

Innovative Catalysts for Oxidative Dehydrogenation in the Gas Phase – Metallic Short Fibers and Coated Glass Fabrics

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This article is dedicated to Professor Dr. G. Zimmermann (Leipzig) in occasion of his 75th birthday.

The catalytic activity of metallic short fibers with chosen alloy components and textures was investigated in the oxidative dehydrogenation (ODH) of propane to yield propene, and of isopropanol to yield acetone. The short fibers were synthesized using a melt extraction process and the properties of the fibers were intensely characterized. A correlation between the structure and the catalytic activity of the material was established. Optical microscopic, DSC, XRD, REM and EDX methods were used to characterize the fibers. Selective results of the dependency of the temperature on the propane conversion are presented in this work. A yield of more than 35 % propene is obtained at a propane conversion of 50 %. The ODH of isopropanol to acetone occurred with attractive yields of over 80 %. The results demonstrate the high innovative potential of the metal fiber materials. The use of coated glass fabrics as catalysts for the ODH and total oxidation of propane were also part of this investigation.

1 Introduction

Propene is a very important feed material for the chemical and polymer industries. The required amounts can only be produced with a high capital input. Today, mainly steam cracking processes are used for the production of propene [1]. Other routes include catalytic dehydrogenation and catalytic cracking processes [2]. The oxidative dehydrogenation (ODH) of propane could be a cheap and simple method to meet the requirements of propene production. Therefore, many research groups are investigating appropriate catalysts and reaction conditions. However, until now no real breakthrough has been reached [3–8].

As the catalytic selective oxidation of short chain hydrocarbons needs special reaction conditions to avoid total oxidation, a short residence time on the catalyst as well as low oxygen concentrations in the feed gas are advantageous. It is also important to use catalysts with a small specific surface area and to arrange for good heat removal out of the catalyst bed.

In this paper we present ten different catalysts based on short metallic fibers. These fibers possess a low pressure drop over their fill and a low but adequate specific surface which can be easily changed by varying the fiber geometry. Hence, they could be very interesting catalysts for selective oxidation in the gas phase. The possibility of using mixtures of nearly every catalytically active metal in the production of these fibers is a huge advantage. Gürtler et al. describe wire meshes as catalysts for post combustion, but the fibers

used are based on commercial alloys and so the catalytic properties are very limited [9]. Additionally, their fibers are relatively thick, so they have a small specific surface which could not be varied to such a great extent.

In addition to metallic fibers, we also used PVD coated silica glass fabrics as catalysts. In this case the aim was to use a cheap, chemical and temperature resistant support material to produce highly active and stable catalysts.

The selection of the constituents of the alloy and the coatings occurred ad hoc after a model of known mixed oxide catalysts [10,11], only that in this work the catalytically active elements have been supplied in metallic form as constituents of the alloy. Additionally, it was of interest to investigate the influence of the microstructure (crystalline, amorphous, quasi-crystalline) on the catalytic activity and the long term stability of the fibers under reaction conditions.

2 Experimental Part

2.1 Catalytic Tests

2 g of catalytic material are used for the ODH of propane to propene. The feed gas mixture contained 2 vol.-% propane and 1 vol.-% oxygen. The carrier gas was nitrogen. The adjusted volume flow over the catalyst was 25000 cm³/h. This corresponds to a space velocity of 10000 h⁻¹. Temperature conversion selectivity curves were detected. The selectivities to propene and to carbon dioxide and the conversion of propane were determined by an online GC with thermal conductivity detector (TCD) at each temperature measuring point.

The total oxidation tests were carried out with 1 vol.-% propane and 99 vol.-% air in the educt gas mixture. All other reaction conditions were the same as in the ODH tests of propane. Fig. 1 shows a schematic drawing of the experi-

