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HIGHLY POROUS METAL FIBRE STRUCTURES AS CATALYSTS FOR THE SELECTIVE OXIDATION OF PROPANE

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Abstract – The catalytic selective oxidation of saturated hydrocarbons in the gas phase requires specific reaction conditions in order to avoid the total oxidation to carbon dioxide. Therefore, it is advantageous to work in high dilutions. This means that the concentration of the hydrocarbon in the gas flow is low. Also, it is crucial to realise short residence times on the catalyst surface. This was ensured by using catalysts with a small specific surface. In the here presented work, the catalytic activity of different metallic fibre materials was analysed for the selective gas phase oxidation of propane to propene. The catalysts were also submitted to a broad characterisation of their material properties. Among other methods, DSC, optical microscopy, XRD, SEM and EDX were used to find out coherences between the materials composition, microstructure and the catalytic activity. The main focus of this work was on metals made from alloys with different compositions of catalytic active metals. The structure varied from crystalline microstructure over single-phase quasi-crystalline microstructure to amorphous vitreous structure. It was possible to convert propane with the help of the used fibre materials and with an excellent selectivity to propene.

Keywords: catalyst, selective oxidation, fibre

1. INTRODUCTION

Propene is known as a very important feed material for the chemical and plastics industry, but the high amount required can only be produced at high costs. The selective oxidation of propane would be a cheap possibility to acquire the needed amount of propene. Many work groups are involved with the search for suitable catalysts and reaction conditions for this problem [1-3]. To date, however, no breakthrough is reached in this field. In this paper, an overview of the testing results relevant to the desired catalytic reaction, the selective oxidation of propane, is given. A particular attention was turned to the chemical, physical (surface, structure) and mechanical stability of the tested catalysts.

Catalytic structures, made from metallic short fibres, should accomplish the requirements for the selective oxidation. The following properties must be accomplished:

- Low, but adequate specific surface area
- Adherence of short residence time at the catalyst
- Efficient heat removal during the reaction.

It was estimated that fills of metallic fibres could fulfil these demands.

2. EXPERIMENTAL DETAILS

2.1. Melt extraction of metal fibers

Using the crucible melt extraction process (Fig. 1), it is possible to make short fibers from almost any fusible material [4]. A rotating wheel with a notched surface is placed over a melt pool. The rotating extraction device is water cooled and thus generates a high solidification rate. As a result, homogenous distribution of the alloying elements, small grain sizes, reduced segregation and extended solubility, as well as the formation of metastable phases is achieved. The melt extracted fibers typically show a sickle or kidney shaped cross-section.

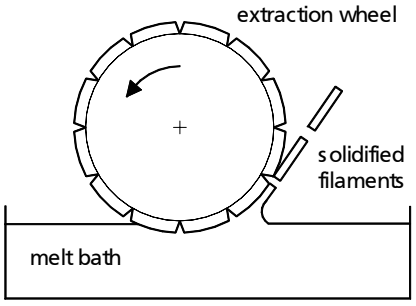

Fig. 1. Schematic drawing of the crucible met extraction process

Fraunhofer Institute IFAM Dresden has improved the crucible melt extraction process to produce fibres of a mean equivalent diameter from 50 to 150 µm in batch sizes of one to several kilograms. The fibre length can be set from 3 to 25 mm with a deviation of approximately ± 15 %. In this work, fibres with the following composition have been produced:

- Cu_3Sn (1); intermetallic phase (38.1 weight-% Sn)
- Cu_3Sn (2); intermetallic phase (38.1 weight-% Sn)
- CuTiNiZrSn; amorphous with intermetallic phases
- AlCuFe; quasicrystalline

Mean equivalent diameter and grain size of the microstructure can be influenced by variation of the extraction parameters, such as circumferential velocity of the extraction wheel and its immersion depth. The fibres have been extracted with a circumferential velocity of the extraction wheel of 5.5 m/s (Cu_3Sn (1); AlCuFe) and 13 m/s (Cu_3Sn (2); CuTiNiZrSn). To get the quasicrystalline structure, the as-extracted AlCuFe fibres were heat treated 3 h at 720 °C.

Table 1 gives an overview of the parameters and catalytic reaction behaviour of the analysed fibres, as described in chapter 3.

2.2. Measuring device to analyse the catalytic activity

For measuring the selective gas phase oxidation of propane to propene, according to the equation

$$C_3H_8 + 0.5\ O_2 \rightarrow C_3H_6 + H_2O \qquad (1),$$

a special measuring device of the Institute of Technical Chemistry and Environmental Chemistry, Friedrich Schiller University Jena, has been used.

