Technological and Economical Aspects of the Metathesis of Unsaturated Esters

M. Sibeijn[a], **E.K. Poels**[a,*], **A. Bliek**[a] and **J.A. Moulijn**[b]
[a]Department of Chemical Engineering, University of Amsterdam, 1018 WV Amsterdam, The Netherlands and [b]Faculty of Chemical Technology and Material Sciences, Delft University of Technology, 2628 BL Delft, The Netherlands

The metathesis of alkenes is a well-established reaction that is applied in various commercial processes. The metathesis of functionalized olefins has not yet been commercialized despite its considerable potential. The conversion of oleochemical feedstocks into specialty chemicals appears especially attractive. In this paper, a process scheme is proposed for the production of 1,18-dimethyl octadecanedioate from pure methyl oleate by metathesis. The chemical and technological bottlenecks are explored, and a rough economic evaluation of this route is given. From these considerations, it is concluded that such a process for the metathesis of functionalized alkenes could be viable only if certain conditions are met. Rapid catalyst deactivation is identified as one of the main obstacles. Feedstock purity, efficient recycling of unreacted feed and multiple catalyst regeneration are crucial for economic feasibility. Rhenium-based catalysts are to be preferred over molybdenum ones because their activation is easier and regenerability is superior. Finally, the direction for future technological and catalysis research is given based upon the results of this work.

KEY WORDS: 1,18-Dimethyl octadecanedioate, feasibility, metathesis, methyl oleate, molybdenum, process, rhenium.

Nowadays, 90% of the chemical products, such as polyesters, polyethers and polyamides, are produced from petrochemical feedstocks (natural oil, gas and coal), whereas only 10% are produced from oleochemical feedstocks (vegetable oils and animal fats) (1). The use of petrochemicals has several disadvantages. The resources are limited (2), the use of petrochemicals adds to the greenhouse effect (there is a net production of CO_2) and the biodegradability of petrochemicals is usually not good (1). In contrast to petrochemicals, oleochemicals are produced from renewable resources, have no net CO_2-production (3) and usually the biodegradabilty is excellent (1). Despite these advantages compared to those of the petrochemicals, the use of oleochemicals is not yet widespread.

There are various causes. Clearly, price and limited availability of natural oils and fats will restrict their application as chemical feedstocks to the higher end of the market. Technologies for the conversion of oleochemical raw materials, however, are not as well-developed as those for petrochemical materials. As more and more companies become interested in the use of oleochemicals, these techniques will improve. Another disadvantage is the fact that most industrial vegetable oil crops in moderate climates give fatty acids (the oleochemical raw materials) with a predominant chainlength of 18 carbon atoms (2). This is a serious limitation. In tropical areas, also shorter, usually saturated chainlengths occur. However, since there is a high demand for fatty acids and derivatives with shorter chainlengths, especially for the production of surfactants (4), a shortage of supply is predicted. Fatty acids and derivatives with a longer chainlength than C18 are also desired. Furthermore, there is a demand for fatty acids with more than one functionalized group, for example di-acids.

In principle, several options are feasible to vary the chainlength of fatty acid esters and derivatives. One of the possibilities is the use of new oil crops, e.g., obtained from new plant species or by genetic modification of existing oil crops, that produce predominantly fatty acids with a shorter [*Cuphea* spp. (2,5)] or longer chainlength [meadowfoam, jojoba (5,6)]. However, agricultural production of these new plants may cause problems (6). The other solution, to change the chainlength of the fatty acids, lies in chemical methods. One of these methods could be metathesis of fatty acid derivatives (2). This reaction can also be used for the production of fatty di-acids and derivatives thereof.

Metathesis of alkenes is a catalytic reaction, in which the carbon–carbon double bonds of alkenes are broken and new bonds are formed. In the metathesis of propene for example, ethene and 2-butene are formed:

$$2\ CH_2{=}CHCH_3 \leftrightarrow CH_2{=}CH_2 + CH_3CH{=}CHCH_3$$

Metathesis is not limited to normal alkenes. Alkenes with functional groups, such as esters, nitriles, ethers and halogens, can also undergo metathesis (7). In Scheme 1, examples are given of possible reactions with unsaturated esters. It clearly shows the versatility of metathesis and its great potential, especially in the field of oleochemical raw materials.

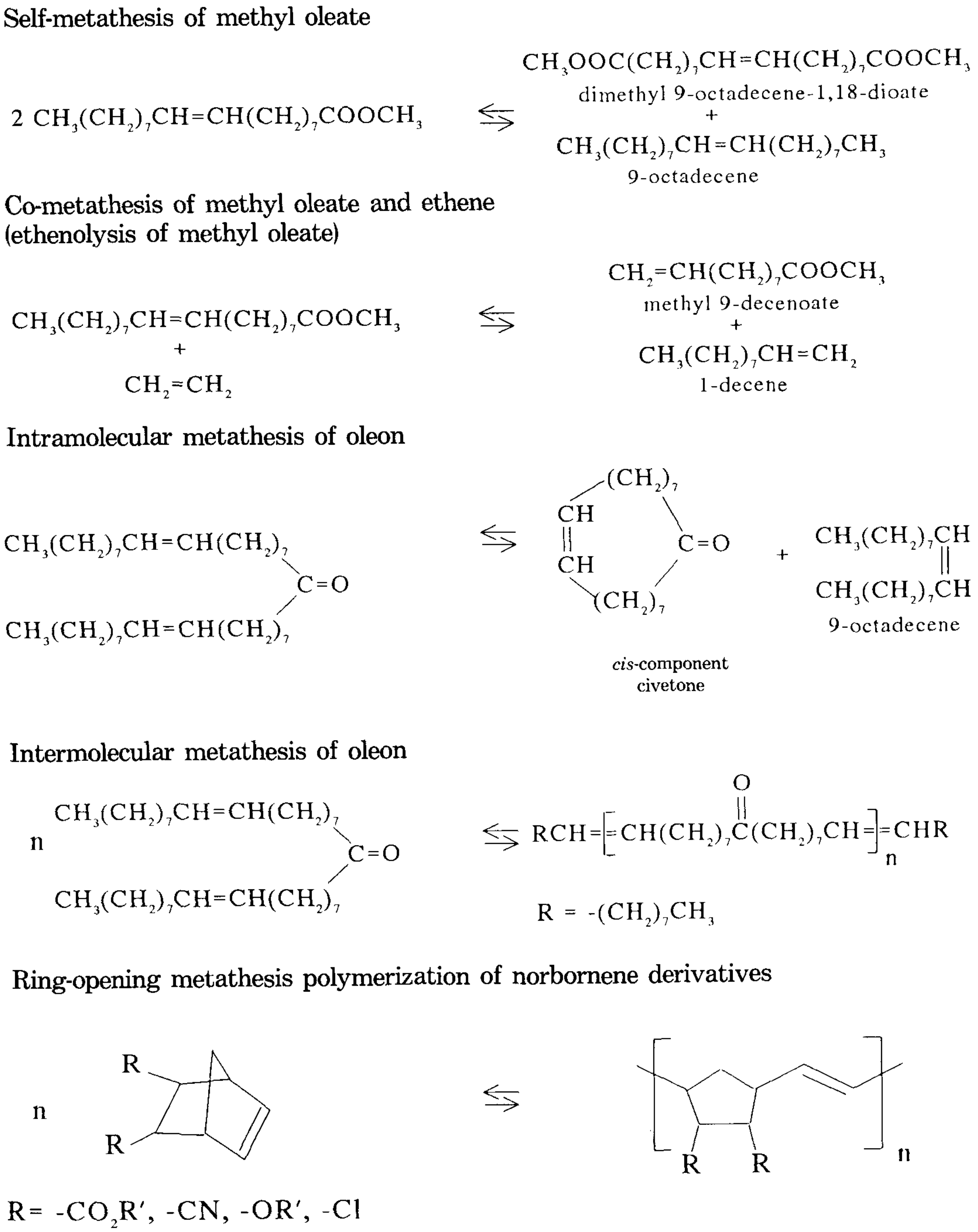
Despite its great potential, up to now no commercial processes exist that use metathesis of functionalized alkenes. In contrast, the metathesis of simple alkenes is applied in several commercial processes [e.g., reversed Phillips Triolefin Process (8,9), SHOP (8,10), Shell's FEAST process (11), Phillips neohexene process (12)]. The main obstacle for the application of the metathesis of functionalized alkenes is their relatively low reactivity, in combination with the low stability of the catalyst systems and their high costs. In this paper, we will consider the metathesis of an unsaturated ester, *viz.*, methyl oleate (methyl *Z*-9-octadecenoate) and investigate whether and how it can be attractive for commercial applications.

CATALYSTS

For the metathesis of simple alkenes, such as propene, many catalysts are active. The most active ones are based on Mo, Re and W (13). The metathesis of functionalized alkenes appears to be more complicated than the metathesis of simple alkenes. Only a small number of the homogeneous catalyst systems that are active in the metathesis of simple alkenes were found to be active in the metathesis of unsaturated esters. An example of such a catalyst is $WCl_6/Sn(CH_3)_4$ (14). Most of the other homogeneous catalyst systems that are active in the metathesis of unsaturated esters and other functionalized alkenes are also based on tungsten (7,15).

---

[*] To whom correspondence should be addressed at Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands.



SCHEME 1

In general, heterogeneous catalysts are preferred for industrial applications, because of easy product separation, the possibility of continuous operation and regenerability. Although many heterogeneous catalysts were already developed for the metathesis of simple alkenes, only in 1977 the first heterogeneous catalyst system for the metathesis of methyl oleate was reported (16), *viz.*, Re_2O_7/Al_2O_3 promoted with $Sn(CH_3)_4$. This catalyst system has been optimized with respect to the promoter and the support material. The most active Re-catalyst now is $Re_2O_7/SiO_2 \cdot Al_2O_3$ (25 wt% Al_2O_3) promoted with tetraethyltin or tetrabutyltin (17). Another catalyst system that is highly active in the metathesis of unsaturated esters was developed only recently. It consists of MoO_3 on SiO_2, which is photoreduced in a CO-atmosphere by an Hg-lamp and subsequently treated with cyclopropane (18; Sibeijn, M., M.N.H. Kieboom, J.G. Nazloomian, P. de Leeuw, A. Bliek and J.A. Moulijn, unpublished data).

In Table 1, the activities (turnover frequency) and the stabilities (turnover number) of the catalysts in the metathesis of methyl oleate are compared with those in the metathesis of simple alkenes, such as propene. It is clear that, for methyl oleate, the activities and stabilities of the catalysts are much lower than for simple alkenes. The huge difference is the main reason that, up to now, no

TABLE 1

Turnover Numbers for Catalysts, Active in the Metathesis of Functionalized Alkenes[a]

Reactant	Catalyst system	Reaction conditions	Initial turnover frequency[b]	Turnover number[c]	Reference number
1-Hexene	3.7 wt% Re_2O_7/Al_2O_3	338°K in solution	n.d.	3000	31
Propene	4.6 wt% MoO_3/SiO_2	480°K 2 bar	0.21	>3000[d]	13
Propene	12.9 wt% WO_3/SiO_2	675°K 2 bar	0.25	>4000[d]	13
Methyl oleate	1 wt% MoO_3/SiO_2 cyclopropane	305°K pure methyl oleate	0.99	468	19
Methyl oleate	5 wt% MoO_3/SiO_2-cyclopropane	305°K pure methyl oleate	0.24	176	19
Methyl oleate	12 wt% Re_2O_7/Al_2O_3-$SnBu_4$	305°K in hexane	0.032	27	17
Methyl oleate	3 wt% $Re_2O_7/SiO_2Al_2O_3$-$SnBu_4$	205°K in hexane	0.20	120	17

[a] For comparison, values for typical simple alkenes are included.

[b] Amount of substrate (mol) converted per mol of W, Mo or Re per second; n.d., not determined.

[c] Total amount of substrate (mol) converted per mol of W, Mo or Re.

[d] Catalyst still active at end of run.

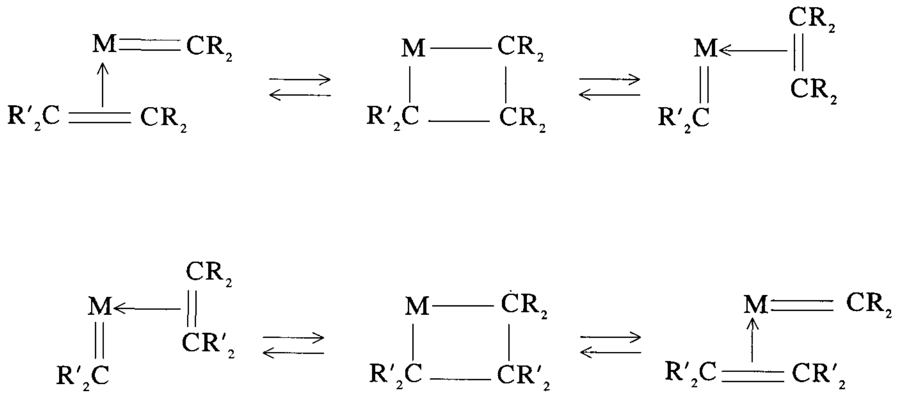
commercial processes have been realized for the metathesis of unsaturated esters or other functionalized alkenes.

Selectivity of the catalysts in the metathesis of functionalized alkenes, such as methyl oleate, is excellent. All known catalysts have a selectivity higher than 97% for the metathesis of methyl oleate. In principle, isomerization of the carbon–carbon double bond by Brønsted acid sites might be expected, especially in the case of acidic supports. However, complexation of the ester group of methyl oleate to the Brønsted acid sites on the support prevents this isomerization. The selectivity only plays a role when less polar substrates than esters are applied.

REACTION MECHANISM OF METATHESIS

Propagation. Today, the metal carbene mechanism, proposed by Hérisson and Chauvin (19), is generally accepted. In this mechanism, the metal carbene is the catalytic active site. After complexation of an alkene to the metal carbene, a metallacyclobutane intermediate is formed. This metallacyclobutane can split up in two ways: The original alkene can be formed back together with the originally present metal carbene, or both a new alkene and metal carbene are formed (Scheme 2).

Initiation. The metal carbene is not initially present on the catalyst, but it is formed prior to reaction. Simple alkenes are able to initiate carbene formation on the catalyst itself (20), but in the case of functionalized alkenes, the metal carbene should be present before introduction of the functionalized alkene. For supported Re_2O_7-catalysts, addition of a promoter, *viz.*, SnR_4 (R = alkyl), is necessary to obtain the Re-carbene (16), while for photoreduced Mo-based catalysts, cyclopropane is needed for the creation of the required Mo-carbene (21).



SCHEME 2

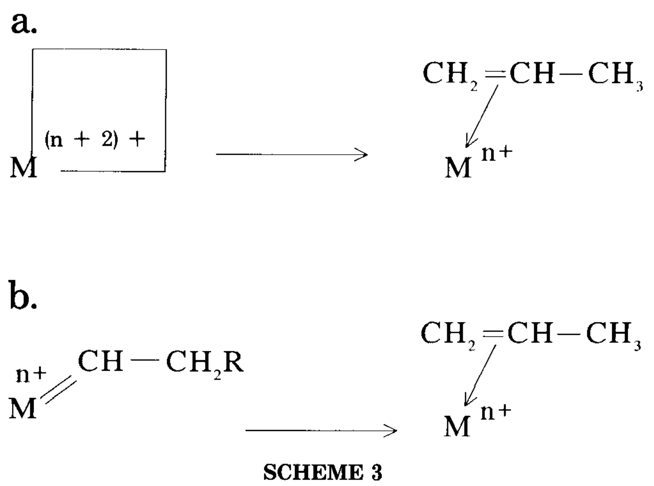
Intrinsic deactivation. In the metathesis of functionalized alkenes, deactivation plays an important role, causing relatively low activities and stabilities of the catalysts in comparison to the metathesis of simple alkenes (Table 1).

In all metathesis reactions (of both simple and functionalized alkenes), deactivation will occur according to the following mechanisms: the formation of stable π-complexes *via* reductive elimination of metallacyclobutane intermediate (Scheme 3a) (22,23) or *via* isomerization of the metal-carbene (Scheme 3b) (23). This type of deactivation is probably an intrinsic property of the metal–carbene complexes. It results in a decrease in the amount of active sites, which can probably not be prevented.

Deactivation by adsorption of polar groups. A completely different type of deactivation is caused by the complexation of a polar group (e.g., an ester group) to the active site. This type of deactivation only occurs in the metathesis of functionalized alkenes. The much lower reactivity of methyl oleate, compared to that of simple alkenes (Table 1), is ascribed to the complexation of the ester group of the substrate on the active site. The reason why there are so few catalyst systems that are also active in the metathesis of functionalized alkenes is probably caused by the sensitivity of most catalyst systems for polar groups. Even the most active catalyst system, silica-alumina-supported Re_2O_7 in combination with tetrabutyltin, is not able to metathesize unsaturated acids or alcohols (7), obviously because the functional groups of these compounds are too polar and easily form complexes with the active sites.

Deactivation by complexation of a functional group can be prevented by the introduction of a protecting group, prior to metathesis. For example, Warwel *et al.* (24) obtained rather high conversions in the metathesis of an unsaturated alcohol when the alcohol group was converted into a trimethyl silyl ether, whereas the alcohol itself deactivates the catalyst immediately and does not show any conversion.

Deactivation by impurities in the substrate. Not only the substrate itself can cause deactivation of the catalyst, but also impurites in the substrate, such as acids, alcohols, water or peroxides. For example, on supported Re_2O_7 catalysts, the active sites are formed by ReO_4 groups that have replaced OH-groups on the support (25). When water is present in the substrate, the bond between the ReO_4 groups and the surface is hydrolyzed, and the remaining ReO_4^- ions are not active for metathesis.



SCHEME 3

When oleochemicals are used as a substrate, the acid value should be kept very low by means of known ester synthesis and refining methods. Special care should be given toward the purification and storage of the feedstock. During storage, peroxides can be formed by auto-oxidation. In Figure 1, the effect of the peroxide number (a measure for the concentration of peroxides in the substrate) is shown on the activity and stability of 3 wt% $Re_2O_7/SiO_2 \cdot Al_2O_3$ promoted with tetraethyltin. It is clear that the presence of peroxides reduces the activity and stability of the catalyst strongly. Therefore, thorough purification of the substrate prior to metathesis is required. In the case of methyl oleate, this can be achieved by storing the methyl oleate on silica–alumina at low temperatures (26) or by a conventional bleaching earth treatment followed by distillation.

