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Catalysis Today 30 (1996) 33–39

CATALYSIS TODAY

Catalyst research — one of the cornerstones of modern chemical production [1]

W. Büchele [a,*], H. Roos [b], H. Wanjek [b], H.J. Müller [b]

[a] *BASF China Ltd., Tower I, 7th floor, South Seas Center, 75 Mody Road, Tsim Sha Tsui E., Hong Kong*
[b] *BASF Aktiengesellschaft, D-67056 Ludwigshafen, Germany*

Abstract

A modern chemical industry first of all requires an economical chemical production. Most chemical processes contain at least one catalytic step. Due to this fact, catalyst research today is one of the cornerstones of a modern chemical industry. Using the selective hydrogenation of acetylene in the C2-stream of a steam cracker, the hydro-treating of the C4-stream and the hydrogenation of carbon oxides to methanol as examples, this paper emphasizes the importance of catalyst research. The BASF Catalyst H 0-11 and the hydro-treatment process SELOP C4® are presented as results of catalyst research. They form part of an integrated approach which also considers sophisticated process design and intelligent feed stock processing. Finally, BASF Catalyst S 3-86 for the synthesis of methanol serves as an example where catalyst research itself enabled a significant commercial improvement.

Keywords: Catalyst research; Modern chemical production

1. Introduction

Chemicals have become a key factor in every part of life — nutrition, transportation, medicine and last but not least, consumer products. Today, a state of the art chemical production thus forms the vital basis for a successful economy, irrespective of whether this has already developed or is still in the process of developing.

According to available studies, most of the chemical processes are based on catalysts. Catalysts and catalyst development therefore, form one of the cornerstones of successful chemical production.

In the following, we would like to outline the fact that different chemical productions require different strategies as far as research is concerned. We will use the selective hydrogenation of acetylene in ethylene streams, the hydro-refining of the C4-cut and finally the hydrogenation of carbon oxides, as examples to outline such different strategies, all of which focus on catalyst research.

2. Selective hydrogenation of acetylene

The hydro-refining of the C2-cut, i.e. the selective hydrogenation of acetylene in the ethy-

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[*] Corresponding author.

[1] BASF. Prepared for Presentation at: The 1st Global Conference of Young Chinese Scientists on Catalysis Science Technology, Tianjin, September, 1995

SSDI 0920-5861(95)00335-5

lene rich fraction of a steam cracker, is carried out in the so-called C2-converter. This unit is closely integrated into the low temperature fractionation section of a steam cracking plant which forms the basis of a modern petrochemical industry [1].

In the most common way of processing, a so-called tail-end hydrogenation, the deethanizer top fraction contains approximately 0.4%–2.5% (v/v) acetylene. This has to be hydrogenated in order to meet the elevated specifications of both chemical and polymer grade ethylene. Furthermore, the hydrogenation should be as selective with respect to ethylene as possible.

The basic reaction scheme consists of:

- the hydrogenation of acetylene to ethylene
- the hydrogenation of ethylene to ethane and
- the oligomerization of acetylene first to 1,3-butadiene and consequently to what is commonly called 'green oil', a variety of unsaturated compounds with comparably high molecular weights.

From this reaction scheme, it can easily be understood that the only thermally stable compound is ethane. Thus, the reaction has to be controlled kinetically in order to get the required high ethylene gain. This can be achieved by combining measures on the process side with those on the catalyst side.

On the process side, it is favourable to operate at higher space velocities. Furthermore, inhibitors such as carbon monoxide can be added to the feed stream in order to affect the adsorption/desorption behavior on the catalyst surface.

Suitable catalysts [2] must exhibit the following characteristics:

- Moderate activity
- High selectivity
- Minimum formation of 'green oil'

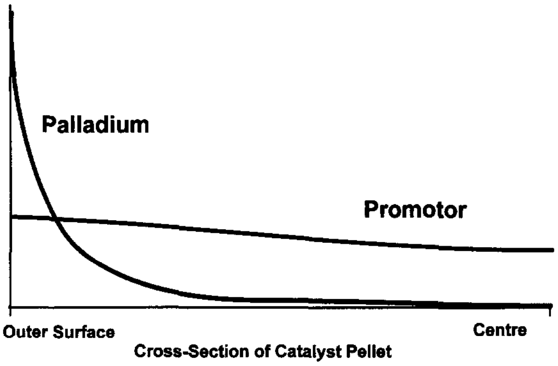

Fig. 1. Distribution of active components.

