## Catalytic systems of nickel chelates and organometallic compounds in cyclohexene hydrogenation

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Catalytic systems NiL<sub>2</sub> (L: 3,5-diisopropylsalicylate I, acetylacetonate II, stearate III, and benzohydroxamate IV) with organometals (Et<sub>1</sub>Al, i-Bu<sub>1</sub>Al, BuLi) were studied. The cyclohexene hydrogenation rate for the most active catalysts, prepared under very mild conditions (30 °C,  $p_0(H_2) = 120$  kPa,  $c(Ni) \approx 2 \text{ mmol dm}^{-3}$ ) was about 0.76 mol min<sup>-1</sup> related to 1 g Ni. Catalytic activity a(i) decreased in order of Ni chelates  $a(I) > a(II) \gg a(III) >$ > a(IV). The optimal ratio was n(Al)/n(Ni) = 3, n(Li)/n(Ni) = 4 for I, and n(Al)/n(Ni) = n(Li)/n(Ni) = 2 for II, III, IV The presence of aromatic compounds slowed down the hydrogenation rate and was accompanied by reduction and sedimentation of nickel in colloid form. The activation energy of cyclohexene hydrogenation using  $Ni(dips)_2 - Et_1Al$ was  $E = 28.4 \text{ kJ mol}^{-1}$  The reaction order with respect to catalyst is equal to one and to substrate zero. The structure of active centre and mechanism of reaction of Ni(dips), with organoaluminium compounds was suggested by means of EPR.

Изучены каталитические системы NiL, (L: 3,5-диизопропилсалицилат I, ацетилацетонат II, стеарат III и фенилгидроксамат IV) с металлоорганическими соединениями (Et<sub>3</sub>Al, i-Bu<sub>3</sub>Al, BuLi). Скорость гидрогенизации циклогексена с наиболее активными катализаторами, полученными при очень мягких условиях (30 °C,  $p_0(H_2) = 120 \text{ к}\Pi a$ ,  $c(Ni) \approx 2$  ммоль дм<sup>-3</sup>) составляла около 0.76 моль мин<sup>-1</sup> в расчете на 1 г Ni. Каталитическая активность a(i) понижалась в последовательности хелатов Ni:  $a(I) > a(II) \gg a(III) > a(IV)$ . Оптимальное соотношение было n(Al)/n(Ni) = 3, n(Li)/n(Ni) = 4 для I, и n(Al)/n(Ni) == n(Li)/n(Ni) = 2 для II, III, IV Присутствие ароматических соединений замедляло скорость гидрогенизации и приводило к восстановлению и осаждению никеля в коллоидной форме. Энергия активации гидрогенизации циклогексена при использовании Ni(dips),-Et<sub>3</sub>Al cocтавляла  $E = 28,4 \text{ кДж моль}^{-1}$ . Порядок реакции по катализатору равнялся 1, а по субстрату 0. С помощью ЭПР спектроскопии сделано предположение о строении активного центра и механизме реакции Ni(dips), с алюмоорганическими соединениями.

More than 200 papers, patents, and reviews [1-4] have been devoted to the Ziegler—Natta-type hydrogenation catalysts. But there are different opinions in many questions, *e.g.* choice of the most convenient transition metal and its ligand, finding of the optimal mole ratio of organometal to transition metal, and determination of the most convenient sequence of the catalyst components addition.

The aim of this work was to find the optimal conditions for preparation of the hydrogenation catalysts based on bivalent nickel salts  $(3,5-diisopropylsalicy-late Ni(dips)_2$ , acetylacetonate Ni $(acac)_2$ , stearate, and benzohydroxamate Ni $(bzh)_2$ ), and organometals (triethylaluminium Et<sub>3</sub>Al, triisobutylaluminium i-Bu<sub>3</sub>Al, and butyllithium BuLi) and to investigate the influence of solvents and some catalytic poisons on the activity of the catalytic systems studied.

## Experimental

Due to the high sensitivity of these catalysts to air and moisture, all the experiments were carried out with purified chemicals in inert atmosphere. Employed solvents (cyclohexane, benzene, toluene, xylene, THF, heptane, diethyl ether, chlorobenzene) were first dried with MgSO<sub>4</sub>, or CaCl<sub>2</sub>, and then with metallic sodium (chlorobenzene with  $P_2O_5$ ) and distilled under argon atmosphere in the presence of small amount of organometallic compound. Nickel components of the catalyst were prepared by the reaction of sodium salt of the appropriate ligand with NiCl<sub>2</sub>.

