Russian Chemical Reviews **63** (11) 937–944 (1994)
©1994 Russian Academy of Sciences and Turpion Ltd

UDC 541.128.49.35

Metal-complex catalysts in the hydrogenation of unsaturated glycerides of natural oils

S R Savel'ev, N F Noskova

Contents

I. Introduction 937
II. Carbonyl, chelate, and other complexes of the Group VIII transition metals 937
III. Ziegler–Natta catalysts 938

Abstract. Information on the use of organometallic catalysts for the hydrogenation of natural oils published since 1979 is reviewed. Organometallic systems of the Ziegler–Natta type are shown to be the most promising. The nature of the catalytic activity of complex organometallic hydrogenation systems is discussed. The bibliography includes 84 references.

I. Introduction

Catalytic hydrogenation is the method mainly used in the treatment of natural oils and fats, and is widely used, for example, in the production of detergents and greases, in the oiling of leathers, and in the preparation of esters, especially in the food products industry.

The industrial production of hydrogenated fats for foodstuffs and for technical applications is carried out in the presence of heterogeneous, suspended catalysts, mainly based on nickel or on nickel–copper (with or without carriers), and also on stationary catalysts.[1] However, heterogeneous catalysts for the hydrogenation of fats have some serious shortcomings: their activity and selectivity are relatively low, and high temperatures and pressures are needed to obtain adequate performance.

In recent years studies of the hydrogenation of fats in the presence of metal-complex catalyts have attracted wide interest. Homogeneous organometallic catalysts offer a high selectivity in the hydrogenation of fats. The most promising metal-complex catalysts were found to be those of the Ziegler–Natta type, with an activity not only much greater than the activity of heterogeneaeous catalysts but also adequate for low-temperature operation. This feature not only safeguards the biological properties of the fats but also offers substantial savings in energy.

In the last 10–15 years there has been a marked jump in our understanding of the nature of the catalytic activity of organometallic catalytic complexes. The combined use of Mössbauer, EPR, and IR spectroscopy, of magnetic susceptibility methods, etc. have made it clear that associated polynuclear complexes are responsible for the catalytic effects.

The aim in this review is to assess the state and the prospects of this new field of study: the development and application of metal-complex catalysts for the hydrogenation of the unsaturated glycerides of oils and fats. Much of the work on the Ziegler–Natta catalysts discussed in the review was carried out at the laboratory for organometallic catalysts of the Institute for Organic Catalysis and Electrochemistry of the National Academy of Sciences of the Republic of Kazakhstan.

S R Savel'ev, N F Noskova Laboratory of organometallic catalysts of the Institute of Organic Catalysis and Electrochemistry, National Academy of Sciences of the Republic of Kazakhstan, 142 ul. K Marxa, 480100 Alma-Ata. Tel. (7-3272) 61-9874

Received 4 July 1994
Uspekhi Khimii **63** (11) 995–1003 (1994); translated by J I Carasso

II. Carbonyl, chelate, and other complexes of the Group VIII transition metals

The main constituents of fats and oils are the triglycerides, containing radicals of saturated (palmitic, stearic, etc.) and of unsaturated fatty acids (oleic, linoleic, linolenic, etc.).

The first review of studies of homogeneous hydrogenation was published by James.[2] It dealt mainly with the work of Shashimoto, Frankel, and Cecchi.

James pointed out that a stage of positional isomerisation of the non-conjugated substrate (triene, diene) into the conjugated analogue precedes the hydrogenation of linolenate and of linoleate in the presence of metal carbonyls and of the phosphine complexes of Pt, Pd, and Ni. The substrate can be activated either directly or after the formation of the mono- or dihydride of the transition metal. Active catalytic systems can be formed after the dissociation of the ligand (as in the case of metal carbonyls), or alternatively they can be formed after solvation (acetylacetonates) or as a result of ligand substitution (platinum tin chloride systems).

Later studies were devoted to the kinetic properties, to establishing the nature of the catalytically active complexes, and to formulating practically convenient catalytic systems.

Ucciani et al.[3] showed that $HCo(CO)_3$ is the active component of catalytic sytems based on $Co_2(CO)_8$. He proposed a catalytic hydrogenation cycle in which the first activation stage includes the conjugation of the unsaturated compound. The description of a cobalt catalyst protected by an envelope of fully hydrogenated palm oil[4] is also of interest.

Of the known metal carbonyls the most promising catalysts for the hydrogenation of fats and oils are the arenechromium complexes, characterised by a high selectivity and a strong suppression of the *cis–trans* isomerisation processes.[5] Hydrogenation takes place slowly [approximately 0.1–0.6 mol H_2 (g-at Cr)$^{-1}$ min^{-1}] at temperatures above 423 K and hydrogen pressures of 2–10 MPa, and the composition of the liquid hydrogenated product is close to the fatty acid composition of oleic acid.

During hydrogenation in the presence of benzoato and polystyrene metal complexes[6] the conjugated esters of soya bean oil showed an enhanced selectivity towards the formation of dienes from trienes in comparison with the hydrogenation of nonconjugated esters, the content of *trans* isomers being only 1%–3%.

The activity of chromium carbonyls is increased by the action of ultraviolet radiation on the catalyst,[7] and also by supporting the catalyst on the surface of poly(phenylsilicon).[8] In the latter case the selectivity of the hydrogenation is also enhanced.

High selectivity is also found in other chromium carbonyl catalysts based on $Cr(CO)_3PPh_3$, which were studied[9] in connection with the hydrogenation of canola oil at 473 K and 1.7 MPa.

Among the chelates the acetylacetonates and bissalicylaldiminates are most often used for the hydrogenation of fatty acids and their methyl esters. The main advantage of these systems is the almost complete absence of conjugated dienes and *trans* isomers among the products (<0.1%). In the presence of palladium acetylacetonates hydrogenation is carried out at 323–353 K and 0.5–5.0 MPa (see Refs 10 and 11). Chelates of Pd(II), Pd(0), Ni(0), and Rh(I) were studied in the hydrogenation of the methyl esters of the acids in soya bean oil.[12] The reaction with $NaBH_4$ was used to activate the complexes. With high metal contents in the substrate (1–2 mass%) the hydrogenation proceeds at 323–373 K and 0.5–1.0 MPa with a selectivity close to that of heterogeneous catalysts.

By supporting the palladium complexes on phosphinated polystyrene[13] the reaction could be carried out under mild conditions (213–353 K and 0.1 MPa) with a low Pd content in the substrate (40 mg Pd per 1 kg of ester).

Workers at the Petrochemicals Synthesis Institute of the Russian Academy of Sciences have recently synthesised new highly active catalysts, based on complexes of palladium with ligands containing nitrogen and supported on Al_2O_3, for the hydrogenation of the triacetylglycerides of fats.[14–16] The catalysts performed successfully in tests on a large laboratory pilot plant model of an industrial hydrogenation reactor. IR spectroscopy results led to the conclusion[14–16] that in this case the catalytic activity is due to the hydride forms of palladium produced during the reaction.

The properties of cationic rhodium catalysts have been studied in depth during the hydrogenation of methyl linoleate and its isomers under mild conditions, using $[Rh(NBO)L_2]^+PF_6^-$ (L = $P(i\text{-}C_4H_9)_3$, $P(C_2H_5)_2(C_6H_5)$, and $P(CH_3)_3$; NBO is norbornadiene).[17] The course of the reaction depends on the nature of the ligand (catalyst). Thus, whereas in the presence of a catalyst with L = $P(C_2H_5)_2(C_6H_5)$ the hydrogenation of methyl linoleate proceeds through a conjugated intermediate state, when a catalyst with L = $P(CH_3)_3$ is used one of the C=C bonds is directly hydrogenated.