To a constant flow of gaseous propane, a flow of pure nitrogen was added in order to dilute the hydrocarbon. Subsequently, air was added to ensure the required amount of oxygen in the flow of educt gases. In this way the flow contained 0.8 to 1 vol-% propane and 1 vol-% oxygen. The reactor with a diameter of 2 cm was equipped with approximately 2 g of the catalytic material, and the flow through the reactor was adjusted to 25000 cm^3/h. Space velocity amounted approximately 10000 h^{-1}. The reactor and the gas transfer lines to the analytic device were heated. This was important to avoid condensation of products in the gas flow lines, especially of water vapour. Analysis was performed by an online gas chromatograph (GC) with a thermal conductivity detector (TCD).

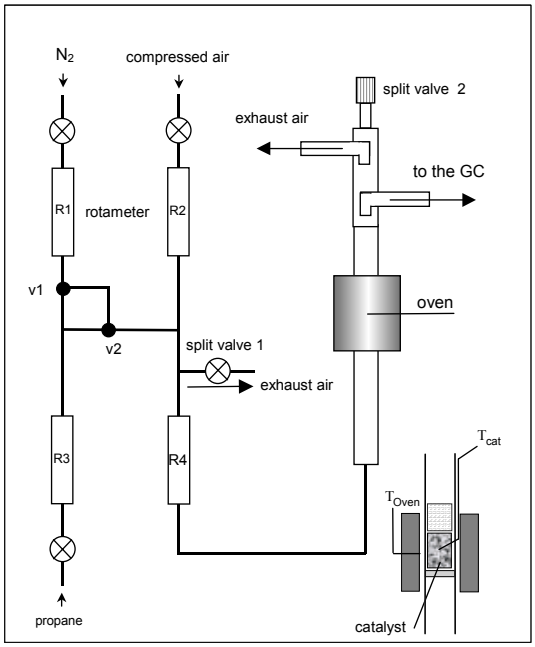

Fig. 2. Schematic drawing of the measuring device

Thus, it was possible to determine conversion, selectivity and yield of all products that were generated.

3. RESULTS AND DISCUSSION

The used metallic short fibres had been analyzed before and after the catalytic testing. In this paper only the typical structural parameters of the initial state in relation to the catalytic behaviour will be discussed.

3.1. Catalyst made from Cu_3Sn fibres

The Cu_3Sn fibres, made from copper with 38.1 weight-% tin, an intermetallic phase in the binary system Cu-Sn, are characterised by a single phase homogeneous crystalline structure. Fig. 3 shows the micrograph of the cross-section of some fibres. The grain size of the crystalline structure was quantified with by image analysis. The average grain size of the Cu_3Sn fibres varied with the extraction conditions and was determined with 26 µm and 13 µm (see table 1).

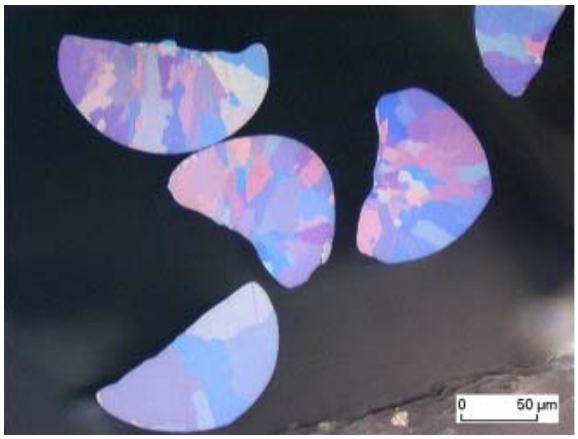

Fig. 3. Cross section of Cu_3Sn (2) fibres (optical metallography; polarised light)

Fig. 4 shows a SEM image of the surface of a Cu_3Sn (2) fibre. Grain-boundaries and very smooth grain surfaces can be seen.

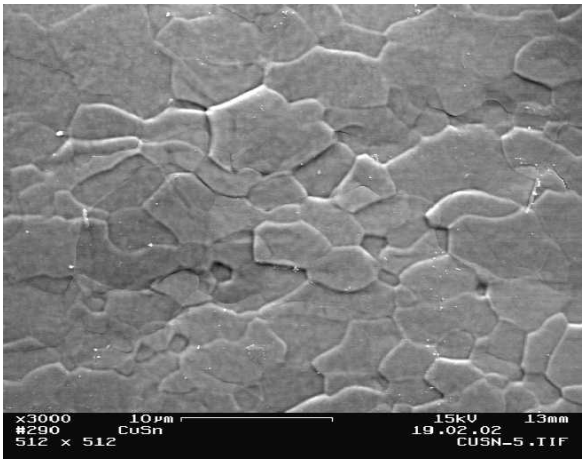

Fig. 4. SEM image of the surface of a Cu_3Sn (2) fibre

Fig. 5 shows the conversion of propane using Cu_3Sn (2) fibres as catalyst. Furthermore, the achieved selectivity of

propene and other products is illustrated. The selectivity of propene is very low. However, water, which would normally be formed during the reaction, could not be detected. Therefore, the catalyst might be used for reforming processes and thus for the extraction of hydrogen. This property of the catalyst is the subject of further investigations.