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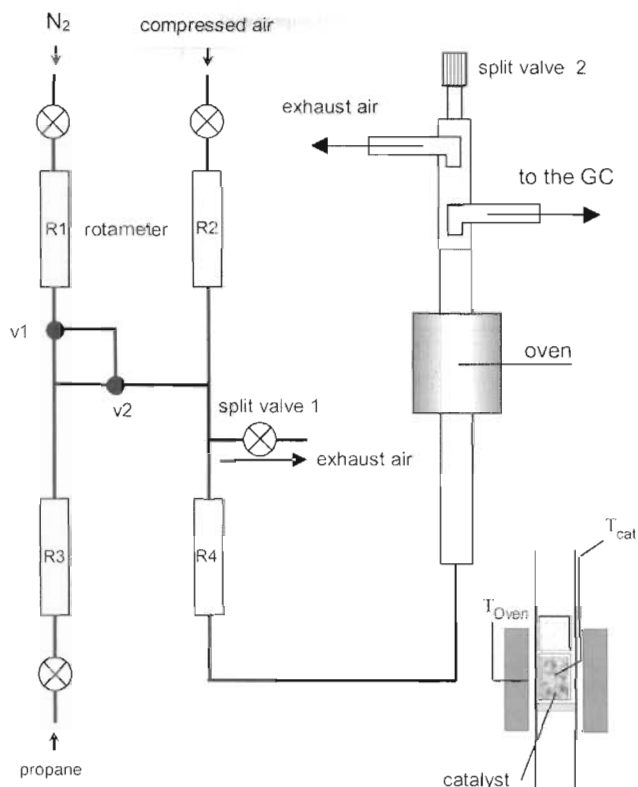


Figure 1. Schematic representation of the experimental set up for testing the catalytic properties of the metallic short fibers in the ODH of propane.

mental set up used for the ODH and total oxidation tests of propane.

The ODH of isopropanol to the product acetone was carried out in a seventeen fold parallel reactor arrangement with online FT-IR detection of the gaseous educt and the products at the reactor exit. The volume flow over the catalyst was $5000 \text{ cm}^3/\text{h}$, which results in a space velocity of 5000 h^{-1} . The concentration of isopropanol in the educt gas was set to 2 vol.-%, the concentration of oxygen was 1 vol.-%. The carrier gas used was nitrogen. As the activity of the catalysts was determined by the detection of temperature conversion selectivity curves, the concentrations of isopropanol, acetone, propene, and carbon dioxide were detected at each temperature step to calculate conversion and selectivities.

2.2 Crucible Melt Extraction (CME) of Metallic Short Fibers

The process of crucible melt extraction (see Fig. 2) makes it possible to produce metallic short fibers in almost arbitrary compositions. A rotating notched wheel is wetted by the molten metal. As the wheel is water cooled, a high cooling rate is reached. So the production of short fibers with a homogeneous distribution of the metals in the composition is achieved. Small grain sizes, a high solubility of the constituents, and metastable or amorphous phases are possible. The melt extracted fibers typically possess a kidney shaped cross section.

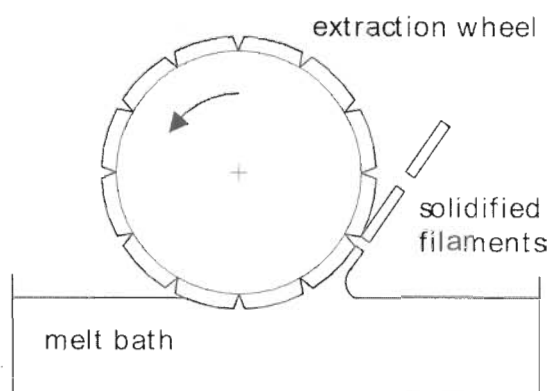


Figure 2. Principle of the production of short metal fibers by melt extraction.

Due to continuous development of the melt extraction process at Fraunhofer IFAM Dresden, the production of fibers with an average equivalence diameter of $50\text{--}150 \mu\text{m}$ is possible in batches of several kilograms [12]. The length of the fibers can be varied between $3\text{--}25 \text{ mm}$ with a deviation of $\pm 15 \%$. For this study, different types of fibers were produced and characterized, Tab. 1. The following compositions were chosen for testing and the most important results are described below.

- CuTiNiZrSn fibers, amorphous with intermetallic phases
- AlCuFe fibers, quasi-crystalline
- Cu_3Sn (1) fibers, intermetallic phase with 38.1 ma.-% Sn
- Cu_3Sn (2) fibers, intermetallic phase with 38.1 ma.-% Sn
- CuNiMnFe fibers, crystalline

The average equivalence diameter and the microstructure can be influenced by the extraction parameters like rotational speed and depth of immersion of the cylinder. The presented fibers were produced with a rotational speed of 5.5 m/s (Cu_3Sn (1)) and 13 m/s (AlCuFe, Cu_3Sn (2), CuTiNiZrSn, CuNiMnFe), respectively. To obtain the quasi-crystalline structure of the AlCuFe fibers, they were annealed in an argon atmosphere at 720°C for 3 h. Tab. 1 presents a summary of the most important fiber characteristics and of the behavior of the fibers in catalytic tests like the oxidative dehydrogenation and total oxidation example.