Systems of the type of $RhBr[P(C_6H_5)_3]_3$ and $[Rh(NBO)diphos]^+$ [where diphos is $(C_6H_5)_2P-CH_2-CH_2-P(C_6H_5)_2$] are active catalysts for the hydrogenation of fats, and they give products containing only low amounts of the *trans* isomers.[18–20]

The use of ruthenium complexes has been discussed,[21–26] and their high selectivity towards the formation of monoenes has been stressed. By depositing the complex $RuCl_3[As(C_6H_5)_3]_2 \cdot CH_3OH$ on montmorillonite and then reducing it to $RuCl_2(H_2)[As(C_6H_5)_3]_2$ (see Ref. 23) those workers were able to hydrogenate jujube oil, which contains the esters of the C_{40-44} acids and C_{20-22} alcohols, and also unsaturated acids in dioxan at atmospheric pressure and 293–318 K. When supported on clay the catalyst is stable and can undergo many cycles without significant changes in structure or in activity.

It has been concluded[26] that the active ruthenium catalyst prepared by dissolving $RuCl_3$ in ROH (R = $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_6H_{13}$, $n\text{-}C_8H_{17}$) is a hydride complex of ruthenium formed by the dissociation of the alkoxide of ruthenium in a hydrogen atmosphere.

III. Ziegler–Natta catalysts

1. Use of the catalysts in the hydrogenation of fats

Systematic studies of the hydrogenation of fats with catalysts of the Ziegler type have recently been reported from laboratories in Czechoslovakia,[27–34] France,[35–39] the USA,[40–42] and Kazakhstan.[43–58]

The first of these groups of workers used the pentadionates,[31] carboxylates,[32] acetylacetonates,[27,28] and n-butyl-salicylaldiminates[29] of nickel and other metals as catalysts, and triethylaluminium and sodium bis-(2-metoxyethoxy)dihydroaluminate, $NaAlH_2(OCH_2CH_2OCH_3)_2$ as the alkylating component. The hydrogenation takes place both with and without a solvent. As reported,[28] the methyl esters of soya bean oil were hydrogenated under mild conditions for a catalyst concentration of 0.05% Ni in the substrate and an Al:Ni component ratio in the catalyst varying from 0.2 to 3.0. The need to use a molar excess of the organoaluminium component has been explained[28] by postulating the hydrogenation mechanism proposed by Sloane:[59]

$$AlR_3 + NiX_2 \longrightarrow R_2AlX + RNiX,$$

$$RNiX + H_2 \longrightarrow RH + HNiX,$$

$$\backslash C{=}C / + HNiX \longrightarrow HC(\backslash)-C(/)-NiX,$$

$$HC(\backslash)-C(/)-NiX + H_2 \longrightarrow HC(\backslash)-CH(/) + HNiX.$$

It is suggested that under the chosen conditions the alkylation of NiX_2 is acceptably fast only at high enough concentrations of triethylaluminium in the reaction mixture. The authors[28] do not limit the role of the aluminium alkyl to the initial activation of the system: they assume the possibility of alkylation of the dimeric nickel compound $(NiX)_2$ formed by the reaction

$$HC(\backslash)-C(/)-NiX + HNiX \longrightarrow HC(\backslash)-CH(/) + (NiX)_2.$$

Systems based on $NaAlH_2(OCH_2CH_2OCH_3)_2$, unlike those based on triethylaluminium, are effective in the hydrogenation of fats even with no solvent (353–423 K, 0.1–2.0 MPa).[27,28]

Since one of the main obstacles to the practical use of Ziegler catalysts in the hydrogenation of fats is the difficulty of separating them from the final product and of using them repeatedly there has been great interest in a method of hydrogenating the esters of unsaturated fatty acids using nickel bis-(n-butylsalicylaldiminate supported on oxide carriers (aluminosilicate or aluminium oxide), or activated $Al(C_2H_5)_3$ or $AlCl(C_2H_5)_2$ (see Ref. 29). At 293–298 K and hydrogen pressures of 0.1–0.15 MPa rapeseed oil was satisfactorily hydrogenated re-using the catalyst three times without any loss of activity [the specific rate of the hydrogenation was W_{sp} = 1.2–20.5 mol H_2 (g-at Ni)$^{-1}$ min^{-1}]. The catalyst was separated from the product by simple filtration.

In the case of an unsaturated catalyst the separation required special procedures such as treating the solution with concentrated phosphoric acid or an aqueous solution of the same acid,[34] and saponification with an aqueous solution of metal hydroxide or carbonate at 313–353 K (see Ref. 33).

French workers have made valuable contributions to studies of the hydrogenation of fats by assigning the Ziegler catalysts to the 'superactive' class.[35] By hydrogenating five tonnes of castor oil in an industrial plant at a relatively low temperature (433 K) and hydrogen pressure (1.5 MPa) they established that the activity of the Ziegler nickel catalysts is 22 times greater than the activity of heterogeneous industrial nickel.[35] They suggested[35] that the low concentration of the nickel (between 10 and 200 ppm) and its high activity should more than outweigh the cost of the Ziegler catalyst.

The hydrogenation of castor oil on these catalysts is selective, and the unwanted 12-ketostearic acid is formed in negligibly small amounts, which is an additional advantage of these systems over the heterogeneous nickel catalysts. Futhermore an original and economical way of separating the catalyst from the product was found. Vigorous stirring of the hydrogenation product with 10% of water at 373 K produces a precipitate from which a final product containing only 0.0001% of Ni can be separated by filtration with 0.2% of coactivator.

The work of the French scientists stimulated world-wide interest, and was patented in 10 countries. These disclosures [36,37] described the hydrogenation of solvent-free soya bean oil with a catalyst prepared from a transition metal salt and a hot concentrated solution of aluminium alkyl, which is undoubtedly the main drawback of this method. A wide range of transition metals was specified as hydrogenation catalysts (Ni, Cr, Ag, Cu, Ni–Ag, Ni–Mn, Ni–Fe, Ni–Cu) in the form of palmitates, stearates, oleates, octoates, etc. Metal complexes supported on oxide carriers (Al_2O_3, SiO_2, Cr_2O_3) were used in some experiments. It was shown that the most active of these catalysts is nickel stearate ($NiSt_2$) [W_{sp} = 16.3 mol H_2 (g-at Ni)$^{-1}$min^{-1}], and that with this catalyst the selectivity of the conversion of dienes into monoenes can reach 76%. Highly selective catalysts based on $NiSt_2$–$CuSt_2$ and on $Ni(acac)_2Py_2$ have a low activity [W_{sp} = 0.63 and 0.9 mol H_2 (g-at Ni)$^{-1}$ min^{-1} respectively].

A modelling method based on the chemical introduction of labels into linolenic, linoleic, and oleic acid chains has been used to explain the mechanism of the selective hydrogenation of fats. [38] It was shown that linolenic acid hydrogenated on a nickel catalyst to the complete conversion of the triene contains not only 3.5%–5.0% of the diene but also 3%–4% of the monoene (the initial concentration of linolenic acid was 7%–10%). Therefore the saturation of the triene is accompanied by saturation of the resulting diene.

Simultaneous saturation of the diene and the monoene takes place during the hydrogenation of the methyl esters of soya bean oil. [39] A catalytic cycle including a complex of Ni(0) with a coordinated diene and monoene has been proposed [39] on the basis of the observation that the oxidative addition of hydrogen takes place after the coordination of the substrate (with the metal) to the so-called 'exposed nickel' by the scheme

$$Ni(OOCR)_2 + Al(C_2H_5)_3 \longrightarrow \longrightarrow Ni(C_2H_5)_2 + Al(C_2H_5)(OOCR)_2,$$

$$Ni(C_2H_5)_2 \longrightarrow Ni^0 + 2(C_2H_5)^{\cdot},$$

$$2(C_2H_5)^{\cdot} \longrightarrow C_2H_4 + C_2H_6.$$

The main conclusion reached [39] in respect of the selectivity of these systems is that the final product contains an enhanced amount of stearate: this is thought to be an unavoidable disadvantage of the nickel Ziegler catalysts.

However, as will be shown below, by using some strictly defined catalyst preparation conditions and an Al-organic component (of the alumoxane type) we can obtain nickel systems in which the hydrogenation of a diene to a monoene takes place with a selectivity of 93%–100%.

A selective catalyst for the hydrogenation of the linolenate to the linoleate in soya bean oil, based on copper stearate with triethylaluminium and diethylmagnesium, has been described. [40] At 443 K, with a hydrogen pressure up to 1.5 MPa and a copper concentration in the oil of 0.1%–0.025%, the concentration of linolenate in the product could be lowered to 0.75% while the concentration of stearate increased from 3.9% to 5.2%. An increase in the activity of these systems was achieved by using trialkylsilicon as the alkylating component, but in this case the selectivity was slightly suppressed. [41]

A detailed description of the properties of copper catalysts and of the methods of increasing their activity has been published. [40] The activity of the copper catalysts is strongly influenced by the nature of the alkylating component, whose favourable effect increases in the sequence

$$Al(C_2H_5)_3 < Al(C_2H_5)_2(OC_2H_5) < < Mg(C_2H_5)_2 < AlH(i\text{-}C_4H_9)_2 < Al(n\text{-}C_4H_9)_3.$$

The addition of aluminium oxide to the $CuSt_2$–$Al(C_2H_5)_3$ catalyst increased its activity five-fold. [42] This activating action of the Al_2O_3 was explained by the adsorption on the carrier of harmful impurities (phosphatides, free fatty acids, etc.) which poisoned the catalyst. An experiment on the hydrogenation of soya bean oil with the addition of various amounts of ethanol has been described. [42] The addition of 0.5% of ethanol lowers the iodine number by 20 units (i.e. it activates the catalyst) as compared with the catalyst without the addition. Additions of 1%–2% of ethanol have the opposite effect, and in the presence of 5% of ethanol the hydrogenation of the oil is almost totally suppressed. According to Koritala [42] this is because of the interaction between ethanol and $Al(C_2H_5)_3$. A concentration of ethanol of 0.5% is sufficient to replace one ethyl group in the $Al(C_2H_5)_3$ by an ethoxy group; the resulting $Al(OC_2H_5)(C_2H_5)_2$ produces a better catalyst with the copper stearate than $Al(C_2H_5)_3$. At higher ethanol concentrations the triethylaluminium begins to decompose.

A programme of studies [43–53] of the hydrogenation of sunflower oil in a solvent (heptane) at 293–353 K involved a wide range of catalysts based on nickel, cobalt, chromium, copper, and iron stearates, and their mixtures with an alkylating agent (triethylaluminium). The following sequence of activities was noted: $NiSt_2 > CoSt_2 \gg FeSt_3 > CrSt_3 > CuSt_2$. The Al:M ratio needed to prepare the catalysts with the greatest hydrogenation activity was strongly temperature-dependent. The kinetic order was zero with respect to the substrate and close to unity with respect to the catalyst and the hydrogen. In every case the selectivity of the hydrogenation of linoleate to oleate increased with temperature and with the concentration of the substrate.

Supporting the stearates of Ni, Co, and Fe on Al_2O_3 increased the activity of the organometallic catalysts in solution, but lowered their selectivity. [45–48] The $NiSt_2/Al_2O_3$–$Al(C_2H_5)_3$ catalyst was proposed for the preparation of tristearin under mild conditions. [49]

The greatest increase in the activity of the catalyst by depositing it on a carrier (almost 60-fold as compared with the unsupported catalyst) was achieved in the $FeSt_3/Ni(OH)_2$–$Al(C_2H_5)_3$ system (see Ref. 50). The maximum rate [225.1 mol H_2 (g-at Fe)$^{-1}$ min^{-1}] was observed for a 50% content of the iron stearate on $Ni(OH)_2$.

With the aim of intensifying the hydrogenation of vegetable oils in solvents, Marusich and Noskova [51] examined the use of donor additives to the $NiSt_2$–$Al(C_2H_5)_3$ catalyst (water, glycerol, the tributyl ester of phosphoric acid, and ethanol). The additives increased the rate of the reaction by a factor of 1.2–1.8. The highest rates were observed for the following ratios between the additive and the nickel: 5:1 (water and ethanol), 1:1 (tributyl phosphate), and 5:1 (glycerol). Unlike Koritala, [42] who attributed the activating effect of ethanol to the formation of ethoxy groups, Marusich and Noskova [51] postulated the formation (in the case of water and ethanol) of alkylalumoxanes, i.e. of compounds containing an Al–O–Al group [$R_2Al(OAlR)_nOAlR_2$]. In fact, special experiments with different alkylalumoxanes [54–81] produced very active, selective, and thermally stable catalysts for the hydrogenation of fats.

Table 1. Effect of the nature of the Al-organic component of an organonickel catalyst on the activity, selectivity, and thermodynamic characteristics of the hydrogenation of the glycerides of sunflower seed oil (for the optimum Al : Ni ratios).

Al-organic catalyst	T/ K	Solvent	W_{sp}/ mol H_2 (g-at Ni)$^{-1}$ min^{-1}	S(%)	$10^2 k$/ min^{-1}	ΔE^*/[a] kJ mol^{-1}	ΔS^*/[b] e. u.
$Al(C_2H_5)_3$	313	Heptane	78.0	87.5	1.8	17.4	−0.24
	423	none	14.8	94.6	–	30.7	−0.20
$Al(i\text{-}C_4H_9)_3$	313	Heptane	76.0	89.0	1.2	24.6	−0.20
	423	none	21.8	93.0	–	26.1	−0.21
$Al(C_9H_{19})_3$	313	Heptane	48.0	90.5	0.29	30.1	−0.19
	423	none	9.0	94.6	–	28.3	−0.19
$Al_{21}O_{19}(C_2H_5)_{23}$	313	Heptane	24.5	91.0	0.9	24.0	−0.16
	353	none	5.9	99.8	–	33.1	−0.22
$Al_2O(i\text{-}C_4H_9)_4$	313	Heptane	72.0	84.5	1.2	19.6	−0.20
	423	none	49.8	99.8	–	22.5	−0.21
$Al_8O_7(i\text{-}C_4H_9)_{10}$	313	Heptane	42.0	85.0	0.5	27.1	−0.18
	423	none	27.7	98.3	–	–	–

[a] ΔE^* is the apparent activation energy. [b] ΔS^* is the entropy of activation.