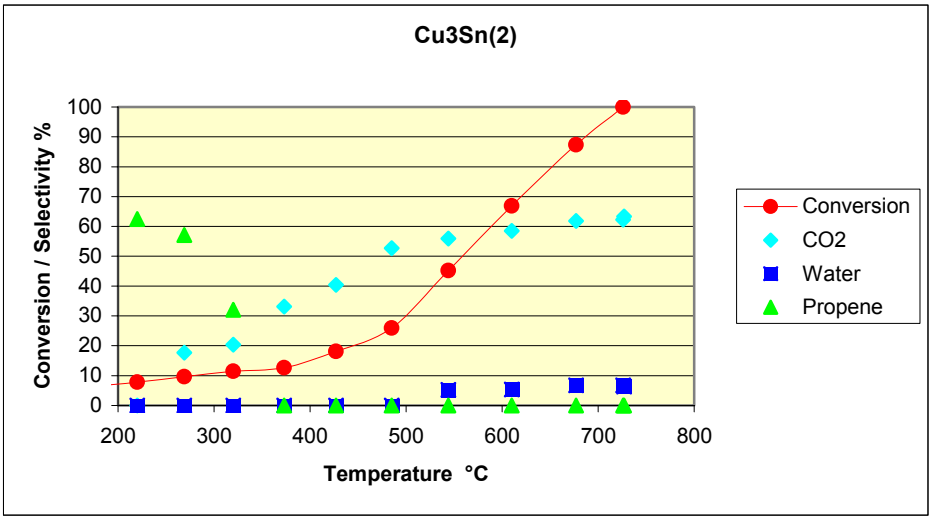

Fig. 5. Conversion of propane with Cu_3Sn (2) fibres as catalyst

3.2. Catalyst made from CuTiNiZrSn fibres

The CuTiNiZrSn fibres, made from a Cu-, Ti- and Ni-rich alloy, are characterised by an amorphous basic structure with crystalline precipitations. Table 1 shows the composition of this alloy and Fig. 6 shows the SEM micrograph of a fibre cross section. In Fig. 6 there can be seen two phases in the fibre. As a result of X-ray diffraction and EDX-analysis, it can be assumed that there exists an amorphous Sn-rich phase (light-coloured) with embedded Sn-depleted crystalline phases (dark-coloured). The SEM investigation of the fibre surface showed a very smooth surface without any structural features.

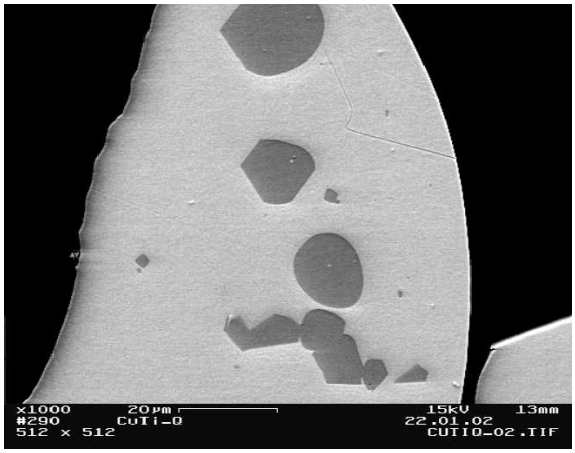

Fig. 6. SEM image of the cross section of a CuTiNiZrSn fibre

Fig. 7 indicates the conversion of propane to propene with the help of the CuTiNiZrSn fibres as catalyst. It is quite evident that the selectivity to propene is comparable to conventional catalysts. Reforming processes are also obtained.