POSSIBLE APPLICATIONS OF METATHESIS OF FUNCTIONALIZED ALKENES

In Scheme 1, the various possibilities of the metathesis of functionalized alkenes are shown. The self-metathesis of functionalized alkenes results in the formation of internal alkenes and of unsaturated alkenes with two functional groups. The latter compounds can be applied in the production of high-performance polycondensates such

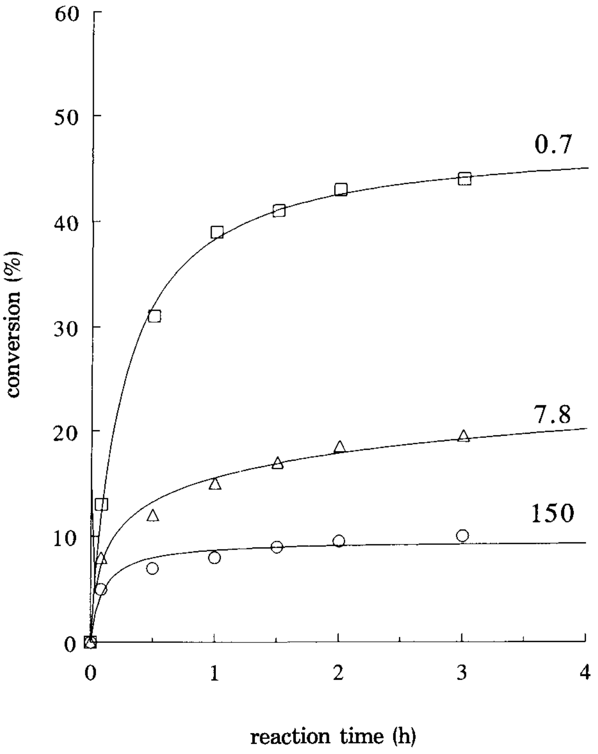


FIG. 1. Conversion of methyl oleate as a function of the reaction time for three samples of methyl oleate with varying peroxide numbers. Reaction temperature, 297°K; molar ratio of methyl oleate/Re/$SnEt_4$ = 120:1:0.6. The numbers in the figure denote the peroxide value in mmol of active oxygen per 2 kg of methyl oleate (taken from Ref. 26).

as impact-resistant nylons, which can be used for the manufacturing of machine parts, *etc.* In the case of methyl oleate, the di-ester obtained after metathesis can also be applied for the production of macrocyclic compounds that are used in perfumes, e.g., civetone (27).

The intramolecular self-metathesis of diunsaturated functionalized compounds, such as oleon, can also be used for the production of macrocyclic compounds. Recently, the successful metathesis of oleon was reported, resulting in a mixture of *cis*- and *trans*-8-heptadecenone, of which the *cis*-component is civetone (28) (see Scheme 1). However, as both stereoisomers are formed during reaction, and separation of these isomers is very difficult, metathesis is probably not suitable for the production of these stereospecific compounds.

The co-metathesis of functionalized alkenes with simple alkenes offers other possibilities. As already mentioned, the co-metathesis of fatty acid derivatives with short alkenes, e.g., a mixture of hexenes, can be used to produce fatty acids and derivatives with a chainlength in the detergent range (29,30). A large excess of simple alkenes can force this reaction to the product side (see Scheme 1). The modest value of these products, however, even at the relative shortage envisaged in the near future, cannot justify their synthesis by metathesis at the current state of the art, as will be clear from the remainder of this paper.

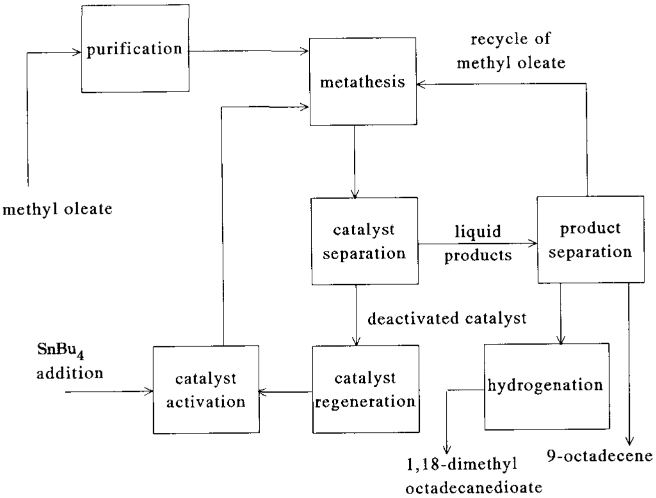
Metathesis of fatty acid derivatives and normal alkenes can also be used for the production of insect pheromones, which can be used as biological pesticides, although the applications are somewhat limited. The pheromones synthesized by metathesis are usually not identical to the insect pheromones, because the latter consist of a specific mixture of *Z*- and *E*-components. Actually the metathetically produced pheromones can be used in disrupting techniques, in which the male insect loses its way to a female by the large excess of sex attractants. Field experiments have shown that pheromones obtained by metathesis can indeed be used for this purpose (31).

Another interesting reaction is the so-called ethenolysis (i.e., the co-metathesis with ethene) of fatty acid derivatives. The reaction can be applied in the synthesis of ω-unsaturated functionalized alkenes, which can be used for the production of nylons after functionalization of the olefinic bond. The ethenolysis product of methyl oleate, methyl 9-decenoate, can be converted into the ω-amino-acid and subsequently used for the production of nylon-10, which could replace nylon-9 and nylon-11.

At present, there are no commercial processes that use the metathesis of functionalized alkenes.

TECHNOLOGICAL ASPECTS

Several technological aspects should be considered in the design of a process based on metathesis. In this paper, we will consider the metathesis of methyl oleate, and we will investigate its potential for commercial application. Scheme 4 presents a process for the production of 1,18-dimethyl-octadecanedioate (a saturated diester) *via* self-metathesis of methyl oleate. Obviously, for some applications, the free di-acid is preferred over the diester, but the consequential saponification step is neglected here for simplicity. We will also only consider the use of pure methyl oleate (purity <98%). In a commercial process, commercially available "methyl oleate" will be used. This "methyl oleate" contains 70% methyl oleate, a certain amount of saturated esters (*ca.* 8%), other monounsaturated esters (15%) and di- and triunsaturated esters (7%) (based on brochure data). Selective hydrogenation of polyunsaturated acids could enhance the methyl oleate level somewhat. When using one of the recently commercialized high-oleic acid-containing oils, such as high-oleic sunflower oil, levels of *ca.* 85% methyl oleate should be possible. Because the saturated esters will act as catalyst poisons, the reactivity of commercially available methyl oleate will be somewhat lower than that of pure methyl oleate. Also, the selectivity to the mentioned diester will be less because the other unsaturated esters will react with methyl oleate. It depends on the required product specification whether this commercially available methyl oleate can be used.



SCHEME 4

Catalysts. The choice of the substrate usually determines the type of catalyst and the reaction conditions. Homogenous catalysts are suited for ring-opening metathesis polymerization, because the catalyst remains in the product. For the production of acyclic alkenes, heterogeneous catalysts are preferred because of their easy separation from the product stream and their regenerability. So far, no simple recovery for homogeneous catalysts has been reported (32).

Most of the substrates used for the production of fine chemicals do not allow extreme reaction temperatures. Therefore, the choice of catalyst is limited to those that are active at mild temperatures. When the substrate is a functionalized alkene, such as methyl oleate, only supported Re_2O_7 promoted with tetraalkyltin and photoreduced MoO_3 catalysts promoted with cyclopropane are available.