Noskova and co-workers [69, 70] used a wide range of aluminium trialkyls (R = C_2H_5, i-C_4H_9, C_9H_{19}) and alumoxanes (R = C_2H_5 and i-C_4H_9 and n = 0, 2, 4, 8, 18, and 21) as alkylating components, and found that in the absence of a solvent the selectivity of the hydrogenation is almost unaffected by the nature of the alkyl radical (Table 1). Therefore the ratios of the stability constants of the complexes with linoleate and with oleate and those of the rate of transformation of linoleate and oleate are not very different for complexes with different R. On the other hand the suppression of the rate of hydrogenation at 313 K by increasing the molecular mass of the organoaluminium compound is explained by the decrease in reducing power in the series C_2H_5, i-C_4H_9, C_9H_{19} and by the increased steric hindrance to the activation of the substrate.

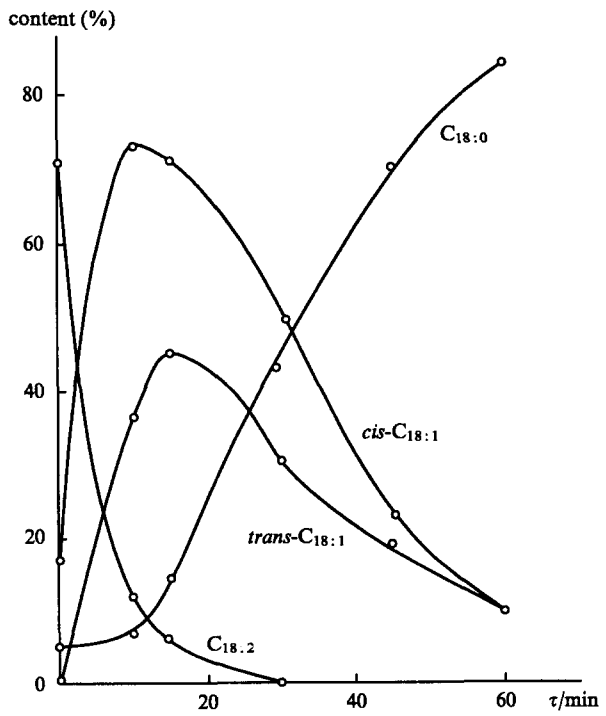


Figure 1. Kinetics of the hydrogenation of sunflower oil: changes in the fatty acid composition of the catalysate obtained on $NiSt_2-Al_2O(C_2H_5)_4$ (Al : Ni = 11, 423 K, 0.05% Ni in oil).

An oil without solvent is hydrogenated more slowly than in heptane (see Table 1). In the absence of a solvent the reaction takes place on all the catalysts with a selectivity of 92% – 100% towards the conversion of linoleate into oleate.

The kinetics of the hydrogenation of sunflower seed oil (1 kg) and the change in the fatty acid composition at 423 K and atmospheric pressure are shown in Fig. 1. The hydrogenation of the linoleate in the presence of 0.047% of Ni in the oil goes practically to completion in the first 15 minutes, during which the concentration of stearate increases from 4.5% to 16%. The rate of hydrogenation of the *trans* unsaturated isomers is lower than the rate of hydrogenation of the linoleate and of the *cis* isomers of oleic acid. After 60 min 11% of the *trans* isomer of oleic acid is the only unsaturated acid remaining in the oil.

Comparing the activities of the organometallic catalyst $NiSt_2-(i\text{-}C_4H_9)_2Al_2OAl(i\text{-}C_4H_9)_2$ with that of the industrial heterogeneous catalyst DM-3 (USA) showed that in the presence of the former a 60% – 63% conversion of the ester is achieved in 10 – 15 min of hydrogenation at 423 K, whereas in the presence of DM-3 the same extent of conversion requires 60 min at 473 K.

Using Ziegler catalysts based on $NiSt_2-Al(C_2H_5)_3$ at 423 K under a pressure of 1.0 – 9.0 MPa the hydrogenation of the ethyl esters of fatty acids can be controlled towards the formation of saturated fatty acids. [71]

A catalyst similar to the Ziegler systems was obtained [72] by activating $Ti(C_5H_5)Cl_2$ with magnesium. The authors stressed [72] that this catalyst is effective in the hydrogenation of methyl linoleate at room temperature, but only in the presence of triphenylphosphine.

2. Nature of the catalytically active complexes

A detailed study [69] of the catalysts based on $FeSt_3-Al(C_2H_5)_3$ by Mössbauer, IR and EPR spectroscopy, magnetic susceptibility, and other methods allowed their structure to be established. High-spin Fe(III) and Fe(II) complexes were detected, and also polynuclear (at the transition metal) associated formations containing bound iron ions. All the complexes are mutually in a dynamic equilibrium depending on the genesis of the catalyst (relative concentrations of aluminium and iron, temperature of the process, carrier, nature and concentration of the solvent and of the gases, atmosphere, time of formation of the complex, presence and nature of a substrate). Polynuclear associations are formed as a result of the interaction of complexes of different valencies between the transition metal and the trialkylaluminium. Calculations of the number of transition metal ions in the association showed that for an Al/Fe ratio of 7 – 9 up to several tens of iron ions may be present.

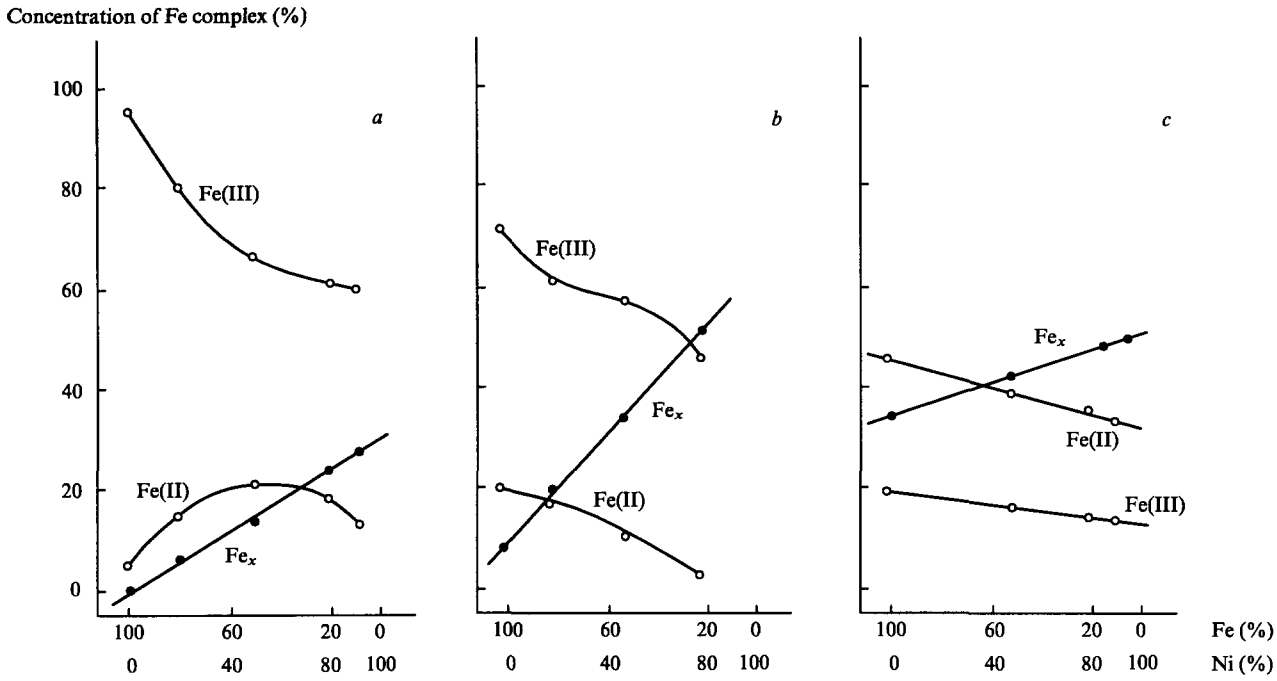


Figure 2. Changes in the concentration of the iron complexes as a function of the composition of the mixed $NiSt_2-FeSt_3-Al(C_2H_5)_3$ (293 K, $[\Sigma M] = 0.28 \times 10^{-3}$ mol); Al : ΣM: (*a*) 2; (*b*) 4; (*c*) 7.

