

The IRS–DR study of interaction of the supported catalyst based on the organic nickel chelate with carbon monoxide and ethylene

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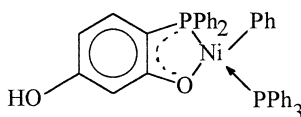
Abstract

The interaction of the supported catalyst based on the organic nickel chelate compound (I) with carbon monoxide and deuterated ethylene has been studied using IRS–DS. The surface nickel compound (SNC) interacts with carbon monoxide in the same manner as the initial nickel complex (I). The reaction of SNC or nickel complex (I) with CO yields nickel acyl complex (V) (a product of the CO insertion into the Ni–Ph bond), ester (VIII) and various nickel carbonyls (VI). According to the IRS data, the interaction between SNC and deuterated ethylene gives a polymer. The subsequent carbon monoxide introduction results in the same products as in the case of the CO reaction with SNC. The interaction between ethylene and SNC pretreated with carbon monoxide does not lead to polymerization. © 1998 Published by Elsevier Science B.V. All rights reserved.

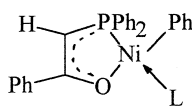
Keywords: Organic nickel chelate compound; Supported nickel catalysts; IRS–DS; Carbon monoxide

1. Introduction

The organic chelate nickel complexes (I–III) are known as homogeneous catalysts for ethylene oligomerization [1].



(I)



(II - III)

(II) : L = PEt₃

(III) : L = PPh₃

Where L in (II) is PEt₃ and L in (III) is PPh₃. These systems show high activity and enormously high selectivity in the linear α -olefins formation without introduction of any co-catalysts. Peuckert and Keim [2] and later, Klabunde and Ittel [3] and Ostoja Starzewski [4] found that in some cases, in the presence of organic nickel chelate complexes (ChNC), polymerization giving polyethylene (PE) proceeds rather than ethylene oligomerization.

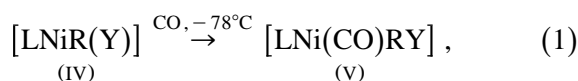
Recently, the data on the synthesis and study of chelate nickel complexes which are polymer supported and used for ethylene polymerization have been published [5]. These catalysts are synthesized directly in a polymerization reactor in the presence of a polymer support which contains the functional groups required for the

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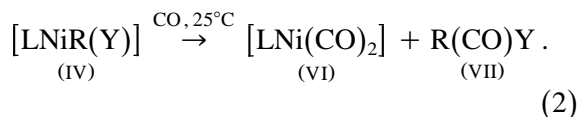
nickel complex formation. Isolation of the supported catalysts from the reaction medium leads to their deactivation [5].

We have prepared the supported high-activity nickel catalysts for ethylene polymerization by means of the nickel complex (I) interaction with inorganic supports-magnesium hydride and silica treated with aluminium trialkyl. The data on the catalyst composition as well as on the ethylene polymerization and co-polymerization with α -olefins over these catalysts are presented in Ref. [6].

Klabunde et al. [7] show that in the presence of some organic nickel chelate compounds, the co-polymerization of ethylene with carbon monoxide may be performed. The character of the interaction of the nickel compound with CO depends on the chelate ligand of nickel compound and the reaction conditions. In Refs. [8,9], it was shown that at low temperatures the interaction of the organic nickel chelate with CO yields nickel acyl complex (V) (reaction 1).



where L = bpy, (R₃P)₂; Y = -OAr, -NR₂, -OC(O)R; and R is Ar, C_nH_{2n+1} and n = 1–3. This compound is stable at room temperature and can be individually isolated. Nickel carbonyls (VI) and the corresponding esters (VII) are produced over some nickel compound at room temperature, independently of the molar [CO]/[Ni] ratio (reaction 2).



The present work is about the study of the composition of the surface nickel complexes (SNC) in the supported catalyst produced by the nickel complex (I) reaction with silica pretreated with triisobutylaluminium (TIBA) and of the interaction of these complexes with carbon monoxide and deuterated ethylene.

2. Experimental

Silica Davison 952 (surface area is 260 m² g⁻¹, pore volume is 1.6 m³ g⁻¹) was used as a support.