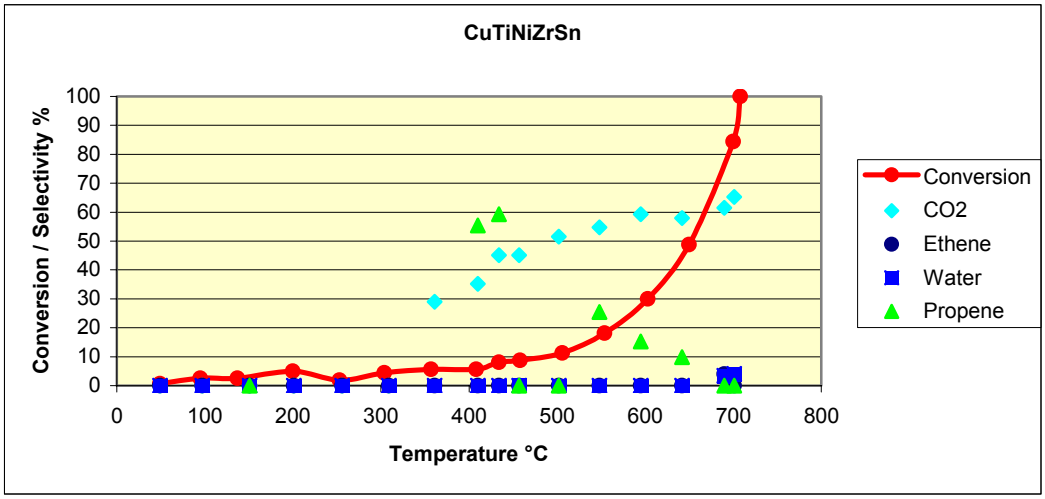

Fig. 7: Conversion of propane with CuTiNiZrSn fibres as catalyst

3.3 Catalyst made from AlCuFe fibres

The microstructure of the AlCuFe fibres with the composition 42.4 % Al, 40.75 % Cu and 16.85 % Fe (weight-%) in the as-extracted condition is illustrated in Fig. 8. There can be seen a typical dendritic structure. In order to get the quasicrystalline structure, the fibres were heat treated at 720 °C for 3 hours.

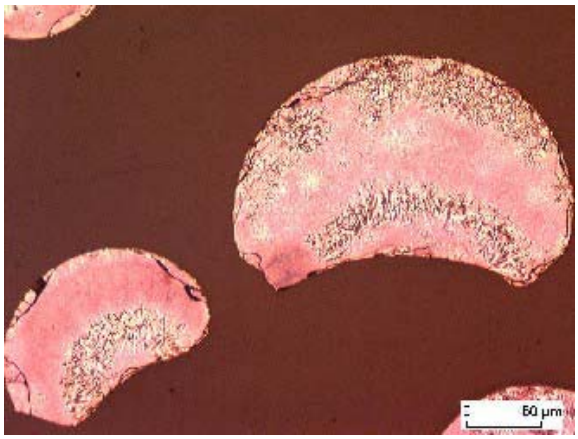

Fig. 8. Cross section of AlCuFe fibres in the as-cast condition (optical metallography)

The X-ray diffraction analysis showed the metastable β-phase (AlFe) and the icosahedric quasicrystalline equilibrium phase after melt extraction. After the heat treatment only the quasicrystalline equilibrium phase was found. The metallographic analysis of the cross section after heat treatment shows no crystalline characteristics at all. In contrast to this, the surface of the heat treated quasicrystalline fibres shows a finely structured, fine dendritic, porous pattern. This is illustrated in Figures 9 and 10.

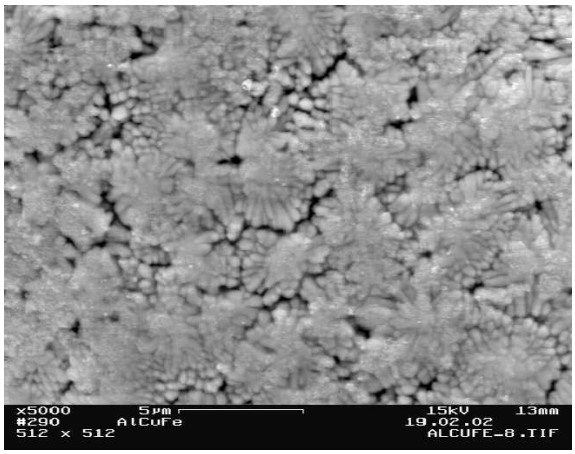

Fig. 9. SEM image of the surface of an AlCuFe fibre in the heat-treated condition

Fig. 10 shows the SEM picture of the edge of a fibre fracture surface. A thin textured oxidized surface layer in nm-dimension is recognisable. This finding is confirmed by results of EDX analyses, which indicated a high oxygen level at the surface.

Investigations on the catalytic activity of the fibres for the conversion of propane demonstrated an excellent selectivity to propene. This result can be seen in Fig. 11. In comparison to the other investigated catalysts, the Cu_3Sn (2) fibres and the CuTiNiZrSn fibres, the quasicrystalline AlCuFe fibres show the best propene-selectivity at high conversion rates.