An analysis of the dependence of the rates of hydrogenation of various unsaturated compounds on the concentration of the complex in the system showed unambiguously that the activity of organometallic catalysts is due to the presence of polynuclear complexes in the system.[60,61]

The polynuclear nature of the active complex was confirmed by a reverse synthesis which gave effective catalytic systems from undoubtedly polynuclear complexes of iron and of iron with chromium.[62-64] Active complexes of organometallic catalysts having a cluster nature have also been suggested.[65,66]

Ideas on the polynuclear nature of the active complexes of hydrogenation catalysts of the Ziegler–Natta type led to the belief that synergic systems could be obtained by mixing (in the synthesis) the salts of different transition metals or by supporting the salt of one transition metal on the hydroxide of another.[50,53,73] It was shown that mixed catalysts are not a simple mixture of the complexes of individual transition metals. The conclusion was that an ion of the second transition metal enters into the composition of the combined polynuclear complex, and forms a single system with the ion of the typical metal. As a result of partial reduction and electron transfer processes the transition metals in the conjugated system of the complex have a mixed valency, which enhances the reactivity of the complex.

The $^{57}FeSt_3-NiSt_2-Al(C_2H_5)_3$ catalysts have been studied by Mössbauer spectroscopy. Parallel tests of their catalytic activity towards the hydrogenation of sunflower oil were also carried out. By processing the spectra it was shown[67] that the system contains a set of iron complexes similar to that found in the system based on $^{57}FeSt_3-Al(C_2H_5)_3$ (see Ref. 60).

The Mössbauer parameters of the corresponding complexes in the two systems have similar values. The Fe : Ni ratio has little effect on the Mössbauer spectra of the complexes, but the relative concentration of the complexes is strongly dependent on this ratio. Fig. 2 shows the relative concentration of the various iron complexes [the high-spin Fe(III) and Fe(II), and the associated polynuclear Fe_x] in the $^{57}FeSt_3-NiSt_2-Al(C_2H_5)_3$ system with 10, 20, 50, and 80 mol% of Ni and a ratio of Al : ΣM = 2, 4, and 7.

For each value of Al : ΣM the relative concentration of Fe(III) complexes decreases as the concentration of nickel stearate is increased, i.e. reduction processes are assisted by additions of $NiSt_2$. At the same time the relative concentration of associated polynuclear complexes increases almost linearly with the concentration of added stearate. The composition of the system is most strongly influenced by an increase in the content of $NiSt_2$ for a ratio of Al : ΣM < 4; for Al : ΣM = 7 these changes are much less marked, and for Al : ΣM > 7 they effectively vanish.

The increase in the content of polynuclear formations can be associated both with the fact that reduction processes are facilitated (as indicated by the most probable mechanism for the formation of polynuclear associations[60,61,68]) and with formation of stable polynuclear complexes when nickel is included in their composition. In the latter case the dynamic equilibrium between the associations and the other transition metal complexes is displaced towards the associations. This seems all the more likely in view of the tendency for mixed (heteroatomic) cluster complexes to be more stable than their analogues with atoms of one transition metal.[66]

The dependence of the composition of the $^{57}FeSt_3-NiSt_2-Al(C_2H_5)_3$ system and of its catalytic activity in the hydrogenation processes of fats on the amount of nickel stearate can be used to identify the complexes leading to hydrogenation. Property–composition correlation dependences show that [as in the systems[61] based on $^{57}FeSt_3-Al(C_2H_5)_3$] polar associated formations are responsible for the activity of the mixed systems, since a straight-line dependence is observed only between their concentration and the rate of hydrogenation (Fig. 3).

As can be seen from Table 1 the entropy of activation calculated for the formation of the intermediate active complex is negative for all the compositions of the catalyst and all the conditions of the process. Negative entropies are usually observed for the interaction of initial reactants including a bimolecular rate-limiting step, whose transition state is reached by the approach of the reactants (for example, the coordination of the substrate molecules with the metal ions),[74] i.e. for reactions passing through an associative transition state, probably by a concerted

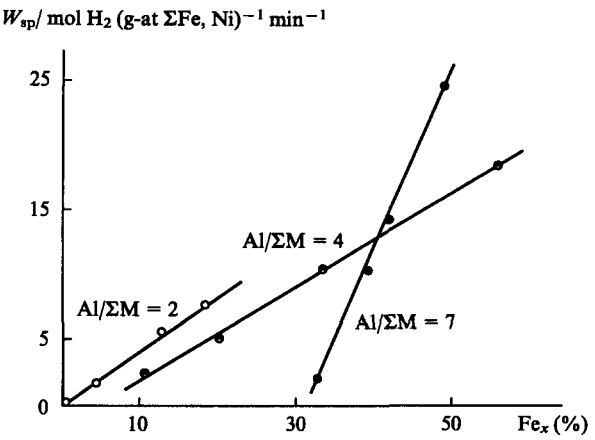


Figure 3. Dependence of the specific rate of hydrogenation of the linoleate from sunflower oil on the concentration of polynuclear Fe complexes in a mixed Ni–Fe catalyst.

(synchronous) mechanism. The latter is usually characterised by a zero or negative entropy of activation, and by a relatively low activation barrier, smaller than the dissociation energies of the weakest chemical bonds assumed in the adjusted process.[66] It can be seen from Table 1 that the apparent activation energy for the process is relatively low (17–34 kJ mol^{-1}). It seems probable that the coordination of hydrogen and of an unsaturated compound on a polynuclear complex involves their strict mutual orientation, with a decrease in the entropy of the active complex, and that a more or less synchronous exchange interaction of the coordinated substrate and hydrogen takes place during the rate-limiting step of the hydrogenation process.