Both catalyst systems have to be activated with a promoter. For supported Re_2O_7 catalysts, this is a tetraalkyltin compound, which is quite toxic. Supported MoO_3 catalysts have to be photoreduced with ultraviolet (UV) light in a CO-atmosphere to generate the active valency, and afterwards, they have to be treated with cyclopropane to generate carbenes. Especially the reduction of the MoO_3 catalysts should become less complicated to make it attractive for commercial applications. UV-reactors have already been developed (33) that might be used for the photoreduction of these catalysts.

The choice of catalyst also depends on the type of process. The process can be carried out batch-wise or continuously. For the production of specialty chemicals, batch-wise production is usually preferred because of its flexibility and its suitability for production of small volumes. Moreover, compared to continuous production, in the case of metathesis of methyl oleate, batch-wise production is more advantageous because no stable production level can be obtained in a continuous process without a complicated catalyst recycle system (17,19). This means that a fixed-bed reactor is out of the question; a continuous-slurry reactor is an option more or less equivalent with batch-wise slurry operation. The smaller catalyst particles applied in the latter case also suppress diffusion limitation and consecutive reactions.

In case a continuous process is desired, a continuous regeneration of deactivated catalyst is needed to maintain a reasonable conversion level. Rhenium-based catalysts could be regenerated at least ten times without any loss of activity. The regeneration takes a considerable time, roughly 4 h, whereas after 3 h the catalyst has lost half of its original activity (34). So, compared to the metathesis reactor, a large regeneration section is required. A rather large amount of catalyst is therefore needed. As rhenium is expensive, it is preferable not to have too much catalyst in stock.

From the results obtained in the batch-wise self-metathesis of methyl oleate over the molybdenum-based catalysts, it can be concluded that these catalysts deactivate even faster than the rhenium-based catalysts (Sibeijn, M., M.N.H. Kieboom, J.G. Nazloomian, P. de Leeuw, A. Bliek and J.A. Moulijn, unpublished data). Moreover, it is expected that the molybdenum-containing catalysts will lose part of their activity, due to sintering of molybdenum during regeneration (at 773°K). As a result, these catalysts are not suited for continuous operation with recycle.

It can be concluded from the above that slurry-type production is preferred. The choice for batch-wise or continuous operation depends on whether the plant is a dedicated one, production volume as well as the fact that batch production allows off-site catalyst regeneration, resulting in a less complicated process design. The catalyst of choice is the rhenium-based one, because its activation is much simpler than that of the molybdenum-containing catalyst, and its regenerability appears to be superior.

Product separation and recycle. Metathesis is an equilibrium reaction. As a consequence, large amounts of unreacted substrate remain in the reaction product. After separation of the products and the substrates, the substrates should be recycled. In all commercial processes described above, a recycle of unreacted substrates is applied. For the metathesis of functionalized alkenes, recycling of the unreacted substrates is crucial because they are rather expensive.

For the separation of the reaction products, several options exist. In all commercial processes described above, product separation is carried out after the metathesis reaction. In the metathesis of simple alkenes, atmospheric distillation can usually be applied. For the metathesis products of functionalized alkenes, this might cause problems because the compounds are rather sensitive to high temperatures. Vacuum distillation can be an alternative. Separating volatile by-products and unconverted methyl oleate from the diester requires a high number of theoretical plates. The residue (the desired product) can subsequently be purified by distillation under high vacuum with much less stringent demands on performance. This latter treatment may be postponed until after the hydrogenation step to limit metal contaminants in the end-product. For high-boiling products, crystallization should be considered, e.g., when saturated (and saponified) free di-carboxylic acid is required, for instance when the application is aimed at a nylon. Extraction is an option when the solubilities of the substrate and the products are sufficiently different. It should not be applied in the metathesis of long-chain esters, such as methyl oleate, because all compounds involved are quite apolar.

Another solution is the combination of catalytic reaction and separation in one reactor. An example of this is catalytic distillation. This operation can only be applied if the volatilities of the substrates and the products are sufficiently different and if the operating temperature and pressure of the reaction agrees with those of the fractionation process. It is attractive for equilibrium reactions, because the products are continually removed. This forces the reaction equilibrium toward the products' side. A possible application for catalytic distillation lies in the ethenolysis of methyl oleate. The products are much lighter than the substrate and are removed continually together with ethene, which can be separated easily from the products and recycled.

This technique can also be applied to the production of a diester *via* metathesis. Instead of carrying out the self-metathesis of methyl oleate, first the ethenolysis of methyl oleate is carried out. After product separation, the ω-unsaturated ester undergoes self-metathesis, resulting in the production of ethene and the unsaturated diester. In this way, high conversions can be obtained, and product separation is much easier than in the case of self-metathesis of methyl oleate. Warwel *et al.* (35) showed that indeed much higher conversions can be obtained in this way than by conventional self-metathesis of methyl oleate.

An alternative for catalytic distillation was recently suggested (C.W.F. Verstraten, and R. Krishna, private communication). Instead of distillation, extraction by an inert gas phase is used to remove the products. In this case, the volatilities of the products have to be sufficiently different. An advantage is that the temperature applied is that of the reaction. Especially for substrates with low thermal stability, this process is preferred. Disadvantages are the high cost of separating the inert gas and usually the low selectivity.

ECONOMIC EVALUATION

An economic evaluation of a process for the production of a saturated diester *via* metathesis of methyl oleate is made below. It is not the purpose of the calculations performed to provide exact numbers, but rather to give a rough impression of the viability of the proposed process scheme and to suggest directions for future research from the derived trends. Scheme 4 gives a possible process. First of all, methyl oleate should be purified thoroughly to prevent unnecessary deactivation of the catalyst by impurities in the substrate, such as traces of water, free fatty acid or peroxides. Subsequently, the metathesis reaction is carried out batch-wise. After the reaction, the catalyst is removed by filtration and regenerated. The regeneration of the catalyst consists of heating it in a dry air stream (Re at 823°K; Mo below 800°K), cooling it in an inert atmosphere (N_2 or Ar) and then reactivating it by a new amount of tetrabutyltin or cyclopropane.

After the removal of the catalyst, the product mixture is distilled to separate the alkenes, monoesters and diesters. The monoesters are recycled. In a process in which commercial "methyl oleate" is used, part of the monoester recycle has to be drained off to prevent a build-up of saturated esters. In the economic evaluation, this loss will be neglected. The saturated monoesters themselves represent only a modest commercial value.

