

HYDROGENATION OF FATTY ACID ESTERS.**I. NICKEL(II) CARBOXYLATE-SODIUM DIHYDRIDOBIS(2-METHOXY-ETHOXO)ALUMINATE CATALYST**

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Factors determining the catalytic activity of the title system, its selectivity and stability have been studied, using hydrogenation of low erucic rapeseed oil as a model reaction. It was found that catalytically active systems are formed already at substoichiometric Al : Ni molar ratios. By contrast to their efficiency, their stability depended strongly on the way of their preparation, the catalysts obtained under solventless conditions being more stable. The selectivity of the above systems determined by a partial hydrogenation of the oil was insensitive to changes of preparation conditions, as demonstrated by similar relative composition of hydrogenated fatty acids as well as by the same level of trans-isomerization.

Although industrial hydrogenation of vegetable oils is based exclusively on heterogeneous catalytic processes, the application of transition metal complexes has long attracted attention (for review of earlier studies see ref.¹, recent advances are reviewed in ref.²). These studies have been initiated not only by common research interest in homogeneously catalyzed reactions but undoubtedly also by the fact that in some cases the high selectivity with respect to formation of monounsaturated products and strong suppression of trans-isomerization were achieved under mild conditions.

Such a behaviour was also observed with some Ziegler type nickel³⁻⁶ and cobalt^{7,8} catalysts. Metal carboxylates were found to be convenient precursors, the active catalytic systems being obtained by reaction of these salts with triethylaluminium^{4-6,8}, ethoxy(diisobutyl)aluminium⁸ and diethylmagnesium⁸. Similar catalysts were obtained by us^{3,7} also on using sodium dihydridobis(2-methoxyethoxy)aluminate (SDMA), $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$. However, a considerable molar excess of the hydride with respect to the nickel precursor was needed to ensure their catalytic activity for hydrogenation of some vegetable oils in hydrocarbon solvents^{3,7}. As due to some favourable properties such as easy and safe handling, high solubility and low inflammability, the hydride could become the agent of choice for Ziegler type catalyst formation, we considered it useful to find ways how to circumvent this problem. For that reason the system was subjected to a more detailed study, special attention being paid to the relations

between basic properties of the catalyst (i.e. its activity, selectivity and stability) and variables involved in the process of its formation (such as metal : hydride molar ratio, component concentrations, temperature, solvent, forming time, passivation etc.). Such data form not only basis for optimisation of the system but also make its comparison with analogous catalysts based on other organoaluminium compounds more reliable. For the above purpose, partial hydrogenation of low erucic rapeseed oil was taken as a model reaction.

EXPERIMENTAL

Chemicals

A refined low erucic rapeseed oil (supplied by Research Institute of Fat Industry, Ústí nad Labem) had the following composition (in wt.%): palmitic acid (C 16 : 0) 4.7, stearic acid (C 18 : 0) 1.4, oleic acid (C 18 : 1) 57.0, linoleic acid (C 18 : 2) 22.1, linolenic acid (C 18 : 3) 9.8, arachidic (C 20 : 0) and gadolenic (C 20 : 1) acid 2.4, erucic acid (C 22 : 1) 2.4, other undetermined compounds 0.2 (acidity number 0.25, iodine value 114.9). Nickel(II) 2-ethylhexanoate was used as a series of samples differing in the Ni concentration from 3.26 to 10.30 wt.% and in the free acid concentration from 0.01 to 4 wt.% (produced by the Northbohemian Fat Industry, Lovosice). Sodium dihydridobis(2-methoxyethoxy)aluminate was a commercial product (Synthesia Kolín, 70% toluene solution, the trade mark Synhydrid). The solvents hexane, benzene and petroleum ether were dried in usual way, distilled and stored under argon.

Catalysts Preparation

In all the methods described below, the process of catalyst formation was made in air, an inert gas (argon) and in hydrogen. The following sequence of the components has been chosen: nickel(II) 2-ethylhexanoate, the solvent, SDMA, and low erucic rapeseed oil. The catalysts prepared were stored under argon.

