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Catalysis at *Lonza*: From Metallic Glasses to Fine Chemicals

Josef Heveling*

Abstract. At *Lonza*, a company which is backwards integrated to light virgin naphtha and liquefied petroleum gas, catalysis is used throughout the entire scale of value added products, starting from bulk chemicals and intermediates up to special fine chemicals. In addition, environmental catalysts are used in order to fulfil the high standards of *Lonza*'s waste management concept. However, the need for the involvement of a dedicated catalysis group is mainly seen at the upper end of the product tree: with increasing diversification the catalysts have to match the complexity of the products and the demand for tailor-made catalysts is increasing. In this sense, also the potential of new catalytic materials is being examined at *Lonza*.

In the following, two examples of a more fundamental approach (amorphous alloys and amorphous/nanocrystalline oxides as catalyst precursors) are given. In addition, a new synthesis of β-picoline is discussed as an example of a straightforward product-oriented approach.

1. Introduction

The Visp plant (Walliser Werke), *Lonza*'s most important centre for Fine Chemicals production, is located in the Rhone Valley in the midst of the spectacular 'Walliser Alpen'. In this region of Switzerland the exposed geographical surface is very scenic; not the least, because the difference between the 'real' surface area and the projected (cartographic) surface is extremely high.

Heterogeneous catalysis is a surface phenomenon too and exposure of an appropriate surface of well matched chemical and physical properties is a prerequisite for catalytic reactions to take place. It is a peculiar paradox that for example in the Netherlands, where the ratio of the geographical to the projected surface is minimal and the people essentially live in a two-dimensional landscape, the effort invested into heterogeneous catalysis is much higher than in Switzerland. It is, therefore, the aim of this article to show that at *Lonza* all the motivating and inspiring models for catalytic surfaces that surround us (compare *e.g. Fig. 1*), were not without impact and have finally pushed the company further into the direction of surface-catalyzed reactions.

2. The Special Situation of *Lonza*'s Visp Plant

In the Swiss context the Visp plant is unique in the sense that it is backwards integrated to a small light virgin naphtha cracker. (The size of this cracker has an absolute European, if not a world minimum.) This means, starting from naphtha (and natural gas), the plant manufactures commodities, organic intermediates and fine chemicals, covering the entire scale of value added products. A continuous energy supply is guaranteed by *Lonza*-owned hydroelectric power plants and a tie-in with the natural gas pipeline system. The entire plant uses 150000 t of hydrocarbons a year, along with a huge amount of air.

Catalysis is used on all production levels and most products have seen more than one catalyst before they leave the factory. In fact, like the whole chemical industry, also the Visp plant is unthinkable without catalysis! Some of the basic catalytic processes – forming the back bone of the whole operation – are outlined in *Scheme 1*. Already at this level the catalytic technologies are quite divers, including homogeneous and heterogeneous transition-metal catalysis in addition to homogeneous and heterogeneous acid-type catalysis. This complex network has to be balanced according to fluctuating market requirements by certain 'release valves'. In this sense, surplus ammonia (hydrogen) can be converted to fertilizers, and surplus acetylene