2.3 Coating of Glass Fabrics

One aim of this investigation was to find a cheap, temperature resistant and chemically stable support material which is easy to coat with catalytically active substances. Hence, silica glass fabrics and basalt fabrics were also used as support materials. The fabrics are stable long term at 1100°C (silica fabrics) and 800°C (basalt fabrics), respectively, and have a specific mass per unit area between $180\text{--}220 \text{ g/m}^2$. The glass fabrics were coated by PVD processes with different metallic coatings as catalytic active layers. The sputter equipment used for coating the fabrics with metallic layers was an Ultra S 150 lab sputter equipment from SURA Instruments GmbH (Jena, Germany). The coating pressure

Table 1. Summary of the material and catalytic properties of the analyzed metallic short fibers at the ODH of propane and isopropanol.

Catalyst, Character of the Fiber	composition	density [g/cm ³]	average fiber geometry		specific surface [m ² /g]	propane: ODH	propane: total oxidation	isopropanol: ODH
	ma.-%		length [mm]	diameter [μm]				
Cu ₃ Sn (1)	Cu 68.1 Sn 31.9	8.94	4.93	136	0.0084 (BET) 0.0044 (optical)	+	-	+
			crystallite grain size: 25.5 μm					
Cu ₃ Sn (2)	Cu 68.1 Sn 31.9	8.94	5.27	70	0.0103 (BET) 0.0061 (optical)	-	+	++
			crystallite grain size: 13 μm					
CuTiNiZrSn	Cu 39.94 Ti 22.58 Ni 13.83 Zr 14.33 Sn 9.32	7.16	9.47	95	0.0277 (BET) 0.0052 (optical)	+	+	++
AlCuFe	Al 42.40 Cu 40.75 Fe 16.85	4.42	10.26	138	0.0418 (BET) 0.0104 (optical)	++	-	-
CuNiMnFe (V447)	Cu 64 Ni 28 Mn 7 Fe 1	8.52	10.3	81.6	0.0077 (optical)	+	+	++
CuNiMnFe (V449)	Cu 88 Ni 10 Mn 1 Fe 1	8.81	11.6	98.4	0.0055 (optical)	-		+
FeCrAlPt	Fe 74.5 Cr 20 Al 5 Pt 0.5	7.2	11.35	89	0.009 (optical)	+	-	-
FeAlPt	Fe 69.5 Al 30 Pt 0.5	5.4	6.06	59	0.0166 (optical)	+	-	-
CuTi 5	Cu 95 Ti 5	8.75	41	137	0.0032	-	+	+
CuSi 1	Cu 99 Si 1	8.68	5.5	136	0.0033			+

was 10⁻³–10⁻² mbar, the sputter gas was argon, and the plasma power was 25 watts.

3 Results and Discussion

3.1 Investigation of the Catalytic Activity of Metallic Short Fibers

The AlCuFe fibers turned out to be very well suited for the ODH of propane to propene. With the help of these fibers, high propene selectivities at reaction conditions with high propane conversion were observed (see Fig. 3). Likewise, the application of the CuTiNiZrSn fibers leads to high propene selectivities at high propane conversions (see Fig. 4). In the case of Cu₃Sn fibers a good total oxidation behavior was observed. The amount of detected water in the product gas was much less than would have been expected according to the reaction equation. It is assumed that part of

the hydrogen formed during the reaction was not oxidized to water. This suspected reforming behavior is a matter of current research (see Fig. 5).