Silica was heated in air at 450°C for 4 h and then dehydroxylated in vacuum at 450°C for 4 h. The dehydroxylated silica was treated with a hexane solution of TIBA at room temperature. Excessive TIBA was removed by washing with hexane.

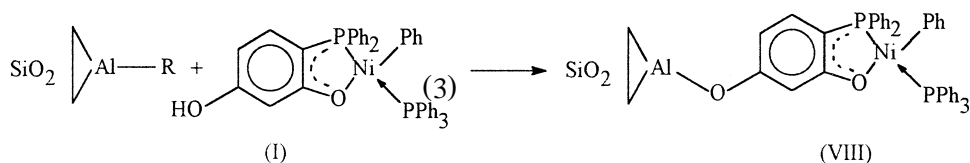
Organic chelate nickel compound (I) was prepared according to the procedure in Ref. [1]. At room temperature, a toluene solution of complex (I) was supported on silica modified with TIBA. Excess unreacted complex (I) was removed by washing with toluene. The prepared catalyst contains 2.0 wt.% Al and 1.36 wt.% Ni.

The IR spectra of diffuse reflection were recorded in a vacuum-tight cell on a Fourier IFS-113V IR spectrometer. The carbon monoxide adsorption was performed at room temperature.

Since the C–H absorption bands of the polymer produced may overlap with the C–H bands of ChNC, the polymerization in situ was studied at the adsorption of deuterated ethylene. The studied sample was treated with deuterated ethylene at the molar ratio [C₂D₄]/[Ni] = 10 either at room temperature or at 50°C for 3 h.

3. Results and discussion

In Ref. [6], we studied the SNC formation by means of IR spectroscopy. It was shown that, at supporting nickel complex (I) on silica modified with TIBA, the nickel complex is anchored via the interaction of the hydroxyl group in the chelate ligand with the surface =Al–R groups of the modified silica. As a result, the SNC (VIII) is produced (reaction 3).

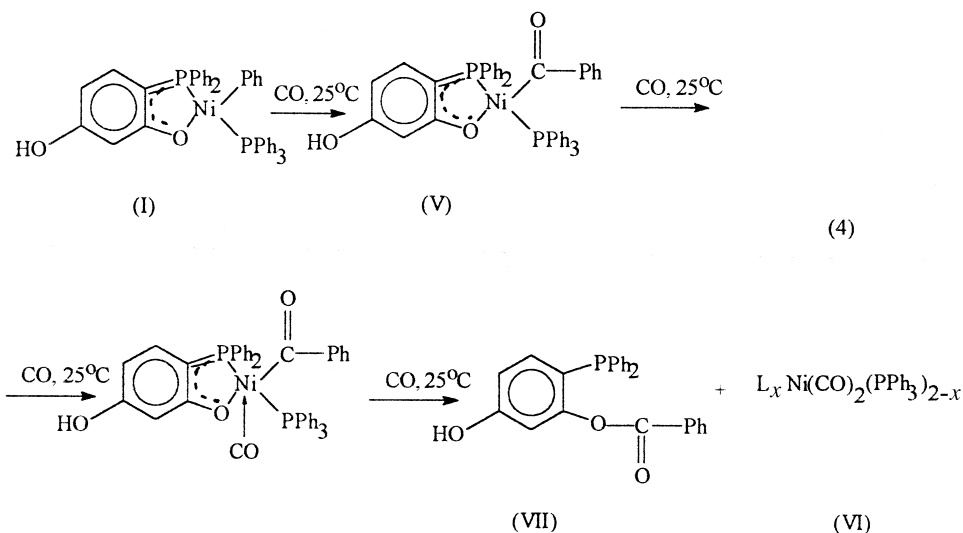


The chelate structure remains the same in the surface complex (VIII). This is evidenced by the presence of absorption band 1560 cm^{-1} in its IR spectrum, corresponding to the C=C conjugation in the chelate structure of nickel complex (I) (Fig. 1(1,2)).

3.1. Interaction of organic chelate nickel complex (I) with carbon monoxide

The IR spectrum shows the presence of new bands 1615 , 1630 , 1700 , 1735 , 1940 , 2000 , 2040 , and 2070 cm^{-1} at the interaction of initial solid complex (I) with carbon monoxide at the molar ratio $[\text{CO}]/[\text{Ni}] = 250$ at room temperature (Fig. 2(1)).