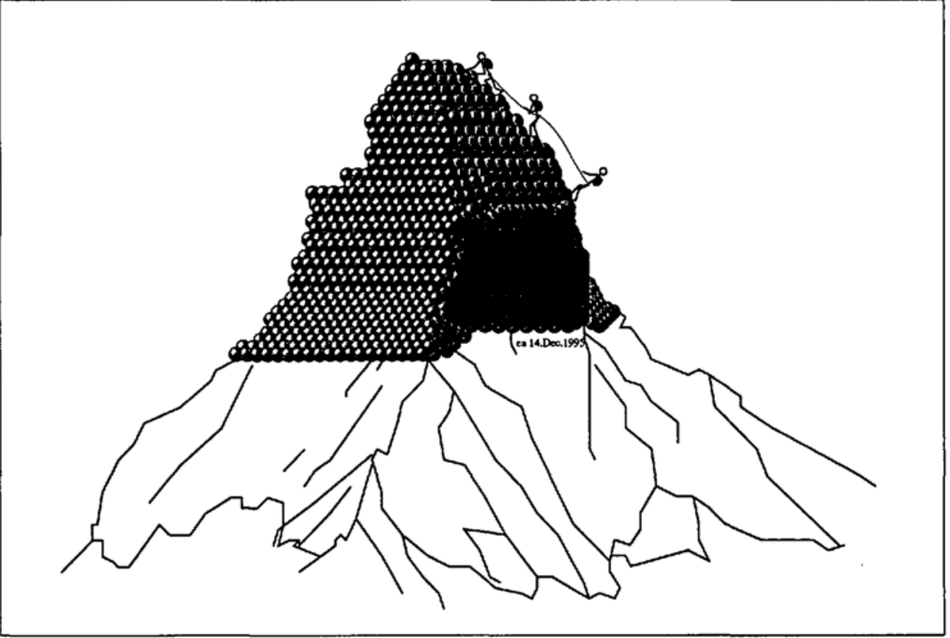


Fig. 1

**Correspondence*: Dr. J. Heveling
Lonza AG, Walliser Werke
CH–3930 Visp

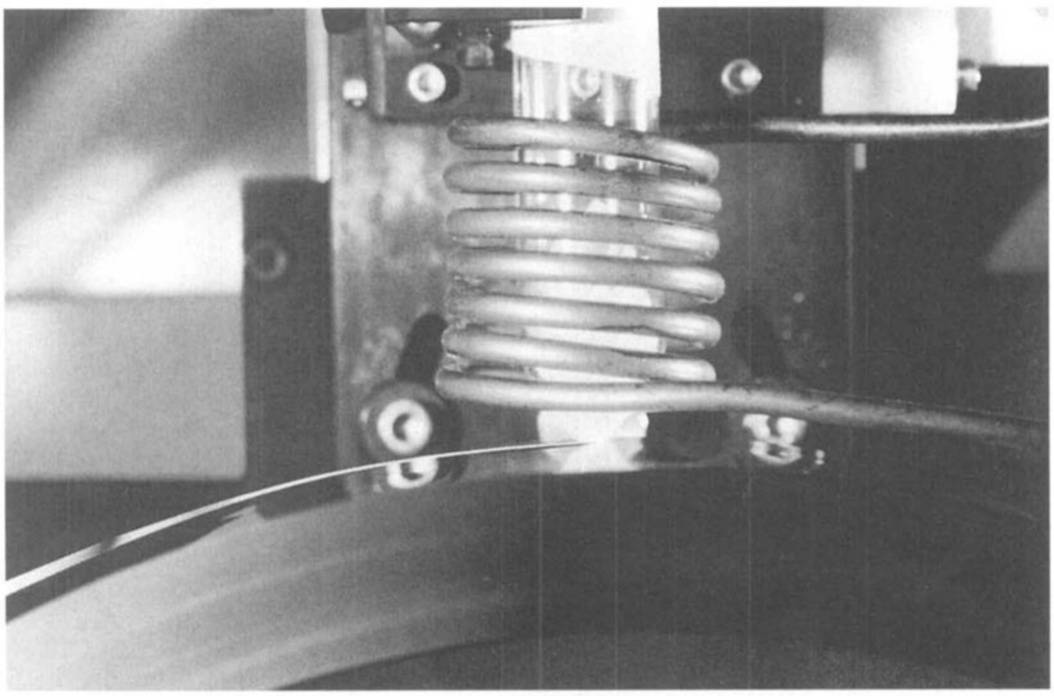


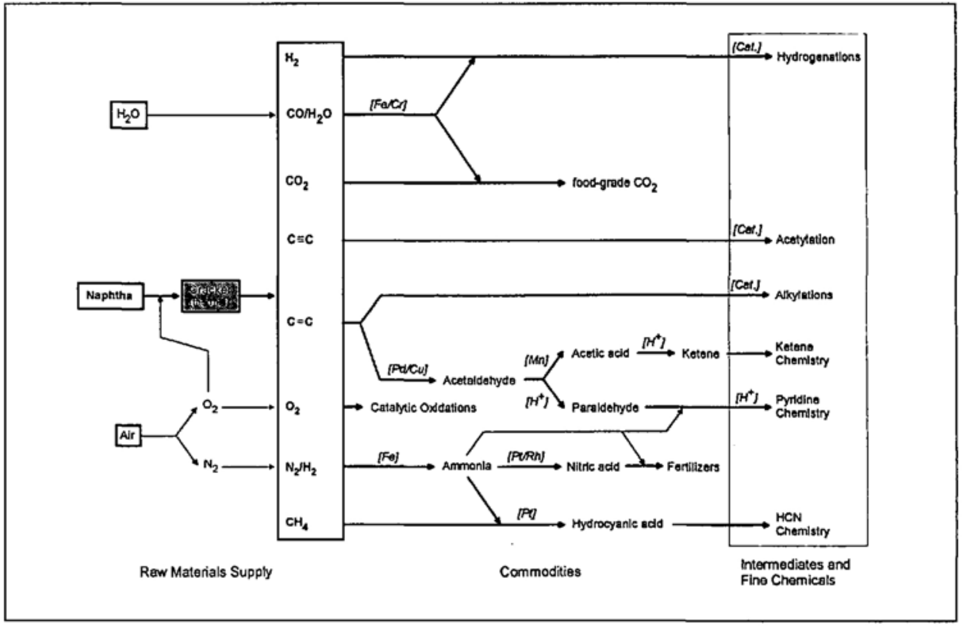
Fig. 2. *A view into the melt spin apparatus.* (The freshly spun ribbon leaves the wheel to the left side.)

can add to the acetaldehyde pool (not shown in *Scheme 1*).

At this level (commodities) it is seldom a problem to acquire existing technologies from various external companies, which have optimized their processes to perfection. Also at the intermediates level catalytic problems can often be solved with existing commercial catalysts or in close cooperation with specialists from catalyst-manufacturing companies.

The year 1984, however, was an important milestone in the history of *Lonza*. It marks the start-up of the Fine Chemicals Complex (FCC). In the fine chemicals business (comparatively low volumes of high value-added, sophisticated molecules) the catalysts have to match the complexity of the products in order to reach the required selectivities. More and more often extensive catalyst tailoring is needed and solution cannot always be found off the shelve. It is, therefore, not surprising that at *Lonza* the need for a dedicated catalysis group was recognized soon after the start (and further extension!) of the Fine Chemicals Complex.

Scheme 1. *Basic Catalytic Processes of* Lonza*'s Visp Plant*



3. How to Lead the Horse to the Water?

Fine Chemistry is a field which is dominated by organic chemists and organic chemistry. In order to successfully implant a catalysis group into this environment, it is advisable to use a Trojan Horse drawn by some far-sighted men or women. Recently, even the term 'catalyst' has come under pressure and the term 'supported reagent' is sometimes used as a synonym by organic chemists, which, to a large extent, is an example of a modern scientific euphemism.

A Trojan Horse is a catalyst in its own right, as it significantly lowers the energy barrier required to achieve an identical goal. At *Lonza*, the catalysis group in the present form was founded in 1988/89, and was then part of Corporate Development/ Basel. At this stage the research was rather fundamental and somewhat outside of *Lonza*'s core business: we were confronted with the problem of activating metallic glasses for catalytic applications, a project which *Lonza* undertook in collaboration with the University of Basel (Prof. *Güntherodt*) and ETH-Zürich (Prof. *Baiker*). At the same time, a group of engineers was looking at metallic glasses for soldering applications. Most of the tools for catalyst testing and characterization were acquired during that time.

