

SOME NEW TRENDS IN CATALYSTS FOR THE SELECTIVE HYDROGENATION OF VEGETABLE OILS

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Hydrogenation is now the most important processing in fats chemistry, in that more than 4 millions tons of hydrogenated products are manufactured every year in the world.

Hydrogenation is commonly used for:

— improving the stability of polyunsaturated oils and keeping their edibility,

— hardening liquid oils,

— converting some non valuable products into valuable ones.

Industrial hydrogenation can be conveniently considered under three headings: the chemical changes involved, the hydrogenation process itself, the equipment used. Each level brings up its own problems, the key of them is undoubtedly the catalyst.

In order to be valuable for industrial purposes, a catalyst requires a lot of qualities:

— a high activity which can be expressed by decrease in iodine value with time and metal weight unit;

— a high selectivity, which can be defined as the ability to partially reduce trienes without increasing saturated. The selectivities are measured with the help of diagrams established from kinetic data, and are expressed by ratios of rate constants;

— a high chemical and physical stability. A catalyst must be resistant to poisons, to thermal peaks, to mechanical erosion;

— a low-cost-price, which is important for further steps such as elimination, regeneration and re-use.

A wide range of industrial heterogeneous catalysts is now availa-

ble, mainly copper and nickel catalysts, which can be associated with another metal, supported by an inert carrier, or protected by a solid organic layer. These catalysts are not soluble in the medium during the whole reaction, and can easily be filtered off at the end.

Some ten or twelve years of research were devoted in order to study homogeneous catalysis for hydrogenation purposes. Homogeneous catalysts are coordination complexes containing a transition metal

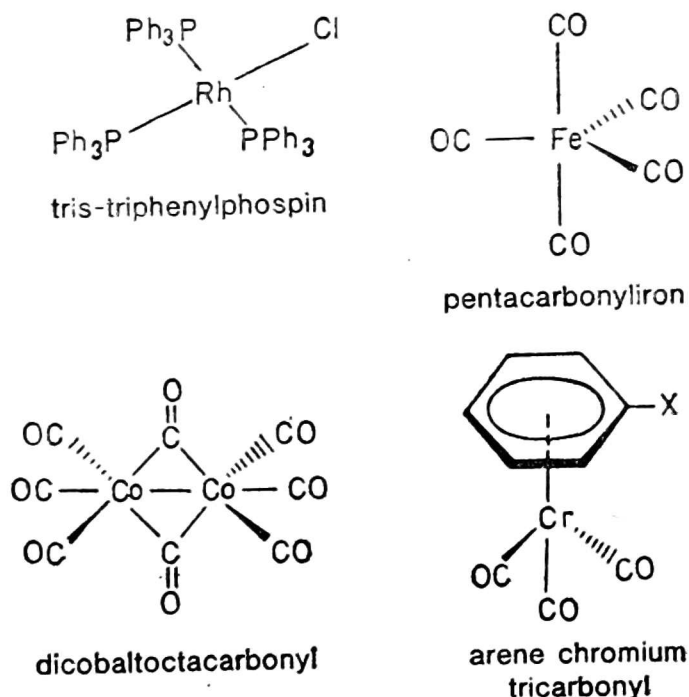


Fig. 1. Catalytic coordination complexes

bound to organic ligands (Fig. 1). The structure and the geometry of such molecular species are well known, their reaction mechanism too, and in fact their behaviour with a given substrate can often be predicted.

These coordination complexes are widely used for industrial applications in petrochemistry, but not yet in fat chemistry. Nevertheless particular reference may be made to some laboratory data summarized on Table 1.

If we compare homogeneous catalysis with heterogeneous catalysis, we find that soluble catalysts exhibit many advantages: high selectivity, limited isomerizations, high stability. A lot of disadvantages must however be pointed out: cost-price, toxicity, sophistication, difficulty of separation, impossibility of re-use.

In most cases it would be valuable to compromise between heterogeneous and homogeneous catalysis. That means to couple the qualities of a soluble complexed metal with those of the same activated solid metal. An approach was attempted by both our Institutes, and we wish to report in that paper the preliminary results achieved.

Table 1

Selective hydrogenation of soybean oil (or methyl esters) catalyzed by coordination complexes

| Catalysts or precursors | Selectivities | | Trans % | References |
|--|------------------|------------------|---------|-----------------------|
| | S _{2,1} | S _{3,2} | | |
| Ni(AcAc) ₂ | 20 | 3.4 | 11.5 | [5] |
| Fe(CO) ₅ | >30 | 2.3 | 26.5 | [3, 9, 13, 16] |
| CO ₂ (CO) ₈ | >30 | 2.6 | 35.5 | [4, 8] |
| PtCl ₂ (PPh ₃) ₂ } SnCl ₂ ·2H ₂ O } | >30 | 1.5 | 80 | [1] |
| XPh-Cr(CO) ₃ | 50 | 4 | >5 | [2, 6, 7, 10, 11, 14] |