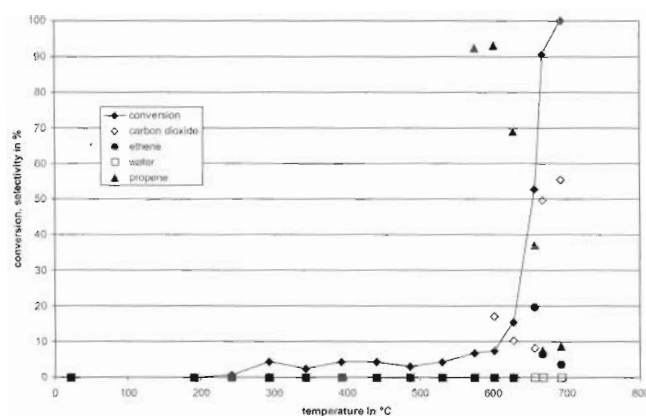


Figure 3. Temperature-conversion-selectivity diagram of ODH of propane with AlCuFe fibers as a catalyst.

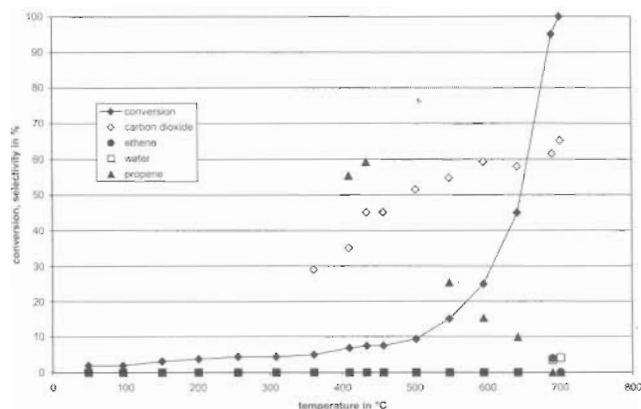


Figure 4. Temperature-conversion-selectivity diagram of ODH of propane with CuTiNiZrSn fibers as a catalyst.

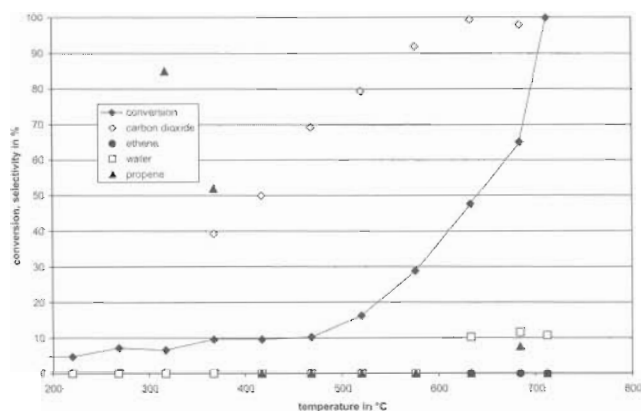


Figure 5. Temperature-conversion-selectivity diagram of ODH of propane with Cu₃Sn (2) fibers as a catalyst.

Some of the fibers showed an outstanding conversion selectivity behavior during the selective oxidation of isopropanol. The fibers Cu₃Sn (2), CuTiNiZrSn, and CuNiMnFe were especially good. With the help of these fibers, nearly complete conversion could be observed at temperatures of

380 °C. The selectivity with regard to acetone amounted to more than 85 %, the selectivity to carbon dioxide was fortunately low at 10–15 % (see Figs. 6–8). A summary of the results obtained from testing the catalytic activity of the fibers for the ODH of isopropanol is presented in Tab. 1.

The overview also contains properties of the analyzed fibers like their composition, geometrical dimensions, and specific surface. The average fiber diameter varied from 70–150 μm depending on the extraction conditions. Thinner fibers are produced by high rotation velocities of the immersed cylinder. One example for this is the Cu₃Sn (2) fiber. Despite the higher fiber diameter of 138 μm, the quasi-crystalline AlCuFe fibers possess a high specific surface. The reason for this is their fine nano-structured surface.

3.2 Structure and Microstructure Analysis of the Metallic Short Fibers

The metallic short fibers were analyzed before and after the catalytic testing to investigate possible changes in the microstructure, the chemical composition, and the surface appearance. It was expected that under reaction conditions diffusion processes in regions near the surface of the fibers occur, so changes in the microstructure of the fibers should be possible. With the help of optical and scanning electron microscopy (SEM) analyses of selected fiber cross sections and surfaces it was possible to judge the long term stability of the fibers under reaction conditions. It was analyzed whether fiber material was lost in the catalytic process.