By 1991, the majority of *Lonza*'s coworkers got used to the idea of Heterogeneous Catalysis (except for an unconvertible hard core) and the catalysis group was to be integrated into R&D Visp. Now, the horse was ready but the water was infected with a very challenging and rather unexplored research field. Nevertheless, in the following the focal point moved gradually from metallic glasses to a much more product-oriented catalyst development for fine chemicals. This, in contrast, covers a very broad spectrum of heterogeneous catalysis and is asking for a generalist

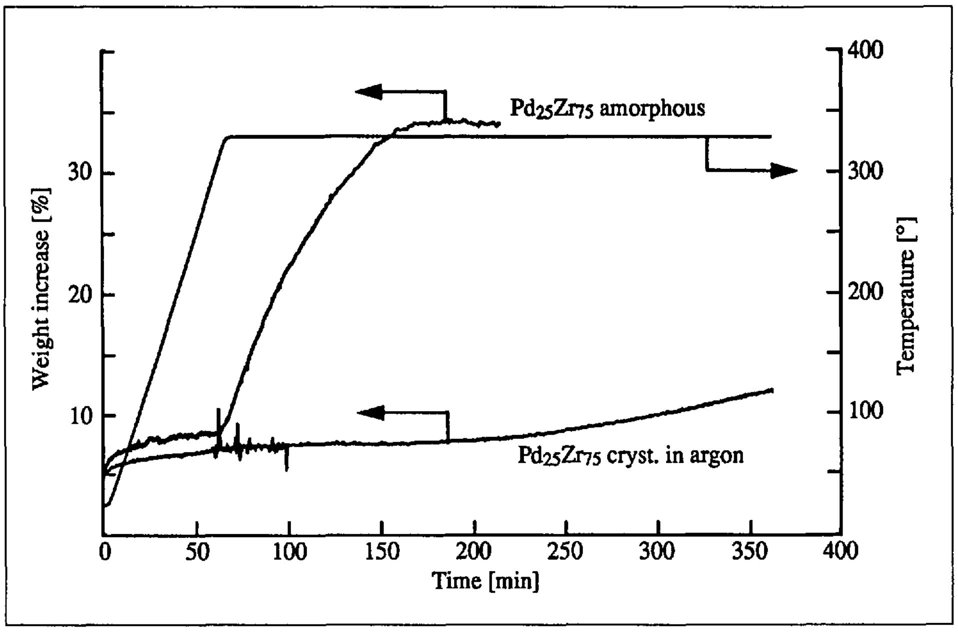


Fig. 3. *Oxygen uptake of an amorphous and a crystalline $Pd_{25}Zr_{75}$ sample when exposed to air* (thermogravimetry)

