

# Layered Double Hydroxides as Supports for Norbornene Addition Polymerisation Catalysts

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Addition polymerisation of norbornene with transition metal catalysts activated by methylaluminumoxane was first realised on heterogeneous catalytic systems. Advanced inorganic functional polymers possessing anion-exchange properties – layered double hydroxides of Al and Zn of hydrotalcite-type – were applied as supports. They possess high polarity and are selective towards polar molecules like organometallic compounds. The activity of immobilised nickel catalysts was found to be higher than that of the homogeneous one. A certain catalytic activity was also found for group 4 phthalocyanines. The polynorbornenes obtained were characterised by gel permeation chromatography and SEM microimaging. The support's morphology influences the shape, density, and dimensions of the resulting polymer particles.

**Key words:** Hydrotalcite, Polynorbornene, Heterogeneous Catalysis

## Introduction

Polyolefins obtained on transition metal (TM) catalysts represent a major part of high performance organic polymers [1, 2]. Olefin polymerisation catalysis by metal co-ordination compounds activated by methylaluminumoxane (MAO) is realised both in homo- and heterogeneous systems. Moreover, the heterogenisation provides a possibility to reduce significantly the amounts of expensive MAO to be used from 10000–3000 down to 500–100 as [Al]:[TM] molar ratio, and also to improve certain properties of the resulting polymers (enhancement of the molecular weight, improvement of tacticity *etc.*).

Known heterogeneous catalytic systems of this type usