</sup>

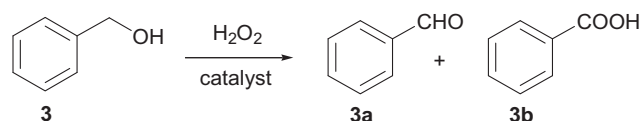
Secondary alcohol	$Y_{\text{ketone}} [\%]$ for MSF	
	V441	V447
2-Propanol ( <b>1</b> )	24	58
2-Butanol	7	11
2-Pentanol	30	61
3-Pentanol	64	54
2-Hexanol	14	18
2-Octanol	38	44
2-Decanol <sup>b</sup>	12 (X=26%)	24 (X=36%)
Cyclopentanol	32	47
Cyclohexanol ( <b>2</b> )	13	38
Cyclooctanol	28 (X=65%)	26 (X=68%)

<sup>a</sup> Substrate: 6 mmol, oxidant: aqueous  $\text{H}_2\text{O}_2$  (60 w%, 4 g), solvent: 30 ml acetonitrile,  $t = 4$  h,  $T = 80^\circ\text{C}$ .

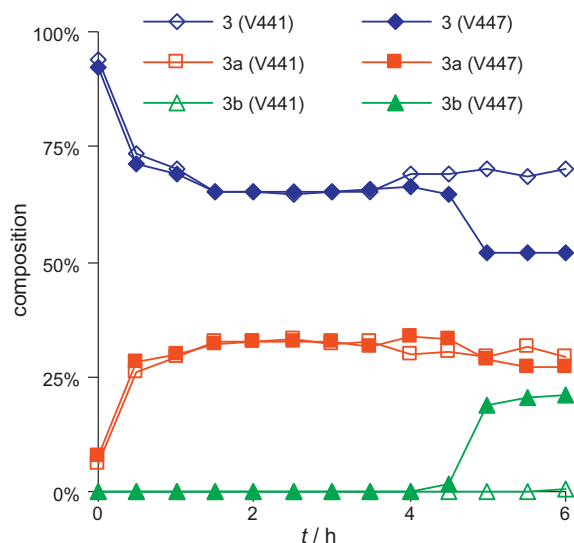
<sup>b</sup> Formation of unidentified side products (X = conversion).

ane ring, respectively. Due to the structural rigidity in case of **2**, its reactivity is significantly lower than in case of the more flexible aliphatic alcohols. Similar to the reaction of 2-decanol, the oxidation of cyclooctanol afforded side reaction products (formation of carboxylic acids indicated by drop of pH) lowering the selectivity for the formation of cyclooctanone to 43 and 38% with V441 and V447 as catalysts, respectively.

Compared to the oxidation of secondary alcohols (Table 7), the similar reaction with primary alcohols is much more difficult, due to the possibility over-oxidation furnishing the corresponding carbonic acid or further reaction products. However, high selectivities for the partial oxidation product benzaldehyde (**3a**) have been found for the oxidation of benzyl alcohol (**3**; Scheme 2) in the presence of fiber catalysts V441 and V447 (Fig. 7) [14–21]. Whereas in the former case the reaction was selective (>99%), application of V447 afforded also the formation of benzoic acid (**3b**) at higher conversion rates. It is remarkable that this side reaction does not affect the overall yield of **3a**. Rather the formation of **3b** resulted from direct oxidation of **3**, which is accompanied by catalyst destruction affording a brownish reaction solution. This indicates dissolution of Mn from the  $\text{Cu}_{64}\text{Ni}_{28}\text{Mn}_7\text{Fe}_1$ -alloy during the oxidation process, affording  $\text{MnO}_2$  as final oxidation product. Additionally, decomposition product benzene was formed at  $t > 4$  h with minor selectivities of 1 and 2% for MSF



**Scheme 2.** Oxidation of benzyl alcohol (**3**) with metallic short fibers.

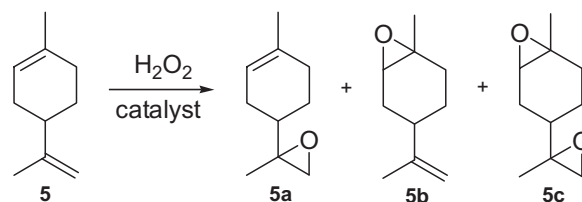


**Fig. 7.** Time dependency of the reaction mixture composition for oxidation of benzyl alcohol (**3**; 6 mmol) using aqueous hydrogen peroxide (60 w%, 4 g) in 30 ml deionized water in presence of MSF V441 and V447 (0.5 g, cf. Table 1;  $T = 80^\circ\text{C}$ ).