Systematic studies of organometallic catalysts for the hydrogenation of fats, and the resulting evidence for the presence of catalytically active polynuclear and polyvalent complexes and of a dynamic equilibrium between the poly- and the mononuclear transition metal complexes, led to the suggestion[56,69,70,73] that

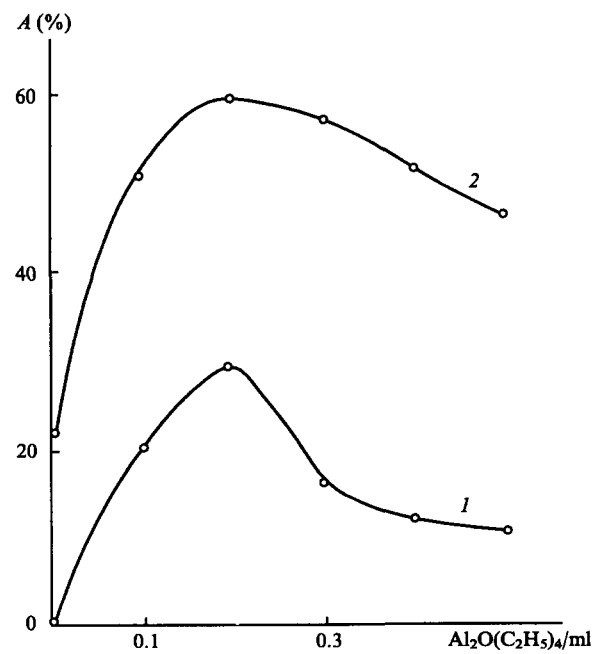


Figure 4. Effect of tetraethylalumoxane additions on the activity (*A*) of a Ni–Cu catalyst in the hydrogenation of sunflower oil at 473 K. Mass of Ni–Cu catalyst: (*1*) 0.03, (*2*) 0.1 g.

these catalysts (like organoaluminium compounds[56]) should be used as additives to heterogeneous catalysts in order to obtain heteropolynuclear and heterovalent complexes (clusters) on the surface of the latter. The following concepts were formulated: (1) the surface of heterogeneous metallic catalysts contains polynuclear (cluster) complexes; (2) there is a similarity between the coordinating powers of the metal atoms on the surface and in the metal complexes;[76–78] (3) like the compounds of the transition metals in solution the surface clusters can interact with Al-organic compounds and form active organometallic catalysts on the surface.

Thus, as shown in Fig. 4, the addition of tetraethylalumoxane to a low-activity nickel–copper heterogeneous catalyst of the VNIIZh-2 type (Ni:Cu = 1:2) increased its activity from 3%–20% to 30%–60%. The experimentally observed dependence of the activity of the catalyst on the amount of added alkyl-alumoxane can be explained by the similarly extremal relationships found in Ziegler catalysts.

Initially, at low concentrations of the Al-organic compound, the activity of the heterogeneous catalyst increased, both as a result of the faster reduction of the metals on the surface (according to ESCA data) and as a result of the formation of coordinated systems with the Al-organic compound on the surface. A further increase in the amount of Al-organic compound led to complex formation and blocking of the transition metal atoms on the surface by aluminium, which lowered the activity of the catalyst. This effect can be clearly seen at low concentrations of the heterogeneous catalyst (0.02%), when the Ni–Cu catalyst is almost completely inactive under the chosen conditions but the addition of tetraethylalumoxane can 'revive' it.

We shall complete our review of this series of papers[43–58,63,64,69,70,73] by summarising their most significant results.

The problem of synthesising a new generation of catalysts for the transformation of fats called for the development of concepts on the nature of the catalytically active complexes, for a detailed study of the changes in activity produced by changes in the genesis conditions (relative amount of the catalyst components, temperature, hydrogen pressure, concentration of catalyst, nature of the organic radical in the organoaluminium component of the catalyst, etc.), and for the determination of the kinetic and thermodynamic characteristics of the hydrogenation process and also of the selectivity and stability of the catalytic systems and of the composition of the final product.

Starting from a qualitative examination of the structure of the active polynuclear complex, and from Mössbauer spectroscopy data on the effect of the nature of the added compound on the irreversible or reversible (depending on the nature of the substrate) decomposition of this complex,[60] it was suggested that a substantial destabilisation of the polynuclear complex during the coordination of compounds such as fats in a solvent is caused by the localisation of charge on one bond of the resulting π complex induced by the strong π-acceptor properties of the substrate. In order to prevent the decomposition of the complex and to create an excess electron density on the conjugation chain in the polynuclear system it was suggested that donor additives should be used and that the nature of the aluminium component should be changed [replacing the traditional $Al(C_2H_5)_3$ by alkylalumoxanes]. These new concepts led to the development of a qualitatively new approach to the synthesis and production technology or organometallic Ziegler catalysts which overcame the serious shortcomings of AlR_3 catalysts (fire and explosion hazards) responsible for limitations and complications in the use of organometallic catalysts.

In the construction of catalytic systems it was possible to increase substantially the stability of the catalyst by creating conditions which suppressed the association of the polynuclear complexes (preparation of the catalyst in a vegetable oil, supporting the catalyst on a carrier). These changes allowed the catalysts to retain their initial activity for long periods.

Table 2. Hydrogenation of vegetable oils in n-heptane in the presence of metal-complex catalysts.

Catalytic system	Reaction conditions		% M in oil	Oil	W_{sp}/mol H_2, (g-at M)$^{-1}$ min^{-1}	S(%)	Ref.
	T/ K	p_{H_2}/ MPa					
$Co_2(CO)_8$	473	3.0[a]	0.09	Soya	1.0	83	3
$Pd(acac)_2$	333	1.5[a]	0.006	"	9.0	89	11
$H_2PtCl_2-SnCl_2$	313	0.1[a]	0.004	"	0.1	97	83
$Ni(acac)_2-Al(C_2H_5)_3$	293	0.12	0.05	MESO[b]	20.2	90	27
$Ni(acac)_2-NaAlH_2R_2$	293	0.12	0.05	"	17.2	91	27
$NiSt_2-Al(C_2H_5)_3$	373	1.0[c]	0.025	Soya	16.3	73	27
$NiSt_2-CuSt_2-Al(C_2H_5)_3$	393	2.0[c]	0.05	"	0.62	91	31
$Ni(acac)_2Py_2-Al(C_2H_5)_3$	333	3.0[c]	0.1	"	0.9	95	36
$CuSt_2-Al(C_2H_5)_3$	473	1.5[c]	0.05	"	2.0	95	42
$NiSt_2-Al(C_2H_5)_3$	293	0.1	0.1	Sunflower	21.0	84	84
	313	0.1	0.1	"	33.0	86	84
	333	0.1	0.1	"	79.0	92	84
$FeSt_3-Al(C_2H_5)_3$	293	0.1	0.4	"	1.2	82	47
	313	0.1	0.4	"	2.0	86	47
	333	0.1	0.4	"	2.8	90	47
$CoSt_2-Al(C_2H_5)_3$	293	0.1	0.1	"	20.0	81	45
	313	0.1	0.1	"	33.0	95	45
$CuSt_2-Al(C_2H_5)_3$	333	0.1	0.4	"	0.08	84	84
50%-$FeSt_3/Ni(OH)_2$ — $-Al(C_2H_5)_3$	313	0.1	0.1	"	59.0	83	50
	333	0.1	0.1	"	149.0	93	50
$NiSt_2-Al_2O(C_2H_5)_4$	333	0.1	0.05	"	200.0	93	55, 70
$NiSt_2-Al_2O(C_2H_5)_4$	353	0.1	0.05	"	4.8	99	55, 70
	473	0.1[c]	0.05	"	64.0	100	55, 70

[a] Solvent: acetic acid. [b] MESO are the methyl esters of soya bean oil. [c] The reaction was carried out without a solvent.

Thus, Ni-organic catalysts with alumoxanes in oil showed no loss of activity after three years' storage in closed vessels.

The new ideas on the polynuclear character of the catalytically active complex led to the synthesis of mixed Ni–M catalysts (M = Fe, Co, Cr, Cu). Using the $NiSt_2-FeSt_3-Al(C_2H_5)_3$ system an increase in the number of heteropolynuclear complexes was achieved, and a straight-line dependence of the activity of the complexes on the concentration of $NiSt_2$ was established. The position of the maximum on the rate–composition curve for mixed catalysts under different conditions is determined by the Ni : M ratio (M is the transition metals), i. e. we have a cluster effect.