These data indicate that the above interaction yields acyl complex (V), nickel carbonyls (VI) and ester (VII) according to reaction 4.



The formation is proved by the appearance of absorption bands 1700 and 1735 cm^{-1} as characterized in Ref. [7], $\nu_{\text{C}=\text{O}}$ in ether (VII). The presence of two bands may be caused by the different ester surrounding. Thus, band 1700 cm^{-1} may correspond to the ester in the coordination sphere of nickel carbonyl (VI), and band 1735 cm^{-1} may be corresponded to the ester in unbound state.

The character of the organic nickel chelate

interaction with carbon monoxide is affected by the nickel ligands [7]. Thus, complex (II) reacts with CO at room temperature, giving nickel acyl complex, while the interaction of complex (III) with CO leads to the production of nickel carbonyls and the corresponding ester.

Nickel complex (I) reacts with carbon monoxide, giving both nickel carbonyls $\text{Ni}(\text{CO})_2\text{L}_x(\text{PPh}_3)_{2-x}$, where $x = 0-2$, L is ester (VII), or $\text{Ni}(\text{CO})_3\text{PPh}_3$ (IX) ($\nu_{\text{C}=\text{O}} = 2070$,

2000 cm^{-1} [7,10] and nickel acyl complexes (VI) ($\nu_{\text{C}=\text{O}} = 1615, 1630 \text{ cm}^{-1}$) [1,8,9,11].

Besides nickel carbonyls (VI), apparently, nickel tetracarbonyl (X) is produced, which is adsorbed on the sample surface. Absorption band 2040 cm^{-1} seems to refer to the valence vibrations of adsorbed $\text{Ni}(\text{CO})_4$. For the gas-phase nickel tetracarbonyl, the corresponding band is 2057 cm^{-1} [12]. The $\nu_{\text{C}=\text{O}}$ shift by 17 cm^{-1} indicates the variation in the $\text{Ni}(\text{CO})_4$ state.

Thus, the interaction of nickel complex (I) with carbon monoxide is complicated and yields a number of products (reaction 4).

It is worth noting that the nickel carbonyls present on the surface of the solid nickel complex (I) treated with carbon monoxide have bridging carbonyl groups. This is proven by the absorption band 1940 cm^{-1} [13].

3.2. Interaction of the surface nickel compound with carbon monoxide

The IR spectrum of SNC treated with carbon monoxide at the molar ratio $[\text{CO}]/[\text{Ni}] = 250$ at room temperature is close to the spectrum of initial solid complex (I) treated with CO (Fig. 2(1,3)). One can see the production of nickel carbonyls (VI) ($\nu_{\text{C}=\text{O}} = 2000, 2070 \text{ cm}^{-1}$), es-

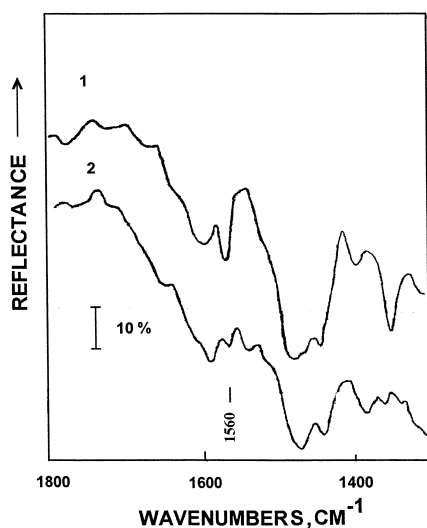


Fig. 1. DRIFT spectrum. (1) Organic nickel chelate (I). (2) SNC.