V441 and V447, respectively. The presence of both catalysts led to an intermediate start of the oxidation reaction indicated by the relative high amount of **3a** formed in the beginning of the reaction.

Beside the oxidation of secondary and primary alcohols the possibility for alkene epoxidation in presence of metallic short fibers has been assessed. Styrene (**4**) and limonene (**5**) have been applied as model substrates. With the same reaction conditions as described previously (Table 7, Fig. 7) styrene oxide (**4a**; Scheme 3) was formed in 1% yield only [16,22,23]. This finding was independent from reaction time, conversion or type of catalyst (V441, V447). As major oxidation product **3a** has been identified in addition to minor amounts of acetophenone (**4b**; <3%) [16]. After 6 h reaction a conversion of 25 and 42% has been found and a product selectivity for **3a** of 38 and 90% has been calculated for the employment of V441 and V447, respectively. Reaction under similar experimental prerequisites with **4a** afforded isomerization to **4b** with selectivities of 69 ( $X = 66\%$ ) and 94% ( $X = 55\%$ ) for oxidation with V441 and V447 ( $t = 6\text{h}$ ), respectively. Also the formation of **3a** was observed. Thus, the formation of **3a** from **4** is a competing reaction pathway to epoxidation (**4a**) and subsequent isomerization (**4b**). The formation of epoxide ring opening products 1-phenylethan-1,2-diol and 2-phenylacetaldehyde has not been observed throughout the experiments.

Concerning the relation to over-oxidation and epoxidation the latter is definitely more pronounced in case of **5** than reported for similar reaction of **4** (Scheme 3). In case of **5** epoxidation is the predominant reaction pathway affording different epoxidation products: 7,8-limonene oxide (**5a**), 1,2-limonene oxide (**5b**), and 1,2;7,8-limonene dioxide (**5c**; Scheme 4 and Table 8) [22–25]. Products **5b** and **5c** exist in different stereoisomeric



**Scheme 4.** Oxidation of limonene (**5**) with metallic short fibers.

**Table 8**

Epoxidation of limonene (**5**; cf. Scheme 4) with  $\text{H}_2\text{O}_2$  and in presence of metallic short fibers<sup>a</sup>.

Catalyst <sup>b</sup>	t [h]	X( <b>5</b> ) [%]	S( <b>5a</b> ) [%]	S( <b>5b</b> ) [%] <sup>c</sup>	S( <b>5c</b> ) [%] <sup>c</sup>
V441	2	1	60	40	0
	4	3	42	58	0
	6	15	34	19	47
V447	2	1	0	>99	0
	4	18	39	12	49
	6	58	41	16	42

<sup>a</sup> Substrate: 6 mmol **5**, oxidant: aqueous  $\text{H}_2\text{O}_2$  (60 w%, 4 g), solvent: 30 ml acetonitrile,  $T = 80^\circ\text{C}$ .

<sup>b</sup> Catalyst = 0.5 g (cf. Table 1).