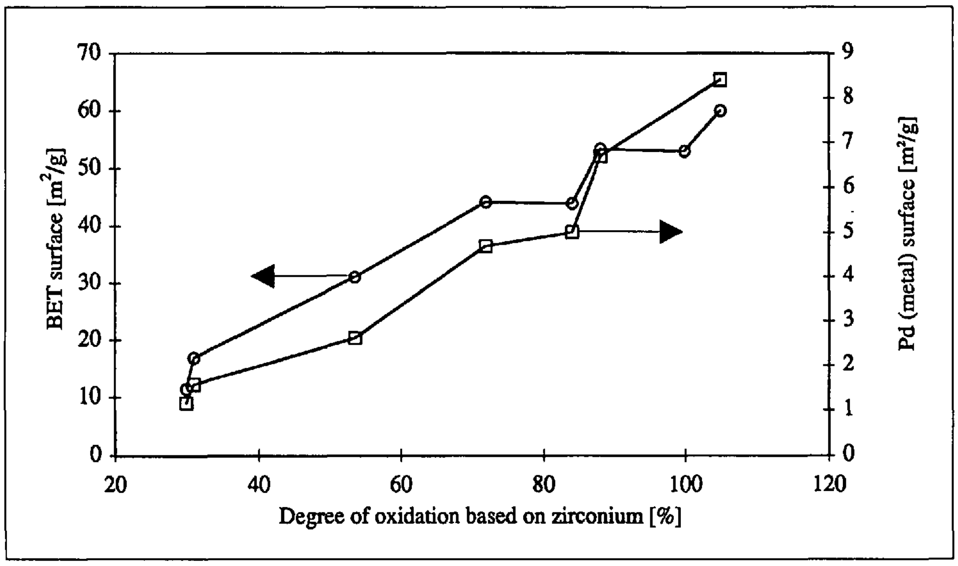


Fig. 4. *Development of the surface area during activation of $Pd_{25}Zr_{75}$*

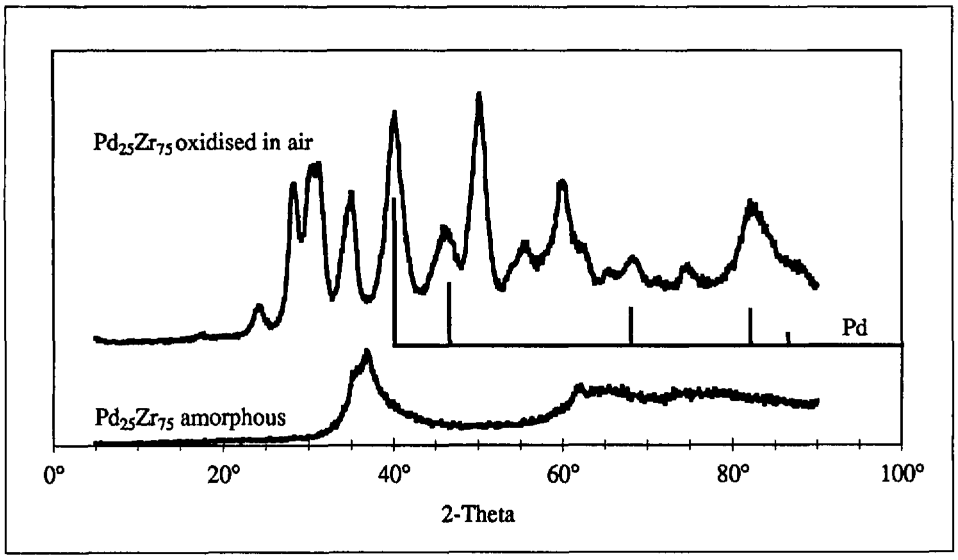


Fig. 5. *X-Ray diffraction pattern of an amorphous and an oxidized $Pd_{25}Zr_{75}$ sample*

rather than a specialist. Catalysis in Fine Chemistry requires the skill and the flexibility to constantly choose the most effective type of catalysis en route to given products. But also today, looking at new materials and their potential for the development of novel high-performance catalysts remains one of the more interesting aspects of our work.

After a résumé of the work on metallic glasses, a recent example from our fundamental catalyst development (innotec) programme will be given, followed by an example of straightforward, product-oriented catalyst development.

4. Metallic Glasses: A Ribbon without Happy End?

Amorphous metals or metallic glasses are rapidly quenched alloys, in which a disordered, thermodynamically metastable state has solidified. By their nature, these materials are of potential interest in catalysis. Amorphous metals can be prepared from the respective alloys by melt-spinning: using this method, cooling rates of *ca.* 10^6 °/s are achieved by casting the molten alloy on a fast rotating copper wheel. The metallic glass is released as a ~10 mm wide and 20 µm thick ribbon. *Lonza* operates one of the few units in the world which can work under Ar as well as *in vacuo*. *Fig. 2* offers a view into the melt-spin chamber during operation.