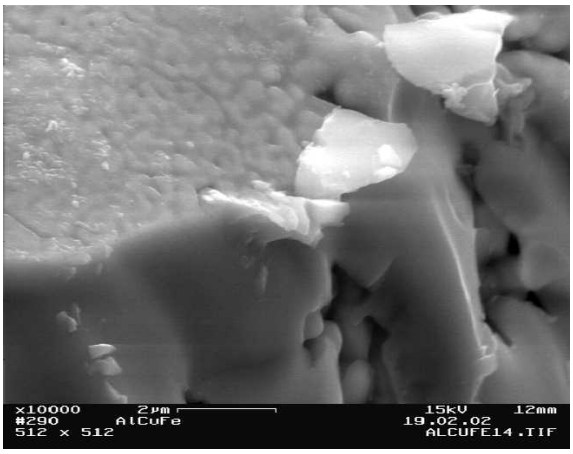

Fig. 10. SEM image of the fractured surface of an AlCuFe fibre (heat-treated condition)

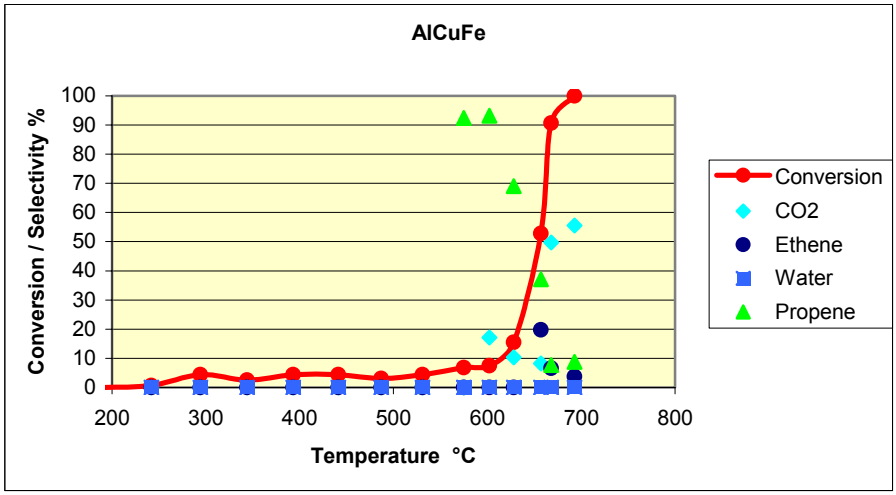

Fig. 11. Temperature-conversion-selectivity diagramm of the conversion of propane with AlCuFe fibres as catalyst

Table 1. Characteristic values of the catalysts, made from melt-extracted fibres

Catalyst	Composition	Density	Mean fibre dimensions		Specific surface area	Propane selective oxidation
			length	diameter		
	[Weight-%]	[g/ cm^3]	[mm]	[µm]	m^2/ g	
Cu_3Sn (1)	Cu 61.9 Sn 38.1	8.94	4,93	136	0,0084 (BET) 0,0044 (optical)	–
			Grain size: 25,5 µm			
Cu_3Sn (2)	Cu 61.9 Sn 38.1	8.94	5.27	70	0.0103 (BET) 0.0061 (optical)	–
			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)	++

Table 1 gives a summary of all tested fibres, their compositions, dimensions and their catalytic activity. It can be seen that the mean fibre diameter varies from 70 to 140 µm, depending on the melt extraction parameters. The thinner fibres had been extracted with a higher circumferential velocity of the extraction wheel of 13 m/s (Cu_3Sn (2); CuTiNiZrSn). In spite of the higher fibre diameter of 138 µm, the quasicrystalline AlCuFe fibres have a very high specific surface area. In particular, the value measured by the BET-method is very high compared to the surface areas of the Cu_3Sn and CuTiNiZrSn fibres. This can be attributed to the finely textured surface constitution of the AlCuFe fibres.

4. CONCLUSION

Melt extracted metal fibres can be used to design catalysts for the selective oxidation of propane to propene. It could be shown that values of the specific surface area of 0.0050 m^2/g up to 0.05 m^2/g are sufficient for the desired reaction.

Chemical composition as well as crystalline structure and surface morphology make melt extracted fibres a well-suited material for certain catalytic applications . The best results for selective oxidation were achieved with the quasicrystalline AlCuFe fibres. The quasicrystalline structure, the chemical composition as well as the very fine oxide scale showing a submicron texture are the reason for this excellent behaviour.

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