Allowance for the polynuclear and polyvalent nature of the active complexes in catalysts of the Ziegler–Natta type, and also in the surface layers of heterogeneous catalysts, led to a method of activation of industrial heterogeneous catalysts by small additions of an organometallic catalyst or of an organic aluminium compound.

The 'construction' of organometallic systems by varying the composition of the cocatalyst, by supporting the active complex on a carrier, or by synthesising it on the surface of a low-activity heterogeneous catalyst allowed organometallic catalysts to be used in some processes of practical importance, such as the selective hydrogenation of fats and the transesterification of glycerides (aimed at accelerating the production and improving the quality of a group of food products manufactured by the 'margarine industry')[79] or the positional isomerisation of non-conjugated linoleate (aimed at accelerating the production of drying oils and of conjugated dienes for organic synthesis).[80–83]

Table 2 summarises the information from various sources on the use of metal-complex catalysts in the hydrogenation of the unsaturated glycerides of natural oils. By outlining the main results obtained since 1979 the Table allows us to compare the effectiveness of metal-complex catalysts of various types.

References

1. A G Sergeev (Ed.) *Gidrogenizatsiya i Pereeterifikatsiya Zhirov i Masel* (Hydrogenation and Ester Interchange of Fats and Oils) Vol. 3 (I) (Leningrad: Maslozhirprom, 1985)
2. B James *Homogeneous Hydrogenation* (Translated into Russian; Moscow: Mir, 1976)
3. E Ucciani, G Cecchi, G Mallet *Rev. fr. Corps Gras.* **24** 225 (1979)
4. E Ucciani, G Cecchi, A Bonfand *Rev. fr. Corps Gras.* **29** 219 (1982)
5. L L Diosady, W F Graidon, S S Koseoglu *Can. Inst. Food Sci. Technol.* **17** 218 (1984)
6. S Koritala, E N Frankel *J. Am. Oil Chem. Soc.* **58** 553 (1981)
7. I A Heldal, E N Frankel *J. Am. Oil Chem. Soc.* **62** 1044 (1985)
8. R A Awl, E N Frankel *J. Am. Oil Chem. Soc.* **58** 557 (1981)
9. P A Berstein, W F Graydon, L L Diosady *J. Am. Oil Chem. Soc.* **66** 680 (1989)
10. I A Heldal, E N Frankel *J. Am. Oil Chem. Soc.* **61** 756 (1984)
11. S Koritala *J. Am. Oil Chem. Soc.* **62** 517 (1985)
12. E N Frankel, J P Friedrich, T R Bessler *J. Am. Oil Chem. Soc.* **57** 349 (1980)
13. C Andersson, R Larsson *J. Am. Oil Chem. Soc.* **58** 675 (1981)
14. N G Bazhirova, A V Novikova, N V Komarov *Kinetika Gidrirovaniya Triatsilglitseridov v Prisutstvii Pd-soderzhashchikh Katalizatorov* (Moscow, 1989) (Kinetics of Hydrogenation of Triacetins in the Presence of Pd-containing Catalysts) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No 3042-I (in Russian)
15. N V Komarov, A N Arutyunyan, V Kh Paronyan *Tsis-transizomerizatsiya v Protsesse Gidrirovaniya Rastitel'nogo Masla na Pd-katalizatore* (*Cis-Trans*-isomerisation in the Hydrogenation of Vegetable Oil on a Pd catalyst) (Moscow, 1990) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No 2295-V (in Russian)
16. N V Komarov, L P Abramova, V Kh Paronyan *Issledovanie i Modelirovanie Protsessa Gidrirovaniya Podsolnechnogo Masla na Pd-katalizatore* (Investigation and Modelling of the Hydrogenation of Sunflower Oil on a Pd catalyst) (Moscow, 1990) Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI), No 2296-V (in Russian)

