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TRENDS IN THE DEVELOPMENT OF EDIBLE OIL HYDROGENATION CATALYSTS

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Over the past nine decades batch hydrogenation of edible oils using slurry Ni catalysts has proved to be a very versatile technique to modify liquid oils. In the UK the first plant using this process was built in 1906 at Crosfield in Warrington and the second was built by Procter & Gamble in the USA a few years later.

In the twenties and thirties this slurry hydrogenation process was studied in the UK by Professor T P Hilditch and in the Netherlands by Professor H I Waterman. In general the slurry Ni-catalysts used at that time were Ni on Kieselguhr. These scientists had already made the important observation that not only is the catalyst activity important, but that the selectivity of the catalyst is an important property as well. Then it was Professor Jacques Coenen who initiated in the early fifties a systematic study of Ni on Kieselguhr catalyst with the main objective being the elucidation of the structure of Nickel-Kieselguhr catalysts in order to reach a better understanding of their catalytic activity for the hydrogenation of unsaturated triglycerides. The main conclusions of his work were:

- activity is determined by the Ni surface area and its accessibility;
- selectivity is also determined by the accessibility of the Ni surface area.

Today, several companies have developed a process for the commercial production of slurry Ni-catalyst which can be used for their application in edible oil hydrogenation. The catalyst quality has been improved continuously and the amount of nickel to be used in the hydrogenation has decreased steadily. The continuous decrease in Ni consumption over the years mainly resulted from the increase in Ni catalyst quality, but also to some extent due to the change in oil type, namely less fish oil and more vegetable oils. Before World War 2 on average an amount of 700 wppm Ni was used whereas after World War 2 this Ni consumption decreased to levels as low as 250 wppm in 1990.

The following companies are the main producers of slurry Ni-catalysts for the hydrogenation of edible oils – Unichema; Sued-Chemie/United Catalyst Inc; Engelhard; Mallinckrodt, and Hoechst. These companies have now commercialised the following types of slurry Ni-catalysts:

- Ni- and sulfided Ni on Kieselguhr as a carrier;
- Ni- on synthetic silicates as a carrier; and
- Ni- and sulfided Ni on alumina as a carrier.

For a very long time Kieselguhr has proved to be an excellent, economically attractive carrier for the manufacture of slurry Ni-catalysts for the edible oil applications. However, a disadvantage of Kieselguhr is the quality variation from batch to batch and its content of various metals. Catalyst manufacturers like to ensure that their products are manufactured to a constant quality, therefore they have always looked for alternatives to Kieselguhr. This activity has led in the '80s to the use of synthetic silicate instead of Kieselguhr and it has been observed that by using synthetic silicates not only the performance from batch to batch could be kept constant much more satisfactorily, but in addition the activity was increased due to:

- an increase in the Ni surface area per gram nickel;
- a decrease of the mean particle size.

Hence, Ni-catalysts possessing a higher activity, a better activity maintenance and usually also a better selectivity were introduced onto the market in the 80s. Mr Ivar Ottesen of DENOFA in Norway presented data which reflect the improvement in Ni surface area at the "Hardening Plant II" session held at the AOCS Annual Meeting in 1995. His data showed that the specific Ni surface areas have changed over the years from 70 m^2/g Ni in 1970 to180 m^2/g Ni in 1993.

The use of alumina as the support has introduced a new range of Ni catalysts possessing a mean pore size considerably larger than could be achieved when using synthetic silicates. The combination of these two properties resulted in catalysts which exhibit excellent activity and selectivity for hydrogenation of edible oils due to the much better accessibility of the whole Ni surface area. For example, it is possible to obtain a 6°C lowering of the slip melting point of soyabean oil if hydrogenated to an IV of 80 (at 120°C, 1.5 bara, using 400 wppm Ni).

The introduction of Ni catalysts based on the use of synthetic silicates and aluminas have been the two most important new developments which we have seen over the past decade.

We expect to see the following developments over the next ten years:-

Batch hydrogenation using slurry Ni-catalyst

A continuation of the use of slurry Ni-catalyst in batch hydrogenation, but less multiple use and more one-time use. Also, less partial hydrogenation and more full hydrogenation followed by interesterification to get the desired oil properties, such as the required functionality.

The following two trends will have a remarkable effect on the catalyst use:

First of all, hydrogenators tend to pay more attention to feedstock refining and, secondly, the re-use practice will slowly disappear. Adequate removal of free fatty acids, metals, phospholipids and other unwanted components is increasingly applied. Therefore, we expect that thorough refining of feedstocks will in the near future become standard practice throughout this whole industry. For example, for the hydrogenation of well refined soyabean oil, very low amounts of nickel (40–50 wppm Ni) are now needed to get in a reasonable time to the required IV value. These procedures will make it possible to partially hydrogenate 12 to 15 batches daily. It has been clearly

proven that single catalyst use results more easily in constant product properties and less manual operation. The main question is what this implies for the Ni-catalyst properties. Manufacturing of catalysts which exhibit a constant quality from batch to batch is known to be a difficult process. Hydrogenators who re-use these slurry catalysts will not immediately observe minor changes in catalyst quality, but companies who use these catalysts only once in well-refined feedstocks will observe minor changes in catalyst quality much earlier.