3.3 Cu₃Sn Fibers as Catalysts

The copper-tin fibers consist of 61.9 ma.-% copper and 38.1 ma.-% tin in the intermetallic phase Cu₃Sn of the binary copper-tin system, so these fibers possess a homogeneous monophase crystalline structure. The average grain size of the crystallites in the Cu₃Sn fibers is 13–26 μm (see also

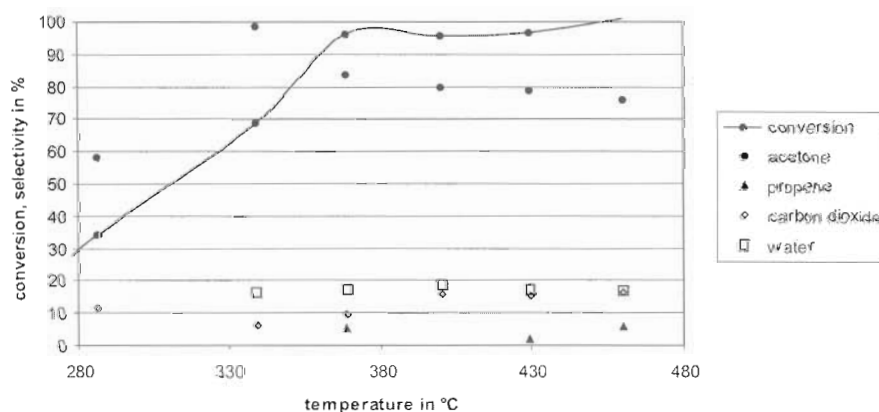


Figure 6. Temperature-conversion-selectivity diagram of ODH of isopropanol with Cu₃Sn fibers as a catalyst.

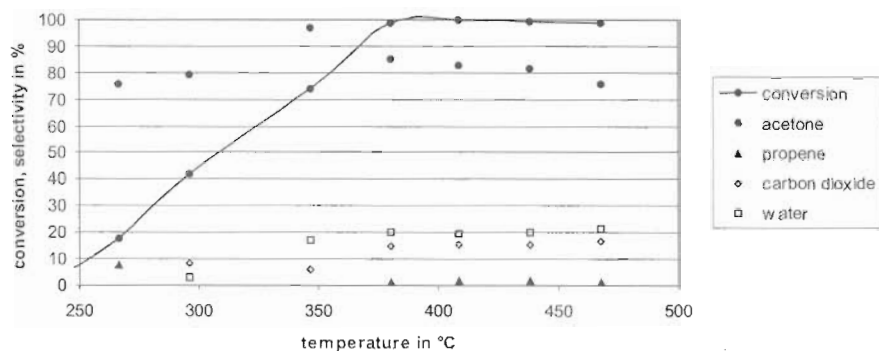


Figure 7. Temperature-conversion-selectivity diagram of ODH of isopropanol with CuTiNiZrSn fibers as a catalyst.

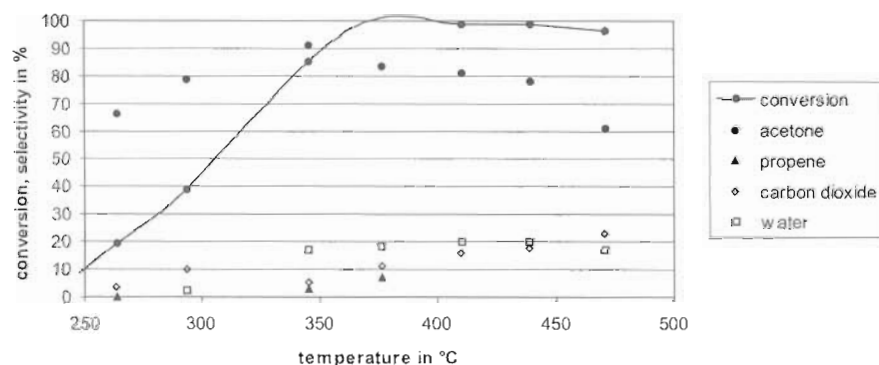


Figure 8. Temperature-conversion-selectivity diagram of ODH of isopropanol with CuNiMnFe fibers as a catalyst.