Table 2

Liquid catalytic system: [Ni⁰ — AIEL₃ — ligands — solvent]
Fr. patent 1974 (IFP.ITERG)
Hydrogenation of soybean oil (same conditions of time and pressure)

| Catalyst | Temp. °C | Catal. conc. ppm | IV | % | | | | | Turn over IV. mm ⁻¹ g ⁻¹ | Select S _{3,2} |
|---------------|----------|------------------|-----|-------------------|-------------------|---------------------------|-------------------|-------|--|-------------------------|
| | | | | C _{18:0} | C _{18:1} | C _{18:2} average | C _{18:3} | trans | | |
| None | — | — | 135 | 4 | 21 | 54 | 9 | — | — | — |
| Supported Ni* | 170 | 200 | 104 | 5 | 49 | 32 | 2.5 | 20 | 26 | 1.8 |
| Ziegler Ni** | 110 | 20 | 103 | 6.5 | 46 | 35 | 1.0 | 17 | 270 | 3.0 |

* Refined and bleached oil.

** Crude oil (1% phosphorus 100 ppm).

1) In the field of homogeneization of metals the starting point is the work of Sloan [17] and Tajima [20] on Ziegler-type catalysts. These catalysts are prepared by adding to a suspension of a transition metal compound in an organic solvent, a powerful reducing organometallic reagent, such as trialkylaluminium compound. The suspension becomes a solution since the metal is reduced and coordinated by suitable ligands.

An example of a nickel-Ziegler [19] is given on Table 2. A slurry of nickel octanoate in heptane and soybean oil, is reduced by triethylaluminium to give a black solution. That solution exhibits a high activity and a good stability toward free fatty acids, phosphorus and sulfur compounds, but not toward oxygen and moisture. The catalytic system was used for the selective hydrogenation of a crude soybean

oil. The results reported here show the different behaviours of homogenized nickel and heterogeneous commercial nickel.

After hydrogenation the separation occurs either by decomposition then filtration, or merely by refining, since the starting oil is crude.

The reductive homogenization of metals via Ziegler-type compounds leads to low cost-price and versatile systems. Such catalysts indeed can be prepared by mixing several metals, by adding ligands, by deactivating for instance.

2) In the field of heterogeneization of soluble complexes two pathways occur:

- The insertion in the framework of an organic polymer,
- The convenient decomposition leading to an efficient divided metal.

Numerous polymeric supported complexes are known, but with few exceptions they were never used for hydrogenation of fats.

Attention must be drawn to these supported complexes (Fig. 2).

- a polystyrene-tricarbonylchromium [15],
- a dimethylaminostyrene-divinylbenzene palladium dichloride, prepared from a basic ion exchanger [12].

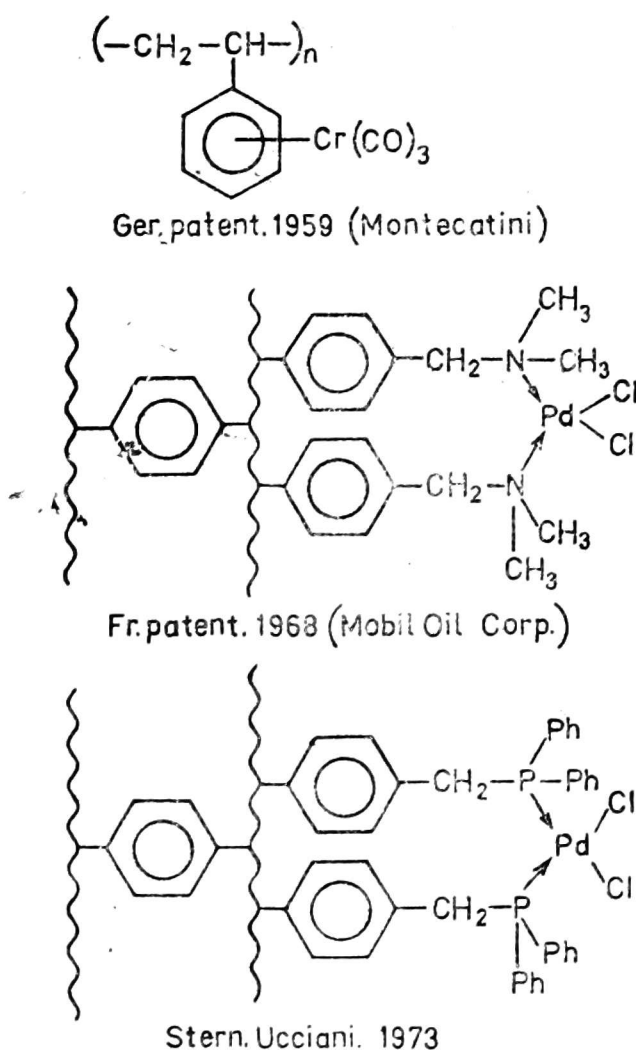
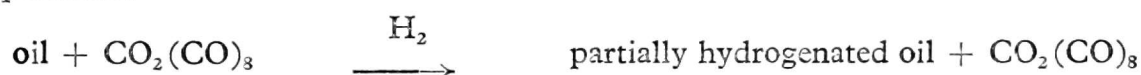