After separation, the alkenes are prepared to be sold, for example as a feedstock for the production of star-branched alkanes (36). The diester should be hydrogenated before it can be used for polymer production.

In our calculations, we will consider the results we obtained in the batch-wise metathesis of "pure methyl" oleate (purity >97%). This is obviously a gross simplification but justified for the limited objectives of this study. Only the variable costs for the production of the diester will be calculated. The variable costs, i.e., costs that are not made when nothing is produced, in our definition include raw materials and recycle streams, by-products, energy, chemicals (e.g., catalysts), effluent treatment, packaging materials, and freight. No losses are considered explicitly. Incomplete methyl oleate recycle is taken into account, however, and may implicitly be considered as a loss. Selling the products in the recycle stream is not taken into account. As we estimated the price of the diester to be about NLG 16.00 per kg of diester, a gross margin of about NLG 6.00 per kg of diester is a necessary minimum for a commercially feasible process (1 NLG = *ca.* \$0.52, DM0.88 and £0.35).

CALCULATIONS

The prices of the compounds are given in Table 2. The price of methyl oleate is rather high because it includes the purification steps. The prices for the diester and the internal alkene are estimated. The price of the diester is chosen toward the maximum price charged for the commercially available C12 dioic acid. This is done assuming that nylon-6,18 possesses similar properties to those of nylon-12 and that the hexamethylene–diamine part of such a product is relatively inexpensive. The price of the internal alkene is probably somewhat high. The costs for the production of the diester are given in Table 3. These prices are estimated from comparable processes.

TABLE 2

Prices of Raw Materials

Compound	Price, NLG/kg
Methyl oleate[a]	2.50
1,18-Dimethyl octadecanedioate	16.00
9-Octadecene	1.50
Support (SiO_2 or $SiO_2 \cdot Al_2O_3$)	10.00
NH_4ReO_4[b]	15000.00
$Sn(n\text{-}C_4H_9)_4$[b]	180.00
$Mo_7O_{24}(NH_4)_6$[b]	250.00
Cyclopropane[b]	1000.00

[a] Including purification; 1 NLG = *ca.* \$0.52, DM 0.88 and £0.35.
[b] Upper limit; estimated from specialty prices (e.g., catalogues of Aldrich, Brussels, Belgium; and Janssen Chimica, Geel, Belgium) to include manufacturing costs, *etc.*

For the calculations for the rhenium-based catalysts, we chose 3 wt% $Re_2O_7/SiO_2 \cdot Al_2O_3$ (24.3 wt% Al_2O_3), promoted with tetrabutyltin (which will be denoted by Re_3-Sn/SiAl), because this catalyst has a much higher turnover number than the alumina-supported catalysts. For the molybdenum-based catalysts, we will calculate the costs for both 1 and 5 wt% MoO_3/SiO_2 because the 5 wt% catalyst has the highest activity per unit weight of catalyst, whereas the 1 wt% catalyst gives rise to the highest turnover numbers. These catalysts will be denoted as Mo_1-CP/Si for 1 wt% MoO_3/SiO_2 and Mo_5-CP/Si for the 5 wt% catalyst. Usually, noble-metal catalysts are considered an investment cost and only regeneration, metal recovery and catalyst preparation are treated as variable costs. Because this approach is not common for molybdenum-based catalysts, the investment in the rhenium is included in the variable costs for a fair comparison between the two options.

In Table 4, the reaction conditions and the results obtained after 3 h of reaction time are given. These values are used for the calculations. The amount of cyclopropane used for Mo_1-CP/Si is rather high. A lower amount of cyclopropane would probably be sufficient. This would increase the profits considerably because cyclopropane is rather expensive.

In Figure 2, the gross margins per kg of diester over Re_3-Sn/SiAl (a), Mo_1-CP/Si (b) and Mo_5-CP/Si (c) are plotted as a function of the number of regenerations of the catalyst, both with and without recycle of unreacted methyl oleate. From this figure, it can be concluded that recycle of methyl oleate has a large positive effect on the profitability of the process. Therefore, we may conclude that the optimal recycle of methyl oleate is crucial for an economically feasible process.

TABLE 3

Estimated Prices of Process Steps

Process operations	Price, NLG/kg
Calcination or regeneration of catalyst	0.75
Reaction, filtration, distillation and hydrogenation	2.15[a]
Finishing	0.10[a]
Bleaching of recycle methyl oleate	0.15

[a] Per kg of diester produced. See Table 2 for values of NLG.

TABLE 4

Reaction Conditions Used and Results Obtained for the Various Catalysts[a]

Catalyst	Methyl oleate/metal (mol/mol)	$SnBu_4$/Re or cyclopropane/Mo (mol/mol)	Conversion (%)
Re_3-Sn/SiAl	240	0.6	50
Mo_1-CP/Si	820	10	50
Mo_5-CP/Si	420	2	42

[a] Reference 17; Sibeijn, M., M.N.H. Kieboom, J.G. Nazloomian, P. de Leeuw, A. Bliek and J.A. Moulijn, unpublished data.