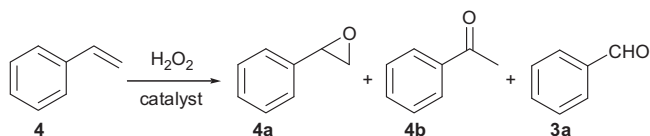
<sup>c</sup> Stereoisomers are summarized.

forms, which is ignored in the calculation of selectivity reported in Table 8. In case of catalyst V447 excellent selectivities for **5b** have been found at very low conversions. Thus, the regioselectivity is comparable to the application of  $\gamma$ -alumina or  $\text{Na}_2\text{WO}_4\text{-PhPO}_3\text{H}_2\text{-[Me}(n\text{-C}_8\text{H}_{17}\text{)}_3\text{N]HSO}_4$  as the catalysts and also 60 w% aqueous  $\text{H}_2\text{O}_2$  as the terminal oxidant [25c,e]. Increase of the reaction time and therefore of conversion afforded predominantly the formation of **5a** and **5c**. Application of metallic fiber V441 revealed lower reaction rates resulting in a maximum conversion of 15% after 6 h. The selectivity ratio is similar to that reported for the employment of V447. The complete absence of over-oxidation products is dedicated to the absence of any (de)stabilizing groups (e.g. aromatic ring in **4**).

### 3.5. Mechanistic considerations

The mechanism of the  $\text{Cu}_3\text{Sn}$ -catalyzed (V441) oxidation reaction with  $\text{H}_2\text{O}_2$  as the oxidant is different to the activation in metal complexes (e.g.  $\text{Cu}^{\text{II}}$ ,  $\text{Ti}^{\text{IV}}$  or  $\text{Mo}^{\text{VI}}$ ) via coordination of peroxy-anions to the metal center [26]. However, it is well known that oxygen is able to oxidize copper very rapidly to its oxides; whereas the formation of cuprous ( $\text{Cu}_2\text{O}$ ) and cupric oxide ( $\text{CuO}$ ) is a diffusion limited process [27]. With increasing layer thickness the relative content of  $\text{Cu}_2\text{O}$ -to- $\text{CuO}$  increases. The presence of hydrogen peroxide as oxidant is also able to furnish the oxidation of Cu-metal in acidic media [28] and reduction of NO to  $\text{N}_2$  is reported also [29]. Both concepts afford the formation of  $\text{Cu}_2\text{O}$  preferably. Thus, the reaction is expected to form  $\text{Cu}_2\text{O}$  by direct oxidation of the metallic fiber and consecutive reaction of the alcohol with the oxide layer furnished the reaction products.

As discussed above reactions with catalyst V447 ( $\text{Cu}_64\text{Ni}_{28}\text{Mn}_7\text{Fe}_1$ ) afforded the formation of  $\text{MnO}_2$  under loss of the structural integrity of the alloyed metal fiber. Apparently, in those case hydrogen peroxide also oxidizes the manganese. The formation of (per)manganate species and of  $\text{MnO}_2$  would account for the higher reactivity of V447 compared to V441, since manganese in those oxidation states is a potent oxidant for alcohol dehydrogenation [30].



**Scheme 3.** Oxidation of styrene (**4**) with metallic short fibers.



#### 4. Conclusion

The application of metallic short fibers of different compositions for liquid phase oxidation has been successfully demonstrated. Results indicated that the fibers are suitable catalysts for the formation of ketones from the corresponding secondary alcohols employing aqueous hydrogen peroxide as the terminal oxidant. In general noble-metal free MSF are significantly more active for reactions in combination with H<sub>2</sub>O<sub>2</sub>. Decomposition reactions of the oxidant are significantly lower than in the presence of noble metals (Pt, Rh, Pd). Contributing to these observations two metallic short fibers have been chosen as model systems for further investigations: intermetallic phase Cu<sub>3</sub>Sn and Cu<sub>64</sub>Ni<sub>28</sub>Mn<sub>7</sub>Fe<sub>1</sub>-alloy. The latter showed higher reactivity, whereas reactions in presence of the former required longer reaction times to reach similar levels of conversion. Despite the variation of various reaction parameters like oxidant-to-substrate ratio or reaction temperature, the oxidations proceed with high selectivity concerning the ketone formation from secondary alcohols. The selectivity for the formation of benzaldehyde from benzyl alcohol reaches a similar high level for Cu<sub>3</sub>Sn, whereas the other material causes over-oxidation to benzoic acid. In summary, it can be concluded that the presented metallic short fibers are interesting materials for liquid phase oxidation catalysis, which may combine the two aspects of catalyst and material design.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.11.038.

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