Tab. 1). The crystal grain boundaries on the surface of the fiber are recognizable in the SEM exposure in Fig. 9. After only three catalytic cycles of the ODH of propane the surface of the fiber is shown by the SEM exposure to be etched and porous. The surface is attacked due to its spongy structure (see Fig. 10). EDX analyses detected a depletion of copper and an accumulation of oxygen at the surface, indicating that copper and/or tin mixed oxides were formed.

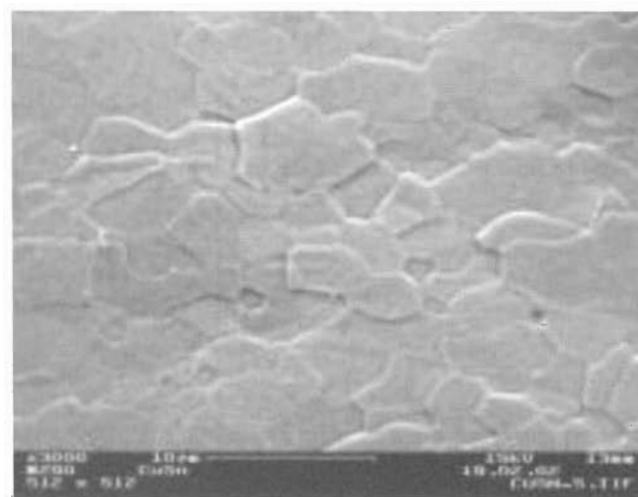


Figure 9. SEM exposure of the surface of a Cu₃Sn (2) fiber before the ODH of propane.

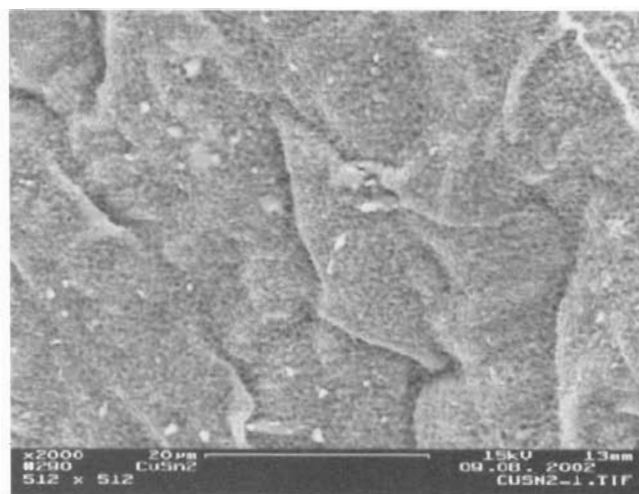


Figure 10. SEM exposure of the surface of a Cu₃Sn (2) fiber after three catalytic cycles of the ODH of propane.

3.4 CuTiNiZrSn Fibers as Catalysts

The CuTiNiZrSn fibers, which are made out of a Cu-, Ti-, Ni- rich alloy, possess an amorphous basic structure with crystalline inclusions. Tab. 1 presents the precise composition of this alloy. Fig. 11 represents a cross section of a fiber in a SEM exposure. There are two different phases distinguish-

able. With the help of XRD and EDX analysis it was proven that the amorphous phase is tin rich (bright) and the crystalline phase is depleted of tin (dark). SEM analysis of the surface of the fibers showed a smooth surface. After five catalytic cycles of the ODH of propane the obtained SEM and EDX exposures demonstrate a disintegration of the fiber volume in single layers. The layers are generated by diffusion processes of single alloy components within the fiber volume. So copper diffuses to the surface of the fiber whereas Ti, Ni and Zr are accumulated in the center. The high oxygen concentration at the surface proves the formation of oxides. The surface is fissured and corroded (see Fig. 12).

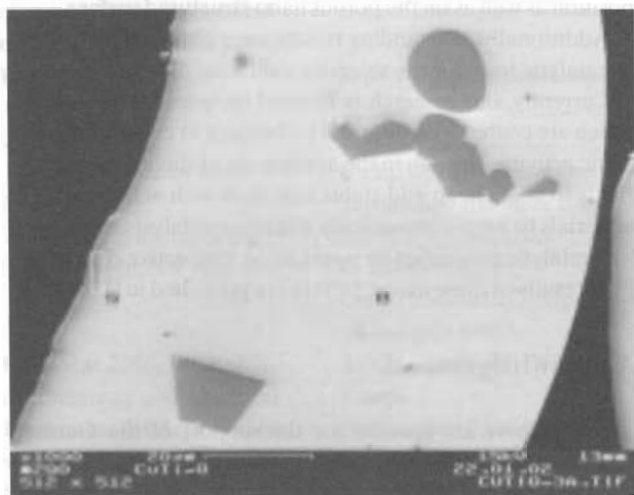


Figure 11. SEM exposure of a cross section of a CuTiNiZrSn fiber before the ODH of propane.