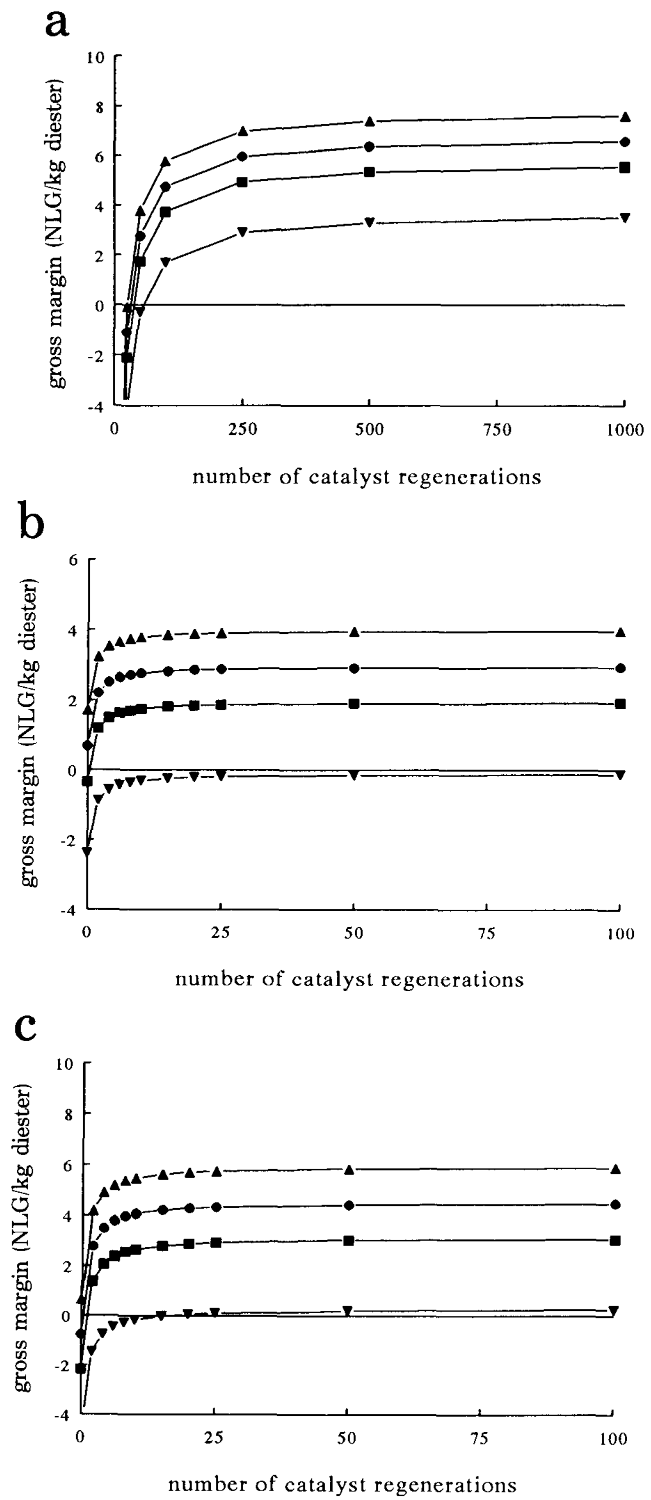


FIG. 2. The effect of the methyl oleate recycle and the number of regenerations on the gross margin for Re_3-Sn/SiAl (a), Mo_1-CP/Si (b) and Mo_5-C/Si (c). Methyl oleate recycle: (▲) 100%; (●) 75%; (■) 50%; (▼) no recycle. 1 NLG = *ca.* \$0.52, DM0.88 and £0.35.

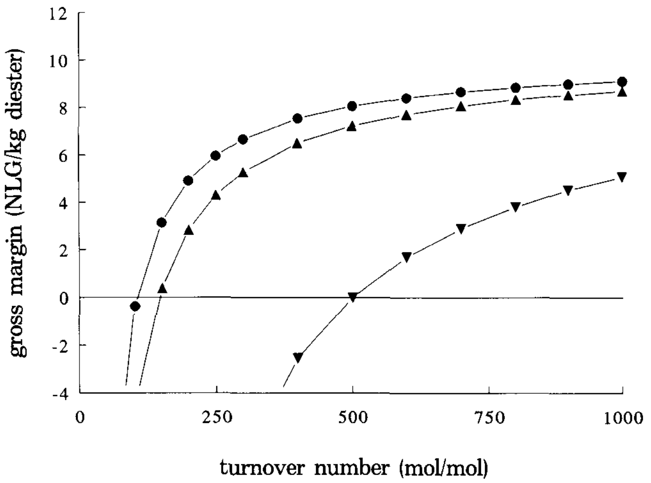


FIG. 3. The effect of the turnover number for Re_3-Sn/SiAl (●), Mo_5-CP/Si (▲) and Mo_1-CP/Si (▼) on the gross margins, assuming that 50% conversion is obtained, a 100% recycle of unreacted methyl oleate is achieved, and that the catalysts can be regenerated 100 times without any loss of activity. See Figure 2 for NLG values.

It is also clear that the number of possible regenerations is important. For the molybdenum-containing catalysts, at least 25 regenerations are necessary when all the unreacted methyl oleate is recycled (100% recycled). For the Re-based catalyst, 250 regenerations are required for 100% recycle of methyl oleate. These figures seem unrealistic at present, however.

Another conclusion derived from Figure 2 is that the catalyst costs appear to form a large part of the total costs. As the number of regenerations is increased, the margins increase as well.

The promoters, $SnBu_4$ but especially cyclopropane, also add considerably to the costs of the process. This is shown in Figure 3, in which gross margins are plotted as a function turnover number, i.e., the molar ratio of methyl oleate to metal atom (either Re or Mo) with 100% recycle of methyl oleate and 100 catalyst regenerations. For all three catalysts, profitability increases considerably with increasing molar ratio. In the case of Re (at 100 regeneration cycles), the decrease in catalyst costs, caused by the higher methyl oleate-to-metal ratio employed, outweighs the effect of the reduction in $SnBu_4$. In case of Mo catalysts, the reduction in the cyclopropane required is the predominant cost-saving result of high turnover number.

Summarizing, a gross margin of NLG 6.00 is realized in some cases for both Re_3-Sn/SiAl and the Mo-CP/Si catalysts (see Figs. 2 and 3). To come to an economically feasible process, it is necessary that the catalysts can be regenerated many times. The rhenium catalyst showed some promise in this respect. It could be regenerated ten times without loss of activity. The regenerability of the molybdenum catalysts was not investigated.

Another condition derived from the above calculations is the recycle of methyl oleate. It should be as high as possible. A full recycle of methyl oleate cannot be achieved, because part of the methyl oleate and products remain adsorbed on the catalyst and is lost during refining and separation processes. Therefore, losses are unavoidable.

The rapid catalyst deactivation is reflected by the low turnover numbers reported in this paper. Improved catalyst stability would greatly reduce catalyst and promoter costs.

Nevertheless, a commercial process that incorporates metathesis of functionally substituted alkenes seems not too far from realization, provided that high-value, specialty products are synthesized.

Thus we conclude that a process for the production of diesters *via* metathesis could be economically viable if the following conditions are fulfilled. Thorough purification of the methyl oleate feed is a first prerequisite. The recycle of unreacted methyl oleate should be as high as possible. It is necessary that the catalysts can be regenerated at least 25 times for the molybdenum-based catalysts and at least 250 times for the rhenium-based catalysts. The molar ratio of methyl oleate to either Re or Mo should be as high as possible, with the condition that 50% conversion should be obtained.

From this evaluation, it is clear that only products with a high added value are candidates for a commercial process in the near future. The real bottleneck for commercialization of metathesis of methyl oleate is the lack of a stable, active catalyst. The Mo-CP catalysts are, in principle, quite promising because they exhibit high initial activities, but the required activation process by a laser beam in a fluidized bed in CO-atmosphere is too complicated for practical applications. The Re-Sn/SiAl catalysts clearly are at an advantage because of their much simpler activation procedure. Moreover, it is expected that the regeneration of the Re-Sn catalysts will be possible many times without loss of activity, whereas for the Mo-CP catalysts it is expected that loss of activity will occur upon regeneration, due to sintering of Mo. Therefore, at present, Re-Sn/SiAl is the most promising catalyst.