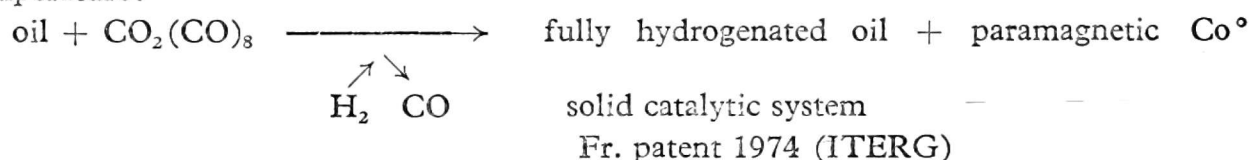
Fig. 2. Supported catalytic coordination complexes

Table 3

of low temperature:



at high temperature:



Hydrogenation of crude soybean oil
temperature 200°C
hydrogen pressure 5 bars
catalyst concentration 300 ppm

| | IV | C ₁₈ : ₀ | C ₁₈ : ₀ | C ₁₈ : ₂ | C ₁₈ : ₃ | trans |
|--------|-----|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-------|
| before | 135 | 4 | 21 | 54 | 9 | — |
| after | 97 | 8 | 49 | 30 | 1.5 | 35 |

turn over ($\Delta \text{IV} \cdot \text{mn}^{-1} \cdot \text{g}^{-1}$): 10

selectivity (S_{3,2}): 2.5

— a diphenylphosphinostyrene-divinylbenzene palladium dichloride [18]. We have prepared and tested it in hydrogenation of soybean oil. It exhibits a good selectivity but decomposition occurs on heating, yielding up organophosphorus fragments.

We have performed some experiments with cobalt as the activated metal coming from complexes (Table 3). The principle is quite simple [21]: dicobalt octacarbonyl is dissolved in soybean oil and the solution is heated at elevated temperature under hydrogen pressure until gas absorption is achieved. The complex is fully destroyed, and on cooling the catalytic metal is quenched in the solid hydrogenated fat, which can be stored and used in that form. The catalytic preparation shows a low activity but a good selectivity in the hydrogenation of crude soybean oil. The outstanding feature of the metal is its paramagnetism, which allows a clean separation and a re-use, on leaving the catalyst to stand into the reactor.

All these new catalysts should improve, in the future, the industrial hydrogenation of oils in that they help to economise on material and energy, since the hydrogenation can be performed on crude oils, at low temperature, with but few parts per milion of metal.

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NIEKTÓRE NOWE KIERUNKI W KATALIZATORACH DO SELEKTYWNEGO UWODORNIENIA OLEJÓW ROŚLINNYCH

Streszczenie

Zarówno w chemii, jak technologii katalitycznego uwodornienia zwykle różni się procesy heterogenne, w których stosowane są różnorodne metale aktywowane i procesy homogenne, gdzie stosuje się kompleksy koordynacyjne.

W przypadku uwodorniania kwasu linolenowego w olejach roślinnych, takich jak: sojowy czy rzepakowy, sytuacja jest prosta: heterogeniczne katalizatory są dostępnymi przemysłowymi produktami (Ni, Cu, Cu-Cr), podczas gdy katalizatory homogeniczne są ciągle laboratoryjnymi odczynnikami (Co, Fe, Cr-kompleksy).

Po przeprowadzeniu badań, pojawiły się nowe możliwości, które można uznać za pomost między heterogeniczną a homogeniczną katalizą.

Przedyskutowano 2 przykłady: 1) homogenne katalizatory, 2) heterogenne katalizatory. Podano kilka przykładów zastosowania takich katalizatorów, zarówno w przypadku tłuszczów technicznych, jak i olejów jadalnych.

Э. Уччиани, Р. Штерн

НЕКОТОРЫЕ НОВЫЕ НАПРАВЛЕНИЯ В КАТАЛИЗАТОРАХ ДЛЯ СЕЛЕКТИВНОЙ ГИДРАТАЦИИ РАСТИТЕЛЬНЫХ МАСЕЛ

Резюме

В химии и технологии каталитической гидратации обычно различают гетерогенные процессы, в которых используются разные активированные металлы, и гомогенные процессы в применении координационных комплексов.

В случае гидратации линоленовой кислоты в растительных маслах, таких как соевое или рапсовое масло, дело представляется просто: гетерогенные катализаторы являются общедоступными промышленными продуктами (Ni, Cu, Cu-Cr), тогда как гомогенные катализаторы представляют собой все еще лабораторные реагенты (Co, Fe, Cr-комплексы).

После проведения исследований, возникли новые возможности, которые можно считать помостом между гетерогенным и гомогенным катализом.

Обсуждались два случая: 1) гомогенные катализаторы, 2) гетерогенные катализаторы. Приводится несколько примеров использования таких катализаторов, как в случае технических жиров, так и съедобных масел.