Due to their small surface area, the catalytic use of metallic glasses as such is of limited value. The metastable amorphous state is, however, an interesting precursor for often unusual solid-state reactions and an understanding of the transformations leading to more active catalysts is crucial for successful applications. By way of example, this is demonstrated for $Pd_{25}Zr_{75}$. The thermogravimetric experiment in *Fig. 3* shows that an amorphous sample of $Pd_{25}Zr_{75}$ rapidly takes up oxygen in a temperature region, where the same sample, which was precrystallized under Ar, remains almost completely inert. In parallel with the uptake of oxygen the total surface area increases by a factor of $>10^3$. At the same time Pd becomes increasingly exposed to the surface, as was determined by CO adsorption (*Fig. 4*). In this way, by appropriate activation, a catalyst is obtained which contains finely dispersed Pd in a matrix of stoichiometric and substoichiometric ZrO_2 [1]. *Fig. 5* shows the conversion of $Pd_{25}Zr_{75}$ to the active catalyst form as seen by X-ray diffraction; even the activated sample is still partially amorphous, which points to a close interaction of all its constituents. Similar results can be obtained for metallic glasses based on Ni/Zr or Cu/Zr.

The catalytic activity of such activated amorphous metals was demonstrated by a series of test reactions, *e.g.* over $Pd_{25}Zr_{75}$ *trans*-hex-2-enal is reduced with high selectivity to hexanal, while $Ni_{64}Zr_{36}$ is active for both the C=C bond and the carbonyl group hydrogenation. In this case, depending on the reaction time, hexanal or hexanol can be obtained in high yields (*Table*).

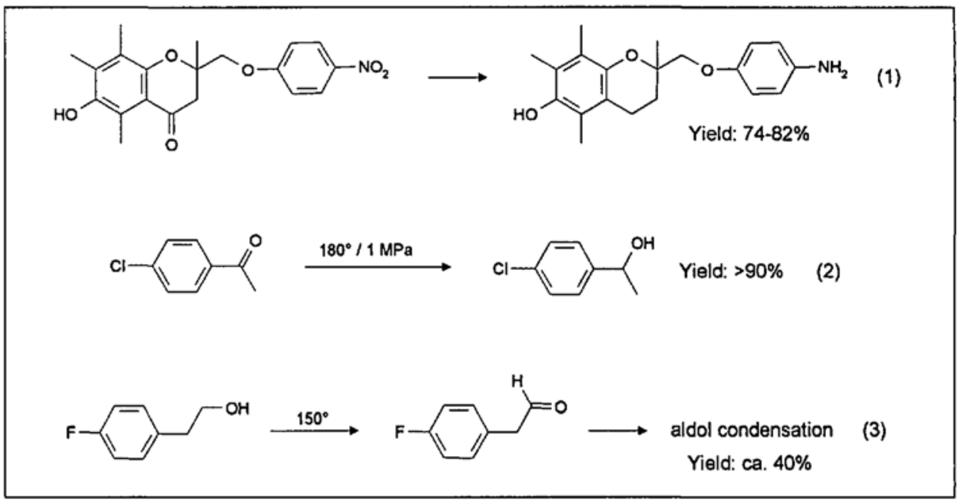
Other reactions tested include the hydrogenation of cinnamaldehyde, the hydrogenation of substituted phenols to cyclohexanols, the conversion of tetralone to tetralol and tetraline, and the highly selective cycloamination of 5-aminopentan-1-ol to piperidine over $Cu_{70}Zr_{30}$ [2].

Catalysts based on metallic glasses show often very high performance, when the activity is based on turnover numbers per exposed surface atom (see [3] for an example from methanol-synthesis catalysts). However, depending on their composition and the metal contents, metallic glasses are comparatively expensive catalysts and their practical use is only justified in cases where they offer clear advantages over conventional catalyst and where the product can tolerate the price. Up to now, a commercial breakthrough has not been achieved.