17. P van der Plank, A van der Ent *J. Am. Oil Chem. Soc.* **57** 343 (1980)
18. W I Bland, T C Dine, R Iobanputra *J. Am. Oil Chem. Soc.* **62** 924 (1985)
19. M Berglund, C Andersson *J. Am. Oil Chem. Soc.* **61** 1351 (1984)
20. I A Heldal, E N Frankel *J. Am. Oil Chem. Soc.* **62** 1117 (1985)
21. T Nishiguchi, K Fukuzumi, F Kimura *Gukaguku* **32** 726 (1983)
22. C Bello, L Diosaky, W Graydon *J. Am. Oil Chem. Soc.* **62** 1587 (1985)
23. M Taqui Khan, M Siddiqui, in *V Mezhdunar. Simp. po Svyazi mezhdu Gomogennym i Geterogennym Katalizom (Tez. Dokl.)* (Abstracts of Reports at the Fifth International Symposium on the Bond between Homogeneous and Heterogeneous Catalysis) (Novosibirsk: Institute of Catalysis, Siberian Division of the Academy of Sciences, USSR, 1986) p. 226
24. M Taqui Khan, S Samad, M Siddiqui *J. Mol. Catal.* **50** 97 (1989)
25. US P. 4 963 295; *Ref. Zh. Khim.* 17 R 1 355P (1991)
26. D Mudesh, C S Narasimhan, K Ramnarayan *Ind. Eng. Chem. Res.* **28** 1261 (1989)
27. P Svoboda, J Hetfleijs, J Soucek *Chem. Prum.* **30** 89 (1980)
28. Z Vankova, P Svoboda, J Hetfleijs *Chem. Prum.* **31** 132 (1981)
29. Czech. P. 209 695; *Chem. Abstr.* **98** 34 276h (1983)
30. Czech. P. 197 143; *Chem. Abstr.* **97** 55 589g (1982)
31. Czech. P. 197 144; *Chem. Abstr.* **97** 109 783w (1982)
32. Czech. P. 209 573; *Chem. Abstr.* **98** 18 465p (1983)
33. Czech. P. 216 087; *Chem. Abstr.* **101** 24 073h (1984)
34. Czech. P. 214 531; *Chem. Abstr.* **101** 191 167w (1984)
35. G Cecchi, E Ucciani *Riv. Ital. Sostanze Grasse* **56** 235 (1979)
36. French P. 2 259 896; *Chem. Abstr.* **95** 63 729w (1980)
37. US P. 4 038 295; *Chem. Abstr.* **94** 9 712h (1980)
38. G Mallet, E Ucciani *Rev. fr. Corps Gras.* **27** 71 (1980)
39. G Cecchi, G Mallet, E Ucciani *Riv. Ital. Sostanze Grasse* **58** 228 (1981)
40. US P. 4 273 722; *Chem. Abstr.* **97** 13 826p (1982)
41. S Koritala *J. Am. Oil Chem. Soc.* **58** 701 (1981)
42. S Koritala *J. Am. Oil Chem. Soc.* **59** 309 (1982)
43. N F Noskova, D V Sokol'skii *Kinet. Katal.* **23** 1382 (1982)
44. N F Noskova, N I Marusich, G N Sharifkanova, in *V Vsesoyuz. Konf. po Kataliticheskim Reaktsiyam v Zhidkoi Faze (Tez. Dokl.)* (Abstracts of Reports at the Fifth All-Union Conference on Catalytic Reactions in the Liquid Phase) (Alma-Ata: Nauka, 1978) p. 144
45. G N Sharifkanova, N F Noskova, D V Sokol'skii *Zh. Prikl. Khim.* **52** 2422 (1979)
46. N I Marusich, N F Noskova, D V Sokol'skii *Zh. Prikl. Khim.* **52** 2558 (1979)
47. N F Noskova, A Zh Kazimova, D V Sokol'skii *Zh. Prikl. Khim.* **54** 653 (1981)
48. T A Petrova, N F Noskova *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* (5) 27 (1980)
49. USSR P. 1 062 251; *Byull. Izobret.* **47** (1983)
50. A Zh Kazimova, A R Brodskii *Zhidkofaznaya Ochistka Gaza Okisleniem i Vosstanovleniem Primesei* (Liquid-Phase Scrubbing of Gas by Oxidation and Reduction of Admixtures) (Alma-Ata: Nauka, 1985)
51. N I Marusich, N F Noskova *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.* (5) 31 (1980)
52. N F Noskova, N I Marusich, A Zh Kazimova, in *XIV Chuguevskoe Vsesoyuz. Soveshchanie po Khimii Kompleksnykh Soedinenii (Tez. Dokl.)* (Abstracts of Reports at the XIVth Chuguev All-Union Conference on the Chemistry of Complex Compounds) (Ivanovo: Ivan. Chem. Technol. Inst., 1981) p. 396
53. N F Noskova, S R Savel'ev, T A Petrova *Izv. Akad. Nauk Kaz. SSR., Ser. Khim.* **6** 42 (1983)
54. S R Savel'ev, N F Noskova, N N Korneev, I M Khrapova, in *V Mezhdunar. Simp. po Svyazi mezhdu Gomogennym i Geterogennym Katalizom (Tez. Dokl.)* (Abstracts of Reports at the Fifth International Symposium on the Bond between Homogeneous and Heterogeneous Catalysis) (Novosibirsk: Institute of Catalysis, Siberian Division of the Academy of Sciences, USSR, 1986) p. 213
55. R S Savel'ev, R L Perkel', N F Noskova, in *VII Vsesoyuz. Konf. po Kataliticheskim Reaktsiyam v Zhidkoi Faze (Tez. Dokl.)* (Abstracts of Reports at the VIIth All-Union Conference on Catalytic Reactions in the Liquid Phase) (Alma-Ata: Nauka, 1988) Part 3, p. 144
56. S R Savel'ev, N F Noskova, N L Melamud, in *The VIIth International Symposium on Heterogeneous Catalysis, Part 2 (Abstracts of Reports), Bourgas, 1991* p. 793
57. S R Savel'ev, N F Noskova, N N Korneev, I M Khrapova *Zh. Prikl. Khim.* **64** 2190 (1991)
58. N F Noskova, A Zh Kazimova, S R Savel'ev *Zh. Prikl. Khim.* **28** 1352 (1992)
59. M F Sloan, A S Matlack, D S Breslow *J. Am. Chem. Soc.* **85** 4014 (1963)
60. A R Brodskii, Candidate Thesis in Chemical Sciences, Institute of Organic Catalysis and Electrochemistry, Academy of Sciences Kaz. SSR, Alma-Ata, 1987
61. A R Brodskii, N F Noskova, D V Sokol'skii, in *VI Evropeiskaya Konf. po Metalloorganicheskoi Khimii (Tez. Dokl.)* (Abstracts of Reports at the Sixth European Conference on Organometallic Chemistry (Riga: Institute of Organic Synthesis, Academy of Sciences Latv. SSR, 1985) p. 75
62. N F Noskova, A Zh Kazimova, N P Ovchinnikova, in *The XXVth Int. Conf. on Coordination Chemistry (Abstracts of Reports), Nanching, China, 1987* p. 734
63. N F Noskova, A Zh Kazimova, N P Ovchinnikova *Kinet. Katal.* **31** 213 (1990)
64. M M Mansurov, G L Semenova, N F Noskova *Zh. Prikl. Khim.* **63** 2003 (1990)
65. F K Shmidt *Kataliz Kompleksami Metallov Pervogo Perekhodnogo Ryada Reaktsii Gidrirovaniya i Dimerizatsii* (Catalysis of Hydrogenation and Dimerisation Reactions by Complexes of the Metals of the First Transition Row) (Irkutsk: Izd. Irk. Russ. Gos. Univ., 1986)
66. A Rufinska, R Giezynski *Wiadomosci Chem.* **34** 291 (1980)
67. A R Brodskii, S R Savel'ev, N F Noskova *Zh. Fiz. Khim.* **63** 1931 (1989)
68. A R Brodskii, V F Vozdvizhenskii, N F Noskova, N I Marusich, D V Sokol'skii *J. Organomet. Chem.* **178** 325 (1979); **179** 139 (1980)
69. S R Savel'ev, N F Noskova *Kinet. Katal.* **34** 1 (1994)
70. S R Savel'ev, N F Noskova, I M Khrapova, N N Korneev, in *IV Mezhdunar. Simp. po Gomogennomu Katalizu (Tez. Dokl.)* (Abstracts of Reports at the Fourth International Symposium on Homogeneous Catalysis) (Leningrad: Inst. Org. Chem. Phys. Acad. Sci. USSR, 1984) Vol. 4, p. 120
71. B Fell, A Kotoko *Fette Wiss. Technol.* **92** 338 (1990)
72. F Scott *J. Organomet. Chem.* **384** 17 (1990)
73. N F Noskova, A R Brodskii, S R Savel'ev *J. Mol. Catal.* **55** 94 (1989)
74. A Nakamura, M Tsutsui *Principles and Applications of Homogeneous Catalysis* (Translated into Russian; Moscow: Mir, 1983)
75. G Henrice-Olive, S Olive *Top. Curr. Chem.* **67** 107 (1976)
76. R Augustine, J Van Pappen *Ann. N. Y. Acad. Sci.* **172** 244 (1970)
77. R Ugo *The Vth International Congress of Catalysis (Abstracts of Reports), Palm-Beach, USA, 1972*
78. D V Sokol'skii, Ya A Dorfman *Koordinatsiya i Gidrirovanie na Metallakh* (Coordination and Hydrogenation on Metals) (Alma-Ata: Nauka, 1975)
79. S R Savel'ev, I M Khrapova, N F Noskova, N N Korneev *Zh. Org. Khim.* **25** 283 (1989)
80. S R Savel'ev, N F Noskova, in *Vsesoyuz. Konf. po Primeneniyu Metallokompleksnogo Kataliza v Organicheskom Sinteze (Tez. Dokl.)* (Abstracts of Reports at the All-Union Conference on the Application of Metallocomplex Catalysis in Organic Synthesis) (Ufa: Bashkir Scientific Centre, Ural Division of the Academy of Sciences of the USSR,1989) p. 54
81. S R Savel'ev, N F Noskova, in *III Vsesoyuzn. Konf. po Metalloorganicheskoi Khimii (Tez. Dokl.)* (Abstracts of Reports at the Third All-Union Conference on Organometallic Chemistry) (Ufa: Bashkir Scientific Centre, Ural Division of the Academy of Sciences of the USSR,1985) Part 2, p. 214
82. N F Noskova, D V Sokol'skii, N L Melamud *Zh. Prikl. Khim.* **53** 1830 (1980)
83. L P van't Hof, B G Linsen *J. Catal.* **7** 295 (1967)
84. N F Noskova, Doctoral Thesis in Chemical Sciences, Institute of Organic Catalysis and Electrochemistry, Academy of Sciences Kaz. SSR, Alma-Ata, 1985