Method A. A 250 ml flask equipped with a magnetic stirrer and placed in a thermostatted oil bath was charged with 5.2% solution of Ni(II) 2-ethylhexanoate (0.6 or 1 ml, 0.53 or 0.89 mmol), diluted with hexane to 1% solution and under a reflux condenser, the solution was brought to boil. Then 0.1 or 0.2 ml (0.35 or 0.68 mmol) SDMA (Ni : Al molar ratio = 1 : 0.65 – 0.78) were added dropwise with vigorous stirring, and the reaction mixture was allowed to reflux for another 2 – 5 min. During this period the mixture turned black, indicating catalyst formation. Then 1/10 of the required volume of rapeseed oil was added, the solvent was removed by evaporation in vacuo while hot and the mixture was made up to 100 cm³ by rapeseed oil. Depending on the amount of Ni(II) 2-ethylhexanoate used, the resulting solution contained Ni in 0.03 – 0.05 wt.% concentration. A total of 10 cm³ of this stock solution was taken to hydrogenation experiments.

Method B. This procedure as well as further described Methods C – E represent preparations of the catalyst in a concentrated form. A 100 ml flask was charged with 5.2% Ni(II) 2-ethylhexanoate (1.5 ml, 1.33 mmol), and the solution was diluted with hexane to obtain final Ni concentration 1 or 2.5 wt.%. Then under reflux, 0.31 ml (1.1 mmol) of SMDA were added dropwise while magnetically stirring the reaction mixture (Ni : Al molar ratio = 1 : 0.78). The catalyst prepared was passivated by 5 or 10 cm³ of the rapeseed oil, with simultaneous removal of the solvent by vacuum evaporation. The catalyst concentration was 0.8 – 2.5 wt.%.

Method C. A 100 ml flask was charged with 5.2% solution of Ni(II) 2-ethylhexanoate (2.6 or 5.2 ml, 2.30 or 4.60 mmol) which was then diluted by hexane to final 1 – 2.5% solution. Then, a small amount of the rapeseed oil was added (approximately in the 2 : 1 mass ratio to Ni content). Under reflux, 0.52 or 1.04 ml

(1.8 or 3.6 mmol) of SMDA were added dropwise with stirring (Ni : Al molar ratio = 1 : 0.78) and the reaction mixture was refluxed with vigorous stirring for another 2 – 5 min. Then, 5 or 10 ml of the rapeseed oil were added, the solvent was removed by vacuum evaporation and the passivated catalyst was stored under argon. The resulting Ni content was 1.5 wt.%.

Method D. The procedure *C* was followed up to the stage of the treatment of the prepared catalyst. In contrast to Method *C*, the solvent was not removed by evaporation and no rapeseed oil was added. The resulting Ni concentration was 2.4 wt.%.

Method E. A total of 2.6 ml (2.3 mmol) of 5.2% solution of Ni(II) 2-ethylhexanoate was mixed with 1.9 or 2.6 ml of hardened palm oil (highly hydrogenated and refined sample with iodine value of 0.6 was supplied by the Research Institute of Fat Industry, Ústí nad Labem). Then the solvent was evaporated while hot in vacuo and a total of 0.8 ml (2.77 mmol) of SMDA were added dropwise with stirring (Ni : Al molar ratio = 1 : 1.2) while heating the mixture to the required temperature. After 3 – 4 min, the mixture was set aside and cooled to room temperature. The Ni concentration was 2.5 and 7 wt.%, respectively. To ensure an easier feeding of such solid catalyst to the reactor, immediately prior to measurements, the catalyst sample was diluted with the rapeseed oil and warmed up (the final concentration was 0.78 or 1.4 wt.% Ni with respect to the total content of the rapeseed oil).

Hydrogenation Experiments

Hydrogenation was carried out on an apparatus described earlier⁹, operating under constant hydrogen pressure. The time dependence of hydrogen consumption was recorded automatically. Hydrogenation experiments were performed in the following way. The reaction vessel⁹ was charged with the low erucic rapeseed oil which was then warmed up to the reaction temperature and evacuated. After that the reactor was charged with hydrogen to get small overpressure, and the catalyst sample of known weight was introduced through septum by syringe. The reactor was then once more evacuated to remove traces of the solvent, and hydrogen pressure was set at 0.115 MPa. Hydrogenation was started by switching on magnetic stirring (2 000 rpm). The course of the reaction was followed by recording time dependence of hydrogen consumption. After the hydrogenation sample of the reaction mixture was subjected to analysis on the content of individual C_{18} acid esters, as described below. In exploratory experiments, samples of the reaction mixture were removed at fixed time intervals and their composition was determined analogously.