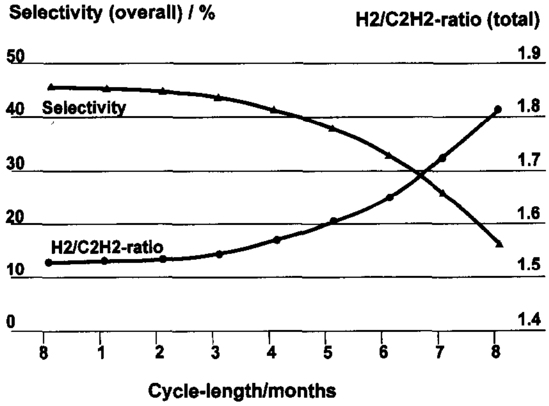

Fig. 2. Selectivity profile of BASF catalyst H 0-11.

The BASF Catalyst H 0-11 is today widely used in the tail-end hydrogenation of acetylene. The significant advantages of this catalyst are based on a specific catalyst design. Silica has been chosen as a carrier material. Due to the lower Lewis acidity of silica, the oligomerization activity is sharply reduced, leading to a significantly lower green oil formation as compared to catalysts based on alumina carriers. Furthermore, the distribution of both palladium (the active component) as well as a promoter is conform to the requirements of the reaction kinetics and of the mass transfer [3] (Fig. 1). The palladium concentration is significantly increased towards the outer surface of the macroporous carrier, resulting in extremely high activity at locations where the mass transfer is high and consequently, the residence time is low. On the other hand, there is practically no active component in the center of the catalyst particle. The advantage of this specific palladium distribution is enhanced by the distribution of the promoter which in fact acts as an inhibitor and thus further increases the selectivity. It is different to that of the palladium, showing only a slight gradient along the extrudate's cross section. In this way, the inhibiting effect is much more prominent in the center of the catalyst pellet as compared to in its outer surface.

This shell type catalyst which is produced by means of consecutive impregnation and drying steps, displays superior performance (Fig. 2). Therefore, only a minor amount of CO, ranging from 0.5 to less than 3 ppm, has to be added to the feed stream. In commercial plants, average ethylene selectivities of up to 40% can be achieved using the BASF Catalyst H 0-11 over a 6-month operating cycle.

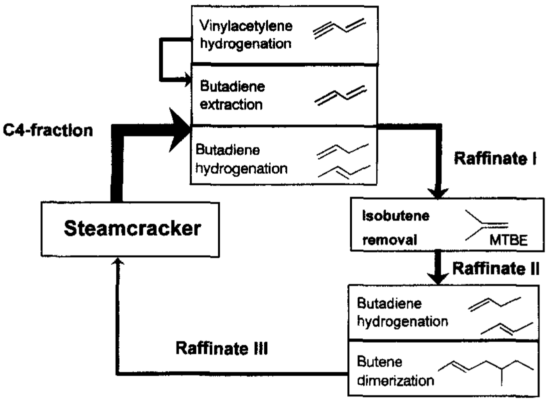

Fig. 3. Efficient processing of the C4-fraction.

3. C4-cut hydro-refining

The hydro-refining of the crude C4-cut is an example of how intelligent feed stock processing combined with sophisticated process technology and specifically designed catalysts, can improve the commercial performance of a steam cracker.

A typical crude C4 stream contains between 35% and 70% (w/w) of butadiene, 20%–28% (w/w) of isobutene with the remainder consisting of butenes as well as butanes. Due to the complexity of the stream, a sequence of consecutive hydro-refining steps must be considered in order to achieve a proper upgrade of this fraction [4]. (Fig. 3).

The first step in conventional processing is the extraction of butadiene using solvents, i.e. n-methylpyrolidone. Due to the fact that the petrochemical industry is facing an increasing over-supply of butadiene, further processes are required in order to upgrade the economical value of the C4-fraction. The selective hydrogenation of butadiene in the crude C4-cut is a new and alternative route in order to achieve a nearly butadiene-free C4-stream, the so-called Raffinate I.

Using SELOP C4®, BASF has now developed a new process for the upgrade of the crude C4-cut by means of selective catalytic hydrogenation. The process is available in different designs featuring up to three different types of specially developed catalysts, all depending on the feed stock composition and the respective product requirements.

By using up to three different catalysts, a practically complete conversion of polyunsaturates, essentially no isobutylene losses, a very high selectivity with respect to butenes and high flexibility with respect to feed stock composition and throughput rates, can be achieved. Furthermore, the formation of by-products such as green oils, oligomers or light gases is minimized.

All three catalysts, BASF Catalysts H 0-12, H 0-13 and H 0-13L consist of palladium on alumina carriers. They do however, differ significantly in terms of the palladium content as well as in the texture of the alumina carrier. Furthermore, special palladium distributions account for a high overall selectivity and simultaneously minimize the tendency towards polymerization. BASF Catalyst H 0-12 is particularly suitable for streams which are rich in butadiene and where high catalyst activity is required. Consequently it has the highest palladium content of 0.5% (w/w). In contrast, BASF Catalyst H 0-13 has been designed for streams with less butadiene. A special distribution of the active component enables control of the isomerization between 1-butene and 2-butene. The highlight of the series however, is H 0-13L [5].

This newly developed catalyst, which has been designed especially for the selective hydrogenation of streams containing medium and low butadiene concentrations, exhibits the following characteristics:

- Macroporous structure, adjusted to the kinetics of the complex reaction scheme related to the crude C4-hydrogenation.
- Significantly reduced bulk density.
- Palladium, exclusively available in the macropores.

Altogether, a superior effectiveness of the active component combined with practically negligible polymerization tendency is achieved.

These three excellent catalysts, combined with optimized process variables enabled the design of a commercially viable process. Besides the catalysts, factors such as the trickle density, the hydrogen to butadiene ratio, process pressure and temperature in particular, mostly affect the overall performance.

In BASF's Antwerp plant, SELOP C4® has been installed since mid-1994 in a two-stage configuration, using BASF Catalyst H 0-12 in the first stage and BASF Catalyst H 0-13 in the second stage (Fig. 4). The hydrogenation is carried out in the liquid phase [6].

The resulting Raffinate I contains more than 96% (w/w) butenes (Table 1). Even with residual butadiene concentrations being as low as 0.1% (w/w), no hydrogenation of isobutylene occurs. The selectivity with respect to butenes reaches approximately 97% (w/w) with an increase in n-butane of as little as 1.1% (w/w).

Table 1
Performance of SELOP C4® process

	Crude C4-fraction	First stage product	Second stage product
Vinylacetylene	0.5	–	–
Butadiene	41.6	3.8	0.1
1-Butene	16.3	36.7	35
trans-2-Butene	6	20.3	23.6
cis-2-Butene	4.6	7.8	9.2
Isobutene	27.9	27.9	27.9
Isobutane	0.6	0.6	0.6
n-Butane	2.5	2.9	3.6

Analysis in % (wt./wt.).

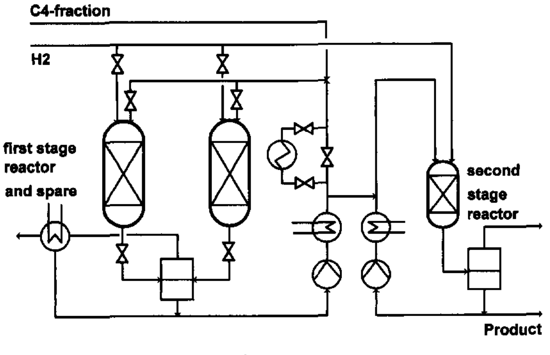

Fig. 4. SELOP C4®-process at Antwerp (B).