The measurements were carried out at 30 °C in a glass apparatus, based on [5], and described in more detail in [6]. Catalytic activity was studied by means of the hydrogen pressure decrease in the system and presented in the form of a graphic function evaluating the initial hydrogenation rate  $v_0$ , *i.e.* the loss of concentration of cyclohexene (in mol dm<sup>-3</sup> s<sup>-1</sup>) vs. the catalyst concentration, or the mole ratio of organometal to transition metal, resp. NMR analysis of the reaction mixture proved that hydrogenation was complete (no C<sub>6</sub>H<sub>10</sub> was found). Then

$$v_0 = -\left(\frac{\mathrm{d}c_{\mathrm{s}}}{\mathrm{d}t}\right)_{t \to 0} = -k\left(\frac{\mathrm{d}p}{\mathrm{d}t}\right)_{t \to 0}$$

where

$$k = \frac{c_{\infty} - c_0}{\langle p_{\infty} - p_0 \rangle} = c_0 / \langle p_0 - p_{\infty} \rangle \qquad (c_{\infty} = 0)$$

 $\langle p_0 - p_x \rangle$  is the average value for 275 measurements.

Components of the catalytic system — solvent, substrate, nickel salt (solution at  $c = 0.1 \text{ mol dm}^{-3}$ , suspension at  $c = 0.02 \text{ mol dm}^{-3}$ , resp.), and solution of organometal ( $c = 0.2 \text{ mol dm}^{-3}$ ), were added into the reaction vessel by syringes up to the whole volume of 20 cm<sup>3</sup> and substrate concentration of 0.5 mol dm<sup>-3</sup>. The catalyst was prepared in two ways:

a) in the absence of substrate, adding 1. solvent, 2. nickel chelate solution, 3. organometallic solution, 4. cyclohexene;

b) in the presence of substrate, adding 1. solvent, 2. nickel chelate solution, 3. cyclohexene, 4. organometallic solution.

## **Results and discussion**

The basic catalytic system investigated here was nickel-bis(3,5-diisopropylsalicylate) with triethylaluminium, further were studied Ni(dips),-i-Bu,Al and

1.6 1.2 v<sub>0</sub>/(mmol dm<sup>-3</sup> s<sup>-1</sup>) 0.8 0.4 NiL<sub>2</sub>-Et<sub>3</sub>Al. L: (1) dips, (2) acac, (3) stearate, (4) 0.0 5 2 3 4 6 (3), (4)).n(AL)/n(Ni) 1.2 1.0 v₀∕(mmot dm<sup>-3</sup> s<sup>-1</sup>) 0.8 0.6 0.4 Fig. 1b. Influence of the ratio n(Li)/n(Ni) on the cyclohexene hydrogena-0.2 tion rate for the catalytic systems NiL<sub>2</sub>-BuLi. L: (1) dips, (2) acac, (3) stearate, (4)0.0 6 5 benzohydroxamate 2 3  $(c(Ni) = 4 \text{ mmol } dm^{-3}).$ n(Li)/n(Ni)

Fig. 1a. Influence of the ratio n(Al)/n(Ni) on the cyclohexene hydrogenation rate for the catalytic systems

benzohydroxamate (c(Ni) = 2 mmol.  $dm^{-3}(1)$ , (2),  $c(Ni) = 4 \text{ mmol } dm^{-3}$   $Ni(dips)_2$ —BuLi, and also other Ni chelates — acetylacetonate, stearate, and benzohydroxamate, with Et<sub>3</sub>Al and BuLi. The solvent usually used was cyclohexane. The optimal mole ratio of the components, and the dependence of the activity upon concentration in various solvents were determined.

The mole ratio of organometallic compound to transition metal influences the activity decisively (Fig. 1). Its optimal value (n(Al)/n(Ni) = 3, n(Li)/n(Ni) == 4 for Ni(dips)<sub>2</sub>, and n(Al)/n(Ni) = 2, n(Li)/n(Ni) = 2 for the other Ni chelates used) is constant for each couple of catalyst components and is independent of the preparation conditions if all reactants are purified and dried thoroughly.

Fig. 2 shows the activity of various catalysts prepared at the optimal ratio of components in the absence of cyclohexene. The highest activity is provided by the systems with diisopropylsalicylate, then with acetylacetonate. The catalysts prepared from stearate are more than one order less active. The lowest activity was observed in the case of benzohydroxamate. This sequence correlates well with the solubility of these nickel salts in cyclohexane. Following decrease of the activity for the examined organometallic compounds was found:  $a(Et_3Al) \approx a(i-Bu_3Al) > a(BuLi)$ . No influence of the time of catalyst preforming and of the employed gas (inert atmosphere Ar, or H<sub>2</sub>) on the activity was observed.



A change of the introduction order of the individual reaction components showed various influence of different organometals. In the preparation of the catalyst in the presence of substrate the catalytic activity increased a little (20 %) for the system Ni(dips)<sub>2</sub>—Et<sub>3</sub>Al, but decreased for Ni(dips)<sub>2</sub>—i-Bu<sub>3</sub>Al. For the

systems with BuLi twofold increase of the catalytic activity in the presence of cyclohexene was observed (Fig. 3). The sequence of activity of nickel salts remained unchanged:  $a(Ni(dips)_2) > a(Ni(acac)_2) \gg a(Ni(stearate)_2) > a(Ni(bzh)_2)$ . Activity of the systems with BuLi was about the same as for the systems with Et<sub>3</sub>Al.



Fig. 3. Influence of the catalyst composition and concentration on the cyclohexene hydrogenation rate for the catalytic systems NiL<sub>2</sub>—BuLi, prepared in the presence of cyclohexene.
L: (1) dips, (2) acac, (3) stearate, (4) benzohydroxamate; (5) Ni(dips)<sub>2</sub> + + BuLi prepared in the absence of cyclohexene.

In the most active catalytic systems prepared here  $(Ni(dips)_2-Et_3Al, Ni(dips)_2-Et_3Al, and Ni(dips)_2-cyclohexene-Et_3Al, -BuLi, -i-Bu_3Al)$  the hydrogenation rate of cyclohexene, at 30°C, H<sub>2</sub> initial pressure 120 kPa, and  $c(Ni) = 2 \text{ mmol dm}^{-3}$ , was around 1.5 mmol dm<sup>-3</sup>s<sup>-1</sup>, *i.e.* 0.76 mol min<sup>-1</sup> related to 1 g Ni and it is one of the highest under such mild condition reported so far [2, 7, 8].

The catalytic activity decreased in the order of employed solvents:  $a(cyclohexane) \ge a(xylene) > a(toluene) > a(benzene) \ge a(chlorobenzene)$  (Fig. 4). Such an influence was observed already by trace amounts of arenes. Similar results were obtained in [9] and explained by  $\pi$ -donor properties of aromates, coordinating the catalyst, Activity of a catalytic system depends on mutual consideration of coordination ability of solvent, and substrate, to the active centre. Though alkyl groups increase the electron density on the benzene ring, steric hindrances cause that cyclohexene hydrogenation goes easier in alkyl-substituted arenes than in benzene. This is in agreement with [10], where a considerably higher influence of steric hindrances than the influence of donor effects of alkylarenes on the catalytic activity was found. Various influence of the absence and of the presence of cyclohexene on the activity of the catalysts prepared from Et<sub>3</sub>Al, and i-Bu<sub>3</sub>Al, can also be caused by a steric hindrance.







(3) toluene, (4) benzene.

In the presence of aromatic solvents the reduction to zerovalent nickel occurs. This Ni precipitates in colloid form, which is characterized by a strong EPR signal with g-value 2.16-2.20, and catalytic system loses its activity. The formation of colloidal nickel was also observed in [11-13].

Traces (*i.e.* from about 0.01 vol. %) of oxygen-containing compounds (especially those with active hydrogen) cause deactivation of the catalyst as they react with its organometallic component. Thus methanol, acetone, water, and air, or oxygen, decomposed the catalytic system. This unfavourable effect of alcohols,

aldehydes, and water, can partly be compensated by appropriate surplus of organometal. The negative influence of etheric solvents (diethyl ether, tetrahydrofuran) is probably caused by the formation of their stable complexes with organometals.

Change of the reaction temperature in the range 20—45 °C had no influence on the optimal catalyst composition (n(Al)/n(Ni) ratio). The activation energy of cyclohexene hydrogenation using Ni(dips)<sub>2</sub>—Et<sub>3</sub>Al ( $c(Ni) = 5 \times 10^{-4} \text{ mol} \cdot dm^{-3}$ , n(Al)/n(Ni) = 4) was determined to be  $E = 28.4 \text{ kJ mol}^{-1}$ ; in good agreement with [7, 14, 15] for similar systems.

The reaction order was determined to be one to the catalyst and zero to cyclohexene. Our equipment was not suitable for an exact determination of the reaction order with respect to hydrogen. Preliminary measurements indicated proportionality of the reaction rate to the hydrogen pressure.