Analytical Methods

The analysis of the samples of reaction mixtures of hydrogenation of the low erucic rapeseed oil on the content of individual fatty acids was made gas chromatographically, using Chrom 5 instrument (Laboratory Instruments, Prague) equipped with a flame-ionisation detector and a column (2.5 m long, 0.3 cm i.d.) packed with 12% 1,4-butanediol succinate on Chromaton N-AW-DMCS (particle size 0.16 – 0.20 mm) under the following conditions: column temperature 205 °C, hydrogen flow rate 20 cm³ min⁻¹ and air flow rate 900 cm³ min⁻¹. Prior to analysis, samples of the reaction mixture were subjected to reesterification by methanol, to convert the triglycerides present to the more volatile methyl esters. As other than C_{18} components have not suffered changes during hydrogenation, the composition determined was expressed as the relative content of C_{18} fatty acids (C 18 : 3, C 18 : 2, C 18 : 1 and C 18 : 0). The method used to reesterification is described below. In some experiments also the extent of trans-isomerization was followed. The isomers with trans-configuration of C=C bond were determined by IR spectroscopy, using Zeiss (Jena) model IR-75 spectrophotometer (10 mass % solution of the methyl esters in CS₂ in 0.1 mm NaCl cell, compared to the pure CS₂ solvent in the comparative cell). The content of trans-isomers was estimated from the intensity of the band at maximum around 960 cm⁻¹ with the aid of calibration by methyl elaidate as a standard.

Reesterification of the sample for analysis. Sample of the reaction mixture (10 – 30 mg) was diluted with petroleum ether or hexane (300 – 600 μ l) and ca 10% volume of 1M sodium methanolate was added (the solution was prepared by mixing 30 ml of methanol with 20 ml of benzene, followed by addition of 7.5 mg of phenolphthalein and 1.15 g of sodium). The mixture was allowed to react for 5 min (which proved to be sufficient time for the triglycerides), then it was acidified by the excess of methanolic hydrogen chloride solution (ca 13% solution was obtained by passing gaseous HCl to methanol) and set aside for another 30 min. The upper layer containing methyl esters was separated and analysed.

RESULTS AND DISCUSSION

A typical course of hydrogenation of low erucic rapeseed oil catalyzed by Ni(2-ethylhexanoate)/SDMA Ziegler systems in the absence of solvents is shown in Fig. 1. Irrespective of the way of catalyst preparation (see discussion later) and of the metal salt (similar results were obtained also with nickel stearate and nickel 2,4-pentanedionate) two stages of the hydrogenation are discernible. The first one is characterized by preferential hydrogenation of polyunsaturated C_{18} acids ($C_{18} : 3$ and $C_{18} : 2$) to monoenoic ones (*cis*- and *trans*- $C_{18} : 1$) with insignificant increase of the saturated product ($C_{18} : 0$). Only after the concentration of linolenic acid decreased to about 2 per cent, the saturated product formation ($C_{18} : 0$) became more pronounced.

By contrast with hydrogenation in aliphatic hydrocarbons which takes place under very mild conditions (usually already at ambient temperature, cf. refs^{3,5,7}), at comparable catalyst concentrations (0.03 – 0.05 wt.% Ni), the above solventless hydrogenation requires the use of elevated temperature (above 80 °C). Under these conditions the hydrogenation rate (measured by rate of hydrogen consumption) becomes comparable to that achieved in solvents.

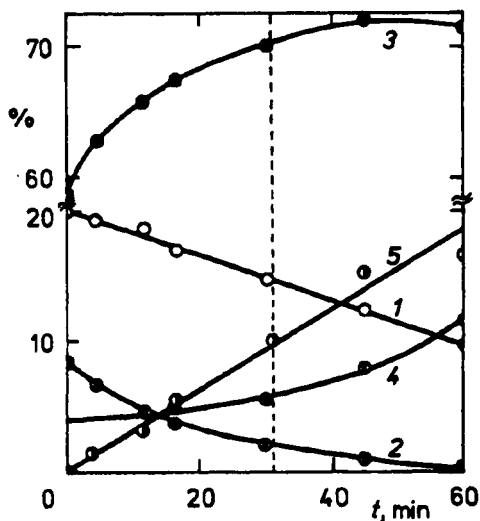


FIG. 1
Hydrogenation of the low erucic rapeseed oil catalyzed by Ni(II) 2-ethylhexanoate/SDMA without solvent at 120 °C, (Ni(II) concentration 0.03 wt.%, Ni : Al molar ratio 1 : 0.85, H_2 overpressure 13.3 kPa). Vertical broken line denotes the content of C_{18} acids at 2 wt.% linolenic acid ($C_{18} : 3$). 1 $C_{18} : 2$, 2 $C_{18} : 3$, 3 $C_{18} : 1$, 4 $C_{18} : 0$, 5 *trans*-isomers. The $C_{16} : 0$ and $C_{22} : 1$ content was constant during the reaction and is not shown

As already mentioned above, the aim of the present work was to characterize the behaviour of Ziegler type catalysts activated by SDMA. Rather high selectivity of these catalysts to the monoene formation (Fig. 1) led us to investigate especially this part of the reaction (i.e. the first stage of hydrogenation). This models the process of partial hydrogenation of vegetable oils, important for ensurance of their oxidation stability (cf. ref.¹⁰).

To evaluate the effect of preparation conditions on the performance of the catalysts, based on a number of preliminary experiments two parameters can be taken: the induction period (defined as the time from the start of stirring the reaction mixture to the appearance of hydrogen consumption found by extrapolating the initial part of hydrogenation curve via tangent) and the time to achieve 4% content of linolenic acid. The performance of the catalysts is further discussed in view of their activity, stability and selectivity.

Catalyst Activity

One of the basic factors determining the catalytic properties of a given Ziegler system is the ratio of nickel to aluminium component. In the case of metal carboxylates as precursors, the eventual presence of the admixture of the free acid should also be considered, since its effect is still controversial. For that reason the catalyst systems were prepared from nickel 2-ethylhexanoates with different level of acid contamination (0.16 to 4 wt.%), using the procedure which eliminated the influence of other factors (the catalyst prepared in solvent was placed into such a volume of rapeseed oil which ensured that the catalyst concentration was that used in proper hydrogenation experiments (Method A, see Experimental)). Data obtained are presented in Table I. The already mentioned division of the time of total hydrogenation to the induction period and to the time to achieve a given degree of linolenic acid hydrogenation finds here further support in the different effect of the Ni : Al molar ratio on both parameters. In general, the decreasing Ni : Al molar ratio decreases more the induction period than the rate of hydrogenation proper. The feature of interest of the studied catalyst system is the fact that the efficient catalyst can be obtained already with substoichiometric amount of SDMA. In this respect the SDMA based catalysts thus differ from analogous systems using triethylaluminium for which two-to fourfold excess of the organoaluminium compound is prerequisite^{4,6}. The results further show that the presence of the free acid does not affect unfavourably the catalyst activity. Furthermore, if the reproducibility of the results is taken into account ($\pm 10\%$), data would indicate that the acid can even promote the catalyst activity, although to a small extent. It is worth mentioning that a similar behaviour of the free acid has been observed for nickel stearate/triethylaluminium catalysts in hydrogenation of cyclohexane¹¹.

Data in Table I further demonstrate that owing to the easy and safe manipulation with SDMA the catalysts can be prepared in air. Their efficiency is however influenced

by the time of catalyst forming, decreasing significantly when the catalyst mixture is exposed to air for more than five minutes (Table II). Prolongation of the time is similarly unfavourable also in the case of the catalyst formed under argon. Furthermore, as

TABLE I

Effect of Ni : Al molar ratio and of the free acid on the catalytic activity of Ni(II) 2-ethylhexanoate/SDMA system in partial hydrogenation of the low erucic rapeseed oil (120 °C, p_{H_2} 0.115 MPa, without solvent, Ni(II) concentration 0.05 wt.%, catalyst prepared by Method A)

Free 2-ethylhexanoic acid, wt.% ^a	Ni : Al molar ratio	Hydrogenation, min	
		induction period	hydrogenation time ^b
0.16	1 : 0.66	4.2	8.7
	1 : 0.74	4.5	9.2
	1 : 0.85	3.3	8.7
	1 : 1.00	2.3	8.3
2.50	1 : 0.65	3.4	7.7
	1 : 0.71	3.3	6.9
	1 : 1.00	1.1	4.6
4.00	1 : 0.51	6.2	7.6
	1 : 0.74	4.9	5.7
	1 : 1.00	0.5	4.6

^a With respect to nickel(II) 2-ethylhexanoate. ^b Time needed to decrease C 18 : 3 content to 4 wt.%.