4. Hydrogenation of carbon oxides

Methanol today is mostly obtained by the low pressure hydrogenation of carbon oxides.

Commercial catalysts for this process consist of CuO and ZnO and operate within temperature ranges of 200–310°C and at pressures of 45–100 bar [7,8]. Depending upon the method of the gas production and the type of reactor system used for the methanol synthesis, there are a wide variety of operating conditions [9]. They differ greatly in terms of pressure, temperature and space velocity. Furthermore, the composition of the synthesis gas, for instance the CO-content or the CO/CO_2-ratio, may also vary significantly depending upon the feed stock employed. Some of these various possibilities are compared in Table 2.

Table 2
Comparison of process conditions

Feedstock	Heavy fuel oil	Off-gas	Natural gas
Pressure (bar)	45	78	100
Temperature			
Inlet (°C)	220	210	200
Max (°C)	260	270	290
SV (h^{-1})	7800	6900	9700
CO (mol-%)	8–20	10–20	3–4.5
CO/CO_2	3.2–5.7	1.7–5.0	1.3–1.5
Reactor	Isothermal	Isothermal	Adiabatic

Catalysts, suitable for the low pressure hydrogenation of carbon oxides under the conditions referred to above, must meet the following basic requirements: high catalyst activity at minimum possible reaction temperatures; high mechanical and thermal stability; high self-guarding efficiency to ensure both effective and selective absorption of poisons which are present in the feed gas and finally, an appropriate chemical design in order to suppress undesired by-product formation.

To ensure that the catalytic activity of a methanol synthesis catalyst is maintained at a high level over a long period of time, the catalytically active phase must be stabilized on a suitable support. Such material must exhibit good dispersibility of the active component combined with excellent thermal stability over a wide range of temperatures. Furthermore, sufficient chemical inertness under the respective process conditions in order to minimize by-product formation, combined with the ability to act as a structural promoter that prevents the sintering of crystallites of the active phases which are obtained after reduction of the catalyst, are required.

BASF therefore has selected a specially designed zinc/alumina oxide as the support material for its high performance catalyst.

The efficiency of a methanol synthesis catalyst furthermore is greatly affected by impurities in the process gas, especially when the latter is derived from partial oxidation of either heavy residue oil or coal. Such poisoning effects are practically always determined by diffusion [10]. A sophisticated approach to minimizing the absorption of catalyst poisons is the protection of the individual active center on a microscopic scale. This can be achieved by embedding them in a matrix which is capable of absorbing the poisons. Such embedding becomes feasible when using precipitation techniques, allowing the production of catalysts with different degrees of dispersion. The existence of such catalysts exhibiting substantially different element distributions, can be verified by means of X-ray fluorescence analysis. A highly dispersed catalyst has a markedly higher capacity for the absorption of catalyst poisons as compared to a catalyst which exhibits improper dispersion.

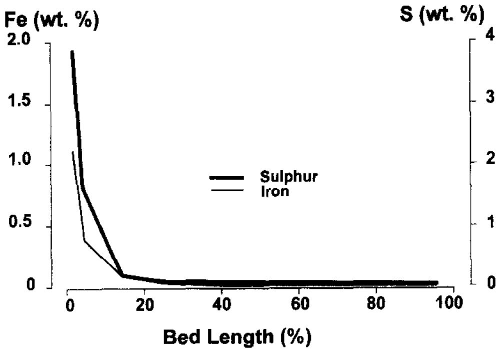

Fig. 5. Self-guarding efficiency.

Poisoning by sulphur compounds, e.g. hydrogen sulphide, limits the catalyst lifetime in many commercial applications. These compounds can be absorbed in a layer at the outer surface of the catalyst particles and can thus block the mass transfer. This fact is exploited in the design of the highly dispersed catalyst in order to ensure the effective absorption of large amounts of sulphur.