Therefore, we expect that the trend to use our nickel catalysts in partial hydrogenation only once, implies for the catalyst manufacturing companies that they need to watch the catalyst qualities which they produce very carefully from batch to batch. Testing of each batch is a must and the implementation and effective use of adequate quality procedures, such as ISO 9001 or ISO 9002, are prerequisites to guaranteeing that the catalyst quality is indeed constant from batch to batch.

Search for better performance

The emphasis to improve the currently used Ni catalyst will remain on improving those properties which will increase the performance in terms of activity, selectivity (in particular to get lower *trans*-fatty acid contents) and filtration rate.

The currently used precipitation and reduction processes result in Ni surface areas as large as 140 mg per gram nickel if synthetic silicate is used as the carrier. However, this surface is not always easily accessible. Some particles may be too large in size so that it takes too long a diffusion time to reach the Ni surface area present in the centre of these large particles. The texture of the particle is the other important factor as to how long the actual minimum pathlength is to reach the centre of the particles. Moreover, in catalysts based on the use of Kieselguhr or synthetic silicates part of the Ni surface is located in pores of a size too small for the large triglyceride molecules. In other words, an improvement of the accessibility can be obtained if the catalyst manufacturing companies have developed methods to control adequately the engineering of the size and the texture of these particles. The ideal architecture of the particles comprises a narrow particle size distribution, a mean pore size just large enough to get an effective diffusivity of the large fat molecules, a uniform pore size distribution and a zig-zag factor not much larger than 1. These wishes sound extremely simple, but in practice it is not easy to get these factors under control. And it will remain the secret of the catalyst manufacturing companies as to how these companies believe that they can improve these properties.

The presence of too many small particles will have a negative effect on the filtration rate. A slow filtration rate and too fast an increase in the cake resistance needs to be avoided by all means. This implies that particles smaller than , say, 2 microns, should not be present in large amounts.

The concern regarding the *trans*-fatty acids issue is well known. In fact the use of any Ni catalyst for partial hydrogenation of multiple-unsaturated triglycerides is accompanied by the formation of *trans*-isomers. Moreover, *trans*-isomer formation is enhanced by the presence of sulfur in the catalysts, by the partial pressure of hydrogen, the temperature. And to some extent also by the presence of components such as phosphatides.

The options for reducing *trans*-isomer formation by changing the process parameters are well known, but it is not easy to get low *trans* levels in combination with appropriate functionality. In order to approach this problem a number of research institutes have tried to develop catalysts which are based on metals other than Ni. We do not believe that these new catalysts will become commercially attractive for the hydrogenation of edible oils because they have not yet shown sufficient advantages to allow commercial production and use to be attractive.

Use of fixed bed technology

The use of fixed bed technology for the hydrogenation of edible oils has been studied by various researchers, but has to our knowledge only incidentally been applied in the former USSR. The main disadvantages are that it can only be used for selective hydrogenation if the metal loading of the catalyst particles is extremely low and the deactivation rate of the catalyst is low as well.

The use of a fixed bed is expected to be attractive only for full hydrogenation of adequately refined vegetable oils. It requires the use of well refined feedstocks in order to obtain sufficiently long run lengths.

This process requires good temperature control. The adiabatic temperature rise for the full hydrogenation of soyabean oil is 200o C. Therefore we expect for this oil a minimum of three consecutive fixed beds with intermediate cooling to ensure that the temperature will not rise above 200°C. The other main pieces of equipment are a hydrogen recycle compressor and a high pressure gas/liquid separator. In order to increase the reaction rate pressures of at least 25 bar should be used. Even at these high pressures the hydrogenation reaction will take place only within a thin shell at the outer surface of the catalyst particle.

The amount and optimal type of catalyst will still have to be evaluated from pilot-plant experiments. All in all we expect this configuration to be an attractive option only for a limited number of hydrogenators. For hydrogenators having a capacity of at least 100–200 ktons per annum it may be an attractive option, but for lower-capacity users the fixed and variable costs could be too high.

Summary

We do not foresee dramatic changes in the area of hydrogenation catalysts for edible oil hydrogenation. Nickel will remain the metal to provide the activity. Improvements for the slurry catalysts have to come from improvements in precipitation technology resulting in greater uniformity of the catalyst particles.

However, we expect that in a limited number of cases fixed bed technology will be applied for the full hydrogenation of well refined oils. In that case palladium on activated carbon could be an alternative to the use of nickel.