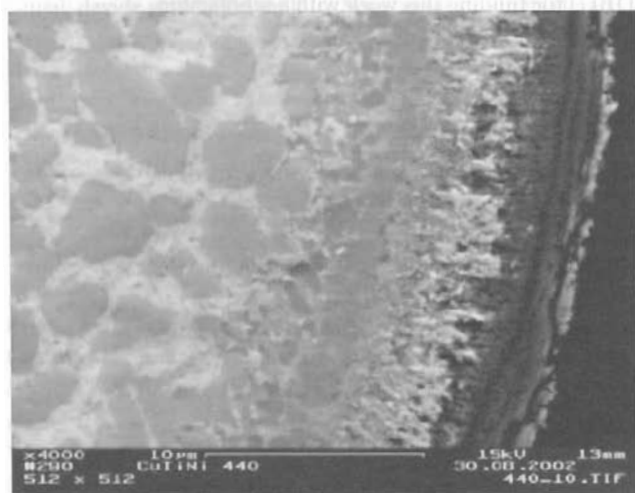


Figure 12. SEM exposure of a cross section of a CuTiNiZrSn fiber after five catalytic cycles of the ODH of propane.

3.5 AlCuFe Fibers as Catalysts

The microstructure of the AlCuFe fibers obtained after the melt extraction possesses dendritic crystals. The fibers

were calcinated at 720 °C for 3 h. After this, no crystalline characteristics could be detected with the metallographic analyses. With XRD exposures only quasi-crystalline icosahedral structures were demonstrated. In contrast to this result, the surfaces of the fibers have a fine structure and are porous rastered. Fig. 13 represents the SEM exposure of a fraction edge of a fiber. There is a thin structured oxide layer on the surface with a thickness in a nanometer range recognizable. This result is supported by the EDX analysis, which reveals a high oxygen concentration on the surface. Fig. 14 shows the fiber surface after five catalytic cycles of the ODH of propane. The oxide layer on the surface is still there. Also, with the help of SEM and EDX exposures on cross sections, no significant changes in the fiber volume are recognizable. The fiber is stable under reaction conditions.

With the presented fibers as catalysts for the selective oxidation of propane to propene, high propene selectives were

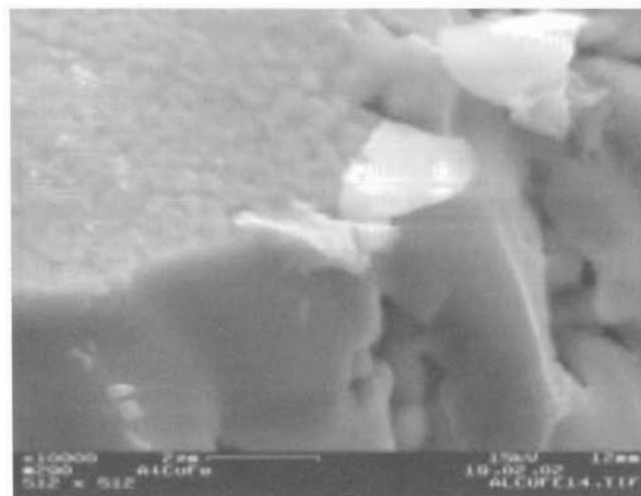


Figure 13. SEM exposure of a fiber break edge of an AlCuFe fiber before the ODH of propane.