Fig. 5 shows the concentration of catalyst poisons on samples of BASF Catalyst S 3-86 which had been on stream for 28 months in a commercial methanol plant based on the partial oxidation of heavy residue oil. In this particular case, the effective self-guarding efficiency due to the high degree of dispersion of the catalyst components has led to the absorption of up to 4% (w/w) of sulphur on the catalyst close to the reactor inlet. Despite this high sulphur level, the catalyst in the lower 80% of the bed was still active. On catalysts with a lower degree of dispersion, the sulphur would be distributed all along the catalyst bed.

Another key factor in methanol plants is the selectivity of the respective catalyst. By-products which may form include higher alcohols [11], carboxylic acids, ketones [12], esters [13], dimethylether [14], Fisher–Tropsch hydrocarbons [15] and methylamine.

There are numerous effects which can cause a drop in catalyst selectivity. Impurities such as ammonia being present in the feed gas for example, may result in the formation of methylamine. Impurities such as alkaline, Fe, Co or Ni present in the catalyst itself, may result in the formation of higher alcohols as well as higher hydrocarbons [15]. Last but not the least, the structural design of the catalyst can also influence the extent of the by-product formation. If for example, an alumina which contains acidic sites is incorporated into the catalyst, this will result in the formation of dimethylether from carbon monoxide and hydrogen. A careful choice of raw materials, their efficient purification and the proper chemical and structural design are therefore of paramount importance if a selective catalyst is to be obtained.

As already discussed in detail, high activity, outstanding chemical and mechanical stability, significant absorption capacity for catalyst poisons and a strong suppression of the by-product formation — all these properties are vital for an advanced methanol synthesis catalyst.

In addition to the selection and purification of the raw materials, the manner in which the catalyst components are precipitated, provides the solution to the optimization problem. Fig. 6 shows different alternatives which may be applied in order to obtain a methanol catalyst. In the first case, only the copper component is precipitated whereas the zinc and the alumina components are added in the form of a suspension. In the second case, copper and zinc are co-precipitated in the presence of suspended alumina. Finally, the third catalyst type is obtained by co-precipitation of all three components. The three alternatives result in three completely different catalysts with in terms of the degree of dispersion and thus their catalytic properties, even if they do have the same overall chemical composition. The same applies if for example, the pH-value, the temperature or the stirring conditions are varied during the precipitation procedure. Furthermore, different catalytic properties are also obtained when parameters are varied at other stages such as filtration, drying or calcination of the catalyst.

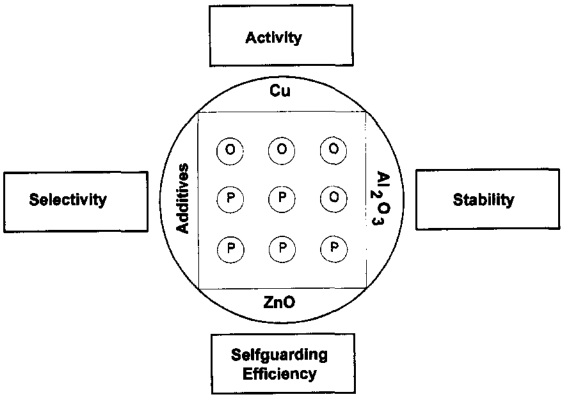

Fig. 6. Precipitation.

After detailed studies of all the various parameters mentioned earlier, BASF Catalyst S 3-86 has finally been developed for the low pressure hydrogenation of carbon oxides to methanol. It is serving as catalyst in the world's largest methanol plant in Chile. In this plant which has an annual capacity of 750 000 mt/year, the catalyst demonstrated its superiority by allowing for actual annual productions which far exceeded the design.

5. Conclusion

Using BASF Catalyst H 0-11 for the selective hydrogenation of acetylene, the SELOP C4® process for the hydro-treatment of the C4-fraction of a steam cracker and BASF's methanol catalyst S 3-86 as examples, we were able to demonstrate that efficient catalyst research represents one of the cornerstones of a modern chemical industry.

This became especially evident by outlining the commercial advantages that can be achieved with a sophisticated catalyst research that leads to higher selectivities, superior resistance towards poisons or to catalysts that are specifically adjusted to the mass transfer requirements of the reaction in question.

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