TABLE II

Effect of formation conditions on the activity of Ni(II) 2-ethylhexanoate/SDMA system in partial hydrogenation of the low erucic rapeseed oil (for conditions and catalyst preparation see Table I)

Time of catalyst formation, min ^a	Hydrogenation, min	
	induction period	hydrogenation time
2.5 ^b	2.5	5.2
3.0 ^b	2.7	4.7
5.0 ^b	5.6	10.4
20.0 ^b	23.5	17.5
3.0 ^c	1.4	10.8
5.0 ^c	2.8	13.2
20.0 ^c	12.5	17.3

^a Ni : Al molar ratio 1 : 0.78, Ni concentration 0.05 wt.%. ^b In air. ^c In argon.

evident from data in Table II, the use of inert atmosphere does not bring any advantages as far as the activity of the catalysts is concerned.

By contrast to the observed favourable effect of hydrogen during formation of Ziegler Ni catalysts supported on NiO (cf. ref.¹²), the presence of hydrogen in our case led always only to the systems which lost rapidly their activity at the very beginning of the hydrogenation.

The catalyst formation is also sensitive to the temperature used. On the basis of the results obtained by one of us¹³ with samples of the catalysts prepared at temperatures varying from 20 to 120 °C using optimum forming time it can be concluded that the catalysts with steady catalytic activity can be obtained only at temperatures close to those used in the hydrogenation (i.e. above 80 °C).

The reason lies in the physical state of the catalysts which at lower formation temperatures are homogeneous solutions very sensitive to the eventual acid admixtures in the rapeseed oil to be hydrogenated. This results in immediate discolouration of the black catalyst solution when injected to the reaction mixture warmed up to the reaction temperature.

On the other hand, the negative effect of the forming time prolongation is due to agglomeration of the catalyst to visible particles, which also proceeds on standing catalyst solution prior to replacement of the hydrocarbon solvent by the rapeseed oil. In both cases these particles begin to settle down. The inactivity of this heterogeneous form of the catalyst was confirmed by experiment with the sample separated from the catalyst solution prepared and stored in hydrocarbon solvent (cf. procedure *D* in Experimental). It should be noted that this process is irreversible and no dissolution of the above black nickel precipitate was achieved under hydrogenation conditions.

As expected, agglomeration is more pronounced for the higher concentrated Ni carboxylate solutions (inactive systems are obtained at 5 wt.% Ni).

Catalyst Stability

The above mentioned limited stability of the so prepared Ziegler nickel catalysts in hydrocarbon solvents sets limits also to their preparative application. This forced us to seek for other methods of catalyst preparation and stabilization. The methods checked are described in detail in Experimental. For purposes of further discussion they are also briefly surveyed in Table III. All make use of favourable effect of the rapeseed oil found by us in preparatory experiments.

The properties of the catalysts and their time changes were then followed using the already described way, yielding the results summarized in Table IV. They show that with the exception of the reference sample and the solventless preparation (Method *E*), all the other modifications of the catalyst preparation leads to unstable catalysts, even though their initial catalytic activity does not differ much from the above mentioned cases.

Catalyst Selectivity

Selectivity of the prepared catalysts has been estimated from the relative composition of the reaction mixture with respect to the content of C_{18} acids at the point where $C_{18} : 3$ content was close to 4% (rel.). Data presented in Table V and obtained with the best samples of each type of the catalyst (*A* to *E*) demonstrate that within the error of chromatographic determination, the C_{18} acid distribution is close to each other.

TABLE III
Survey of methods used to prepare nickel(II) 2-ethylhexanoate/SDMA catalysts

Method ^a	Starting Ni(II) solution (wt.% Ni), solvent	Ni : SDMA molar ratio	Other components added	Final form of the catalyst
<i>A</i>	1, hexane	1 : 0.78	none	0.05 wt.% Ni cat. in rapeseed oil
<i>B</i>	0.8 (2.5), hexane	1 : 0.78	none	0.8 (2.5) wt.% Ni cat. in rapeseed oil
<i>C</i>	1.5, hexane	1 : 0.78	rapeseed oil ^b	1.5 wt.% Ni cat. in rapeseed oil
<i>D</i>	2.4, hexane	1 : 0.78	none	2.4 wt.% Ni cat. in hexane
<i>E</i>	2.5 (7.1), hardened palm oil	1 : 1.2	none	2.5 (7.1) wt.% Ni cat. in hardened palm oil

^a For detailed description see Experimental. ^b 2 : 1 by weight to nickel(II) 2-ethylhexanoate.

TABLE IV
Time dependence of the activity of Ni(II) 2-ethylhexanoate/SDMA catalysts prepared by different Methods *A – E* (see Experimental) in partial hydrogenation of the low erucic rapeseed oil (reaction conditions see Table I)

Method of preparation	Ni content wt. %	Induction period (min) / time of hydrogenation (min) after standing the catalyst for				
		freshly prepared	1 day	3 days	10 days	20 days
<i>A</i>	0.05	1.1 / 4.6	1.2 / 4.4	1.4 / 4.5	2.9 / 4.7	3.1 / 5.2
<i>B</i>	0.80	1.2 / 4.4	1.8 / 5.3	15.2 / 15.6	inactive	
	2.50	2.3 / 3.9	6.5 / 9.1	9.7 / 11.2	inactive	
<i>C</i>	1.50	2.7 / 4.7	8.2 / 6.2	25.1 / 9.5	inactive	
<i>D</i>	2.40	2.5 / 4.7	4.9 / 5.2	7.1 / 5.5	21.5 / 13.5	inactive
<i>E</i>	2.50	1.3 / 4.8	1.3 / 4.9	1.5 / 5.1	2.7 / 5.7	5.2 / 8.1
	7.10	1.2 / 5.9	1.3 / 5.7	1.8 / 9.2	2.7 / 9.2	3.5 / 11.1

In the light of the requirements on the products of partial hydrogenation, the catalysts fulfill most of them: (i) they enable to achieve the required degree of C 18 : 3 conversion under mild conditions at Ni concentrations well comparable with heterogeneous Ni catalysts; (ii) they nearly retain the content of proessential C 18 : 2 acid; (iii) they initiate only low trans-isomerization (in all cases, the trans-isomers did not exceed 5 wt.%).

The only unfavourable property of these systems is the more distinct increase of C 18 : 0 acid, the glycerides of which form a part of solid portions of partially hydrogenated oils.

CONCLUSIONS

The present work documents that sodium dihydridobis(2-methoxyethoxy)aluminate is the agent of choice for preparing Ziegler type Ni hydrogenation catalysts. Similarly to the other Ziegler systems studied so far, their properties are affected by a number of factors, optimization of which results in efficient, sufficiently stable and highly selective catalysts. Furthermore, these catalysts meet also most of the requirements on partial hydrogenation of the low erucic rapeseed oil. In this respect, stress on this aspect of catalyst behaviour in the present work is thus justified. A more detailed study of kinetics of the process using model methyl esters of C₁₈ acids will be reported in a subsequent work.

TABLE V

Composition of the product of a partial hydrogenation of the low erucic rapeseed oil catalyzed by nickel(II) 2-ethylhexanoate/SDMA systems (reaction conditions see Table I)

Method of catalyst preparation	Content of C ₁₈ acids, rel.%			
	C 18 : 0	C 18 : 1	C 18 : 2	C 18 : 3
A	3.4	68.7	23.7	4.2
	3.0 ^a	70.4	22.7	3.9
B	2.9	69.9	22.9	4.3
C	3.0	70.4	22.7	3.9
D	3.0	69.8	23.3	3.9
E	4.1	69.2	22.9	3.8
	3.5 ^a	70.1	22.5	3.9

^a Data obtained with the sample stored for 10 days (see Table III); the content of trans-isomers did not exceeded 5 wt.%.

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