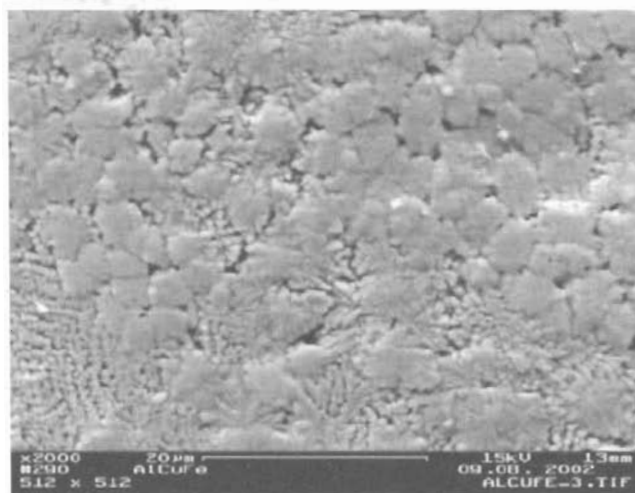


Figure 14. SEM exposure of the surface of an AlCuFe fiber after five catalytic cycles of the ODH of propane.

obtained. The results are shown in Fig. 3. Of all tested fibers, the AlCuFe fibers were the best catalysts for the ODH of propane. The obtained selectivities at high conversions could be of interest for commercial processes.

3.6 Coated Glass Fabrics as Catalysts

The coated glass fabrics were used for the total oxidation of propane. Different coatings cause varying catalytic activities (see Fig. 15). The best catalyst analyzed for the total oxidation of propane was a silica glass fabric with Pt coating. Silica glass fabrics with copper containing coatings give comparatively bad catalysts. There is evidence, especially from the PtRh coated fabrics, that there is transport control of the reaction at higher conversions. So, with an optimized reactor and with optimized reaction conditions, even better results should be possible. The fabrics are also stable long term under reaction conditions, as it is shown in Fig. 16.

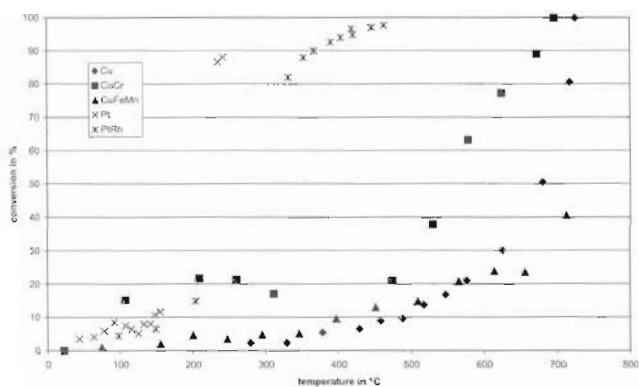


Figure 15. Comparison of different coatings for silica glass fabrics in the total oxidation of propane.

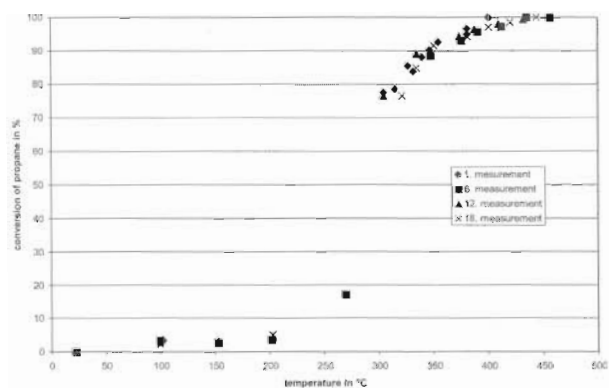


Figure 16. Long term stability test for a PtRh-coated silica glass fabric for the conversion of propane.

4 Conclusions and Outlook

It could be shown that melt extracted metallic short fibers possess a great variability of material composition, microstructure, and surface morphology. This, as well as the optimized specific surface and the low pressure drop over the catalyst bed, make the fibers very well suited for application as catalysts for selective oxidation reactions in the gas phase.

The selected fibers remained stable under reaction conditions over several catalytic cycles. The best result for the ODH of propane was detected with the quasi-crystalline AlCuFe fibers. The excellent catalytic behavior combined with the stability under reaction conditions is based on the chemical composition as well as on the porous nano-structured surface.

Additionally, outstanding results were obtained with fibers in catalytic tests for the selective oxidation of isopropanol.

Currently, our research is focused on iron hollow spheres which are coated with different techniques to enhance the catalytic activity. The aim in the application of this support material is to coat cheap and stable materials with active catalytic materials to form economically attractive catalysts with excellent catalytic properties for application in selective oxidations. First results of these investigations are published in [13, 14].

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