Table. *Hydrogenation of* trans-*Hex-2-enal over Amorphous Metal Catalysts*

Cat	*T* [°]	*p* [MPa]	*t* [h]	Conv. [%]	Selectivity [%] Hexanal	 Hexanol
$Pd_{25}Zr_{75}$	100	0.1	4	95.0	97.0	–
$Ni_{64}Zr_{36}$	130	1	2	96.5	97.5	–
			7	100	–	97.6

Scheme 2. *Examples for Zirconia-Catalyzed Hydrogen-Transfer Reactions*



5. NanoCats: Give Catalysis a Chance!

Life in general and catalysis in particular follow self-organizing principles. A catalyst surface is not static, it is highly flexible and dynamic. A catalyst precursor and a working catalyst are two different objects: the working catalyst is formed under reaction conditions in the presence of the reacting medium and remains rather undefined in most cases. The principle of self-organization has been introduced to the economic world under catchwords like 'lean management', 'matrix structures', 'business teams', and 'empowerment'. In many cases, catalysts could be designed following the same principles.

We have adopted this philosophy in our research project on nanocrystalline/amorphous materials, which was started in 1991. The project is based on the following assumption: Starting with an amorphous or nanocrystalline material, more flexibility is introduced into the systems and – due to high interdispersion – the chances, that a suitable active species is formed, increases. In contrast, a crystalline material has much less *self-organizing driving forces* because it is already in a thermodynamically stable state. It is obvious that this approach follows directly from our work on Zr-based metallic glasses.

Incidentally, in 1991 at *Alusuisse* a ceramics team was working on zirconia for high-performance construction parts. Here, know-how on precipitation and sol-gel technology had accumulated, and a strong cooperation between the catalysis and the ceramics group developed within the *Alusuisse-Lonza Corporation*. Our point of departure was a paper by *Takahashi et al.* using hydrous zirconia as a catalyst for hydrogen-transfer reactions to carbonyl groups [4]. We saw a potential system for chemoselective reductions of multifunctional molecules. Subsequently, the first test reaction was hydrogen transfer from i-PrOH to ketones to give the corresponding alcohols and acetone (*Meerwein-Ponndorf* reduction). This is an equilibrium reaction and with an excess of acetone, alcohols can be converted back to ketones (*Oppenauer* oxidation). In this way, carbonyl groups can be reduced in the presence of certain other functional groups and we were soon able to apply this system to examples of industrial relevance (*Scheme 2*). In the first example, reduction of the carbonyl group is followed by immediate release of H_2O. Subsequently the C=C bond and the nitro group are reduced in one step over a conventional Pd catalyst to obtain the corresponding amine [5]. The third equation of *Scheme 2* is an example of the reverse reaction (*Oppenauer* oxidation); the primary product was added *in situ via* aldol condensation to a second aldehyde and the target molecule was obtained in *ca.* 40% yield.

In the following, the principle of nanocrystalline/amorphous catalyst precursors was extended to mixed oxides and successfully applied to hydrogenation reactions and CO/H_2 chemistry. Amorphous $CuO/ZnO/ZrO_2$, for example, is an effective catalyst for the hydrogenation of maleic anhydride to γ-butyrolactone [6].

6. β-Picoline from 2-Methylglutaronitrile

This is an example of project where not only the target molecule was given but also the starting material; much like a mathematical equation without the law to solve it.

β-Picoline is an important intermediate for the production of agrochemicals and niacin. 2-Methylglutaronitrile (MGN) is available as a side-product of the manufacturing of adipodinitrile, one of the building blocks of nylon-6,6. β-Picoline can indeed be prepared in one step from MGN over a fixed-bed Pd/Al_2O_3 catalyst [7]. In this case, the sequence of a hydrogenation reaction, a cyclization reaction, and a dehydrogenation reaction takes place in one reactor over the same catalyst. It is, therefore, not surprising that the window for the reaction conditions, which allow this reaction to proceed, is very narrow; namely a temperature of 280–290° and a pressure of *ca.* 500 kPa H_2. This reaction is accompanied by a rapid catalyst deactivation, and after the reaction a viscous dark oil can be extracted from the catalyst. This oil has a molecular mass of 500–3000 and is mainly aliphatic in nature. It is probably formed *via* the polymerization of imine intermediates and is the main cause of catalyst deactivation (*Scheme 3*).