FUTURE RESEARCH

Metathesis of methyl oleate has not yet been applied in a commercial process. The results of this study and the economic evaluation have shown that, in principle, such a process is not far from economic feasibility.

In the past, most of the research has been concentrated on the improvement of catalytic activity, the development of a new catalyst and explorative studies on the co-metathesis of functionalized alkenes and simple alkenes. More technological aspects, such as reactor design, the various separation steps required and regenerability of the catalysts, have not been investigated in detail. Therefore, a more technologically orientated study is necessary.

Also, further improvements of the catalysts are necessary. For the Re-based catalysts, it is not likely that further improvement can be achieved, unless a method is found to activate a larger part of the rhenium atoms. The molybdenum catalysts can probably be improved. For example, the activation procedure is rather complicated. It would be easier to perform a thermal reduction in H_2 or CO. Perhaps, this will do for MoO_3/Al_2O_3, on which the Mo^{+6} ions are readily reduced to Mo^{+4}. A subsequent treatment with cyclopropane would then create the active sites. Another option is the development of a different preparation technique, e.g., by chemical vapor deposition techniques. Application of alternative (lower-cost) carbene-generating substances also deserves attention.

Another interesting aspect would be the development of more stable catalysts. It is clear that the stability of the known catalysts is too low. The molybdenum-containing catalysts especially are quickly deactivated. Their initial activity is high, which explains the relatively high turnover numbers achieved with these catalysts. An increased stability would definitely speed up the commercialization of the metathesis of functionalized alkenes.

ACKNOWLEDGMENTS

Sponsoring of this work by Unichema International and careful reading of the manuscript by J.J. Vreeswijk are gratefully acknowledged.

REFERENCES

1. Fabry, B., *Fat. Sci. Technol. 92*:287 (1990).
2. Stein, W., *Fette Seifen Anstrichm. 84*:45 (1982).
3. Richtler, H.J., and J. Knaut, *Fat Sci. Technol. 93*:1 (1991).
4. Kaufman, A.J.,and R.J. Ruebusch, in *Proceedings World Conference on Oleochemicals (Kuala Lumpur, Malaysia 1990) "Into the 21st Century"*, edited by T.H. Applewhite, American Oil Chemists' Society, Champaign, 1991, p. 10.
5. Uehara, H., in *Ibid.*, p. 75.
6. Röbbelen, G., in *Ibid.*, p. 119.
7. Mol, J.C., *J. Mol Catal. 65*:145 (1991).
8. Streck, R., *CHEMTECH 19*:498 (1989).
9. Amigues, P., Y. Chauvin, D. Commereuc, C.C. Lai, Y.H. Liu and J.M. Pan, *Hydrocarbon Processing 69*:79 (1990).
10. Freitas, E.R., and C.R. Gum, *Chem. Eng. Prog. 75 (1)*:73 (1979).
11. Chaumont, P., and C.S. John, *J. Mol. Catal. 46*:317 (1988).
12. Banks, R.L., D.S. Banasiak, P.S. Hudson and J.R. Norell, *Ibid. 15*:21 (1982).
13. Mol, J.C., and J.A. Moulijn, in *Catalysis: Science and Technology, Vol. 8*, edited by J.R. Anderson, and M. Boudart, Springer-Verlag, Berlin, Heidelberg, 1987, p. 69 and references therein.
14. van Dam, P.B., M.C. Mittelmeijer and C. Boelhouwer, *J. Chem. Soc. Chem. Commun.*:1221 (1972).
15. Mol, J.C., in *Olefin Metathesis and Polymerization Catalysts*, edited by Y. Imamoglu, B. Zümreoglu-Karan and A.J. Amass, Kluwer Academic Publishers, Dordrecht, 1990, p. 115.
16. Verkuijlen, E., F. Kapteijn, J.C. Mol and C. Boelhouwer, *J. Chem. Soc. Chem. Commun.*:198 (1977).
17. Sibeijn, M., A. Bliek, J.C. Mol and J.A. Moulijn, *Appl. Catal.*, in press (1994).
18. Kazansky, V.B., and B.N. Shelimov, *Res. Chem. Intermed. 15*:1 (1991).
19. Hérisson, J.L., and Y. Chauvin, *Makromol. Chem. 141*:161 (1970).
20. Ivin, K.J., *Olefin Metathesis*, Academic Press Inc., London, 1983.
21. Vikulov, K.A., I.V. Elev, B.N. Shelimov and Y.B. Kazansky, *J. Mol. Catal., 55*:126 (1989).
22. Spronk, R., A. Andreini and J.C. Mol, *Ibid. 65*:219 (1991).
23. Vikulov, K.A., B.N. Shelimkov and V.B. Kazansky, *Ibid. 72*:1 (1992).
24. Warwel, S., N. Döring and F.J. Biermanns, *Fat. Sci. Technol. 89*:335 (1987).
25. Olsthoorn, A.A., and C. Boelhouwer, *J. Catal. 44*:197 (1976).
26. Siebeijn, M., Metathesis of Unsaturated Esters over Supported Re_2O_7 and MoO_3 Catalysts, Ph.D. Thesis, University of Amsterdam, 1993, pp. 199–204.
27. Tsuji, J., and J. Hashiguchi, *J. Organometal. Chem. 218*:69 (1981).
28. Plugge, M.F.C., and J.C. Mol, *Synlett 7*:507 (1991).
29. Warwel, S., N. Döring and A. Deckers, *Fat Sci. Technol. 90*:25 (1988).
30. Warwel, S., and A. Deckers, *Tenside Surf. Det. 26*:4 (1989).
31. Banasiak, D., *J. Mol. Catal. 28*:107 (1985).
32. Warwel, S., *Erdöl, Ergas, Kohle 103(5)*:238 (1987).
33. Fischer, M., and H. Barzynski, in *Ullmanns Encyklopädie der technischen Chemie, Band 3*, edited by H. Buchholz-Meisenheimer, J. Frenzel and R. Pfefferkorn, Verlag Chemie, Weinheim, 1973, p. 305.
34. Sibeijn, M., J.A.R. van Veen, A. Bliek and J.A. Moulijn, *J. Catal. 145*:416 (1994).
35. Warwel, S., H.-G. Jägers and S. Thomas, *Fat. Sci. Technol. 94*:323 (1992).
36. Nelson, W.T., and L.F. Heckelsberg, *Ind. Eng. Chem. Prod. Res. Dev. 22*:178 (1983).

[Received November 3, 1993; accepted March 22, 1994]