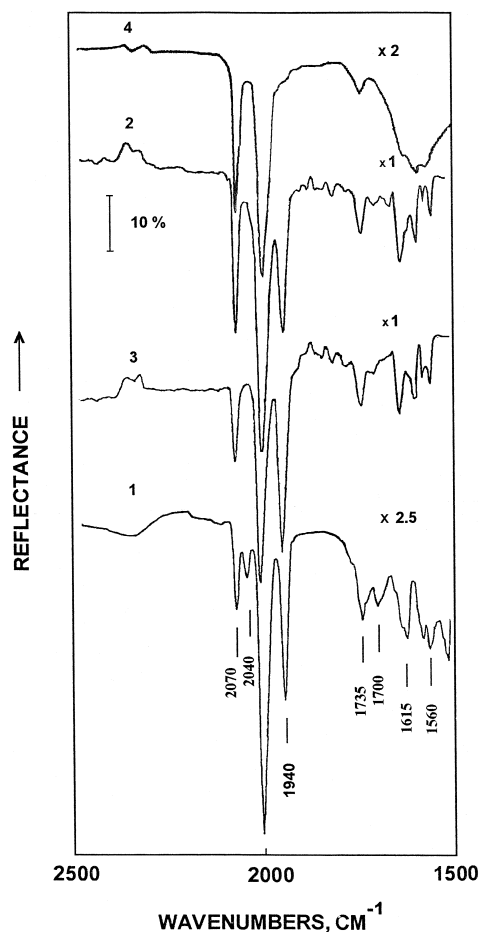


Fig. 2. Differential DRIFT spectrum. (1) Sample of nickel complex (I) is treated with CO at molar ratio $[\text{CO}]/[\text{Ni}] = 250$. (2) Sample of SNC is treated with CO at molar ratio $[\text{CO}]/[\text{Ni}] = 250$. (3) Sample 2 is evacuated for 3 h. (4) Sample of SNC is treated with CO at molar ratio $[\text{CO}]/[\text{Ni}] = 1$.

ter (VII) ($\nu_{\text{C}=\text{O}} = 1740 \text{ cm}^{-1}$) and nickel acyl complexes (V) ($\nu_{\text{C}=\text{O}} = 1630, 1670 \text{ cm}^{-1}$). The absence of absorption band 2040 cm^{-1} indicates that mostly nickel carbonyls (VI) are produced rather than $\text{Ni}(\text{CO})_4$. Moreover, one can see the broad asymmetric bands with maxima at 1640 and 1740 cm^{-1} , which seems to indicate the presence of several acyl complexes and esters. Note that band 1560 cm^{-1} remains. This testifies that only some surface chelate nickel complexes take part in the esters production according to reaction 4.

Nickel carbonyls are known to have low

boiling points [14]. Therefore, heating or evacuating the sample, the surface carbonyls may be removed. Thus, after evacuation at room temperature for 3 h, the number of surface nickel carbonyls is reduced, which is evidenced by the decrease in the intensity of bands 2000 and 2070 cm^{-1} (Fig. 2(2)). At the same time, the intensity of band 1970 cm^{-1} , characterizing the bridging carbonyl groups, grows. The number of nickel acyl complexes (V) remains the same.

The IR spectrum of SNC treated with carbon monoxide at the molar ratio $[\text{CO}]/[\text{Ni}] = 1$ at room temperature is close to that for SNC treated with CO at $[\text{CO}]/[\text{Ni}] = 250$ (Fig. 2(3,4)). The spectrum has no absorption band 1940 cm^{-1} (bridging carbonyl groups). The intensities of bands 2070, 2000 (nickel carbonyls (VI)), 1740 cm^{-1} (esters (VII)), and 1640 cm^{-1} (nickel acyl complex (V)) are much lower.

Thus, the interaction between the supported nickel catalyst and carbon monoxide proceeds according to reaction 4 and yields a number of products, including nickel acyl complex (V) (a product of the CO insertion into the Ni–Ph bond).

3.3. Interaction of the surface nickel compound with deuterated ethylene and carbon monoxide

SNC is known to show high activity in ethylene polymerization [6]. Indeed, after ethylene adsorption on the catalyst at room temperature the IR spectra show the PE production. One can see the intense absorption bands 2195 and 2100 cm^{-1} (Fig. 3(1)), characterizing the C–D vibrations of the $-\text{CD}_2-$ fragment of the polymer chain [13]. Band 1940 cm^{-1} refers to the overtone $\nu_{(\text{C}-\text{C})}$ of the valent vibration of the polymer. The composition of SNC did not change after ethylene adsorption, which is evidenced by the absence of other changes in the IR spectra within 1500–2500 cm^{-1} .

The deuterated ethylene adsorption on SNC pretreated with carbon monoxide does not lead to the spectrum change (Fig. 3(2,3)).

The carbon monoxide adsorption on SNC

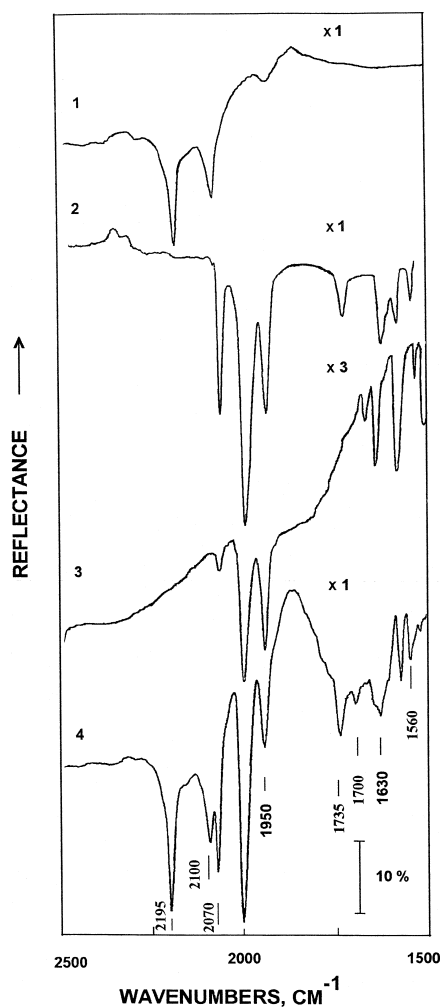


Fig. 3. Differential DRIFT spectrum. (1) Sample of SNC is treated with C_2D_4 at molar ratio $[\text{C}_2\text{D}_4]/[\text{Ni}] = 10$. (2) Sample of SNC is treated with CO at molar ratio $[\text{CO}]/[\text{Ni}] = 250$. (3) Sample 2 is evacuated and then is treated with C_2D_4 at molar ratio $[\text{C}_2\text{D}_4]/[\text{Ni}] = 10$. (4) Sample 1 is treated with CO at molar ratio $[\text{CO}]/[\text{Ni}] = 250$.

pretreated with deuterated ethylene results in the same IR spectrum changes as on the CO adsorption on initial SNC (Fig. 3(2,4)). In this case, nickel carbonyls (VI) ($\nu_{\text{C}=\text{O}} = 2070, 2000, 1950 \text{ cm}^{-1}$), esters (VII) ($\nu_{\text{C}=\text{O}} = 1735, 1700 \text{ cm}^{-1}$) and nickel acyl complexes (V) ($\nu_{\text{C}=\text{O}} = 1615, 1630 \text{ cm}^{-1}$) are produced (Fig. 3(4)). Here, as in the case of SNC untreated with ethylene (Fig. 2(3)), band 1560 cm^{-1} , characterizing the C=C

conjugation in the nickel chelate (I) structure, remains.

In general, the interaction of CO with the catalyst treated with ethylene under conditions leading to the PE production proceeds similarly to the initial catalyst unreacted with ethylene, according to reaction 4. The products include nickel acyl complexes which can result from the carbon monoxide insertion into the nickel–phenyl and nickel–polymer bonds.

4. Conclusions

(1) The interactions of carbon monoxide with the supported catalysts containing the surface organic nickel chelates (VIII) and with the solid initial nickel chelate (I) proceed in a similar manner. In both cases, nickel acyl complex (a product of the CO insertion into the Ni–Ph bond), ester (VII) and various nickel carbonyls (VI) are produced.

(2) According to the IRS data, on the interaction of complexes (VIII) with deuterated ethylene, the polymer is produced. The subsequent carbon monoxide introduction results in the same products as on the reaction between CO and the initial nickel chelate and SNC (nickel acyl complexes, esters and nickel carbonyls).

(3) At the interaction between ethylene and the supported catalyst pretreated with CO at room temperature, the IR spectra show no polymer production.

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