At a temperature below 200° the dehydrogenation reaction is suppressed and at 180°/5 MPa a water-clear, oily substance is formed without obvious catalyst deactivation. It was identified as 1,5-bis(3-methylpiperidino)-2-methylpentane (**I**). Obviously, at low temperature the reaction on the way to β-picoline (PIC) stops at 3-methylpiperidine (MPI), and MPI is *always* present in high enough quantities to quench all imine intermediates. Any excess imine, under the prevailing reaction conditions, will primarily react to give more MPI. In this way the potential source of catalyst poison is scavenged by the intermediate and incorporated into the final product. Hence, the reaction cleans itself, becomes reasonable selective and the catalyst works stable. I was found to be a polyurethane catalyst [8].

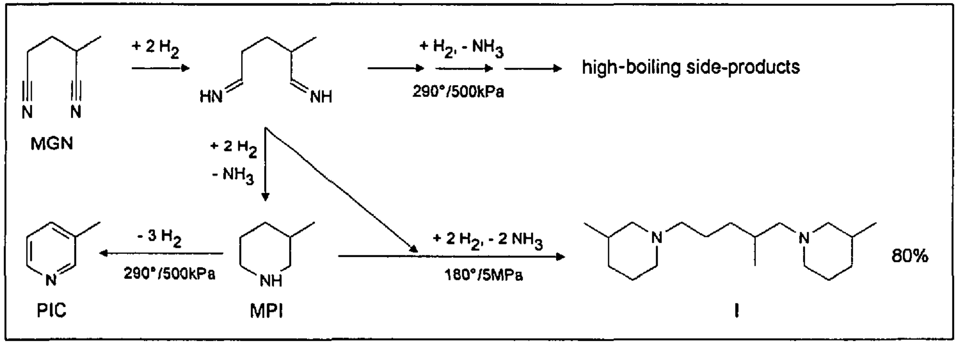
Coming back to the title reaction: It became clear that this equation could not be solved in one step; a route *via* imine intermediates had to be avoided at all costs! The project was now based on 2-methylpentane-1,5-diamine (MPDA) as starting material, which is an MGN-derived intermediate from *DuPont*. MPDA can almost quantitatively be converted to MPI over an acidic catalyst like zeolite ZSM-5, followed by dehydrogenation over an equally efficient and stable Pd catalyst [9]. This route to β-picoline forms the basis for *Lonza*'s new niacinamide process from MPDA as raw material, consisting of four catalytic steps (*Scheme 4*).

8. Other Catalytic Activities at *Lonza*

Catalysis research at *Lonza* is not limited to heterogeneous catalysis. Among homogeneously catalyzed reactions emphasis is put on enantioselective hydrogenations of C=C bonds and imines. In a fruitful collaboration of our organic synthesis laboratories with the catalysis group of *Ciba* a first commercial breakthrough was achieved within *Lonza*'s biotin synthesis: the key step has been considerably improved by implementation of an Rh-catalyzed diastereoselective hydrogenation [10].

In addition, this survey would not be complete without mentioning that within *Lonza* expertise in catalysis is also found in Italy at *Lonza SpA*. Here, the focus lies on selective oxidation reactions. An example to mention is the well-known ALMA-process for the production of maleic anhydride from butane [11]. The most recent addition to a series of plants running world-wide according to this technology was built in Ravenna with a capacity of 50 000 t/a of maleic anhydride.

Scheme 3. *Hydrogenation of 2-Methylglutaronitrile over Pd/Al_2O_3 under Various Reaction Conditions* (simplified)



9. Conclusion

Today catalysis at *Lonza* extends from the development of new catalysts for recognized problem areas within the fine chemicals business to contributions in the synthesis of well-defined target molecules. Catalysis as compared to 'traditional' organic synthesis is looking for short cuts, less raw material consumption, less energy consumption, less waste, less capital investment, and less time (faster). Heterogeneous catalysis in general and enantioselective hydrogenations in particular are important core competencies within *Lonza*'s technology portfolio and are being developed further with great emphasis.

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Scheme 4. Lonza*'s New Route to Niacinamide* (= nicotinamide)