Stability of the Ni(dips)<sub>2</sub>—Et<sub>3</sub>Al catalyst  $(c(Ni) = 2 \text{ mmol dm}^{-3}, n(Al)/n(Ni) = 4)$  during a hydrogenation of several portions or a greater amount of cyclohexene was investigated. 1 cm<sup>3</sup> of cyclohexene (*i.e.* 0.01 mol;  $c = 0.5 \text{ mol} \cdot dm^{-3}$ ) was hydrogenated in 11.5 min with the initial rate of 0.991 mmol $\cdot dm^{-3} s^{-1}$  In hydrogenation of the second, third, fourth, and fifth portion of cyclohexene, the original hydrogenation rate slowed down to 99%, 97%, 89%, and 83.7%, respectively.

Catalytic system Ni(dips)<sub>2</sub>—BuLi ( $c(Ni) = 4 \text{ mmol dm}^{-3}$ , n(Li)/n(Ni) = 4), prepared in the presence of cyclohexene, was studied in hydrogenation adding five portions (or quintuple amount) of cyclohexene in three various ways (A, B, C). The initial rate in all three methods was 1.88 mmol dm<sup>-3</sup> s<sup>-1</sup> and the first portion of cyclohexene was hydrogenated in 6.5 min. In the first method (A) the next portion of substrate was added after the hydrogenation of the previous one

Portion	Method		
	A	В	С
1	1	1	1
2	0.33	0.73	0.92
3	0.22	0.38	0.85
4	0.16	0.25	0.75
5	0.12	0.23	0.68

Table 1

Relative hydrogenation rate of cyclohexene with Ni(dips)2-BuLi

Five portions of substrate were added in various ways: A. after complete hydrogenation of the previous portion; B. just before the completion of the previous portion; C. five portions added at the beginning.

was completed. In the second method (B) the next portion of substrate was added just before the hydrogenation of the previous one was completed. In the third method (C) the quintuple amount of cyclohexene was hydrogenated and hydrogen was supplied after hydrogenation of each one fifth of the total cyclohexene amount (Table 1).

Comparison of A and B shows that substrate is taking part in the formation of the catalytic active centre. Its replacement after the completion of the reaction and its harder recoordination after a new addition of cyclohexene explains slowing down the hydrogenation rate. The observed lower rate if the catalyst was prepared in the absence of cyclohexene can be explained similarly. Method Cindicates that the repeated manipulation with the system in methods A and Bleads to the loss of activity caused probably also by contamination of the system.

In the catalytic system Ni(dips)<sub>2</sub>—Et<sub>3</sub>Al ( $c(Ni) = 1 \text{ mmol dm}^{-3}$ ) additionally to cyclohexene also other substrates were investigated. The comparison of the hydrogenation rates of 1-decene, 1-dodecene, and cyclohexene (Fig. 5) shows that with the increasing steric hindrance of the double bond in alkenes the hydrogenation rate decreases; it is in agreement with [16].



The structure of the catalytic active centre of systems based on  $Ni(dips)_2$  was studied by means of EPR spectroscopy. Two types of paramagnetic species were observed in cyclohexane solution (Fig. 6). g-Value of the first one, and the shape

of the second, depend on the type of employed organometallic compound as well as on the type of chelate ligand. g-Values of the first signal (singlet) for Ni(dips)<sub>2</sub>, or Ni(acac)<sub>2</sub>, with various organometallic compounds are

Ni(dips) <sub>2</sub> —Et <sub>3</sub> Al	g = 2.056
Ni(dips) <sub>2</sub> —i-Bu <sub>3</sub> Al	g = 2.084
Ni(dips) <sub>2</sub> —BuLi	g = 2.110
Ni(dips) <sub>2</sub> —RMgX	g = 2.100 [17]
$Ni(acac)_2 - Et_3Al$	g = 2.051 [9]

g-Value of the second type of signal is 2.0028. Depending on the employed chelate ligand, organometallic compound, and solvent, variously resolved hyperfine structure was observed. The spectra of both paramagnetic species disappear if the system is contaminated with oxygen.



Fig. 6. EPR spectrum of paramagnetic intermediates of catalytic system Ni(dips),-Et,Al in cyclohexane.

The first type of signals was assigned to Ni(I) species with electron configuration  $3d^9$ . g-Value of the second species (2.0028) is characteristic of free radicals. According to the detailed investigations, described previously [17—20] these paramagnetic products are ketyl radicals (ArCO<sup>-</sup> R), formed during the last stage of reaction of the nickel chelate ((ArCOO)<sub>2</sub>Ni) with the organometallic compound (RM).

The highest concentration of both types of paramagnetic products was found at the ratio n(organometal): n(Ni) = 8-10, whereas the highest catalytic activity in hydrogenation is observed before the reduction of the transition metal at the ratio 2-4 (Fig. 7). By increasing the ratio n(organometal): n(transition)metal) the catalyst loses its activity. This decrease of catalytic activity is accompanied with increase of concentration of both types of paramagnetic products.

Though catalytic activity of these systems depends on the order of introduction of reactants, the presence of olefin did not influence the spectral structure of the observed paramagnetic products.



Fig. 7. Comparison of the cyclohexene hydrogenation rate  $v_0$  with the concentration of paramagnetic species c, both as a function of the ratio n(Al)/n(Ni). Catalytic system Ni(dips)<sub>2</sub>—Et<sub>3</sub>Al in cyclohexane.

From the comparison of the optimal catalytic activity with the concentration of the paramagnetic products results that the catalytic active centre are diamagnetic species of bivalent nickel, formed by the alkylation of transition metal chelate (after the primary elimination of hydrogen from the hydroxyl group of diisopropylsalicylate). Generally [21, 16], in agreement with our results, it is assumed that the nickel alkyl rearranges under the nickel hydride formation and coordination of olefin, described by the following common structure



where  $L^1$ ,  $L^2$  are the chelate ligands modified by organometals.

Based on the results [22] and this study the following scheme of reaction of nickel(II) diisopropylsalicylate with organoaluminium compounds can be suggested (Scheme 1).



Scheme 1

## References

- 1. Aspects of Homogeneous Catalysis 1. (Ugo, R., Editor.) Carlo Manfredi, Editore, Milano, 1970.
- Sokolskii, D. V and Noskova, N. F., Katalizatory tipa Tsiglera—Natta v reaktsii gidrirovaniya. Nauka, Alma Ata, 1977.
- 3. James, B. R., in *Advances in Organometallic Chemistry*, Vol. 17, p. 319. Academic Press, New York, 1979.
- 4. Reguli, J. and Staško, A., Chem. Listy 76, 1085 (1982).
- 5. Vilím, J. and Hetflejš, J., Chem. Listy 70, 188 (1976).
- 6. Reguli, J., CSc. Thesis. Slovak Technical University, Bratislava, 1982.
- 7. Tzinmann, M., Bull. Soc. Chim. Fr., Part 1, 193 (1981).
- 8. Duinker (Shell Int. Res. Maatschappij N. V.): Neth 396137 (1965); Chem. Abstr. 63, 9878.
- 9. Noskova, N. F., Marusich, N. I., and Sokolskii, D. V., Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR 1970, 3.
- 10. Lipovich, V. G., Shmidt, F. K., and Kalechits, I. V., Kinet. Katal. 8, 1300 (1967).
- 11. Tkáč, A. and Staško, A., Collect. Czechoslov. Chem. Commun. 37, 573 (1972).
- 12. Shmidt, F. K., Tkach, V. S., Kalabina, A. V., and Saraev, V V., 2-oi sovetsko-frantsuzskii seminar po katalizu, p. 165. Kiev, Sept. 1974.
- 13. Van Ommen, J. G., van der Ploeg, H. J., van Berkel, P. C. J. M., and Mars, P., J. Mol. Catal. 2, 409 (1977).
- 14. Lipovich, V. G., Shmidt, F. K., and Kalechits, I. V., Kinet. Katal. 8, 939 (1967).
- 15. Feldblum, V. Sh. and Konovalova, V. T., Neftekhimiya 17, 197 (1977).
- 16. Lapporte, S. J., Ann. N. Y Acad. Sci. 158, 510 (1969).
- 17. Staško, A., Tkáč, A., Přikryl, R., and Malík, L., J. Organometal. Chem. 92, 253 (1975).
- 18. Staško, A., Tkáč, A., Malík, L., and Adamčík, V., J. Organometal. Chem. 92, 261 (1975).
- 19. Staško, A., Malík, Ľ., Tkáč, A., Adamčík, V., and Maťašová, E., Collect. Czechoslov. Chem. Commun. 44, 1731 (1979).
- 20. Malík, Ľ., Staško, A., Maťašová, E., and Tkáč, A., Org. Magn. Resonance 15, 83 (1981).
- 21. Jolly, P. W. and Wilke, G., *The Organic Chemistry of Nickel*, Vol. 1, 2. Academic Press, New York, 1975.
- 22. Staško, A., Chem. Zvesti 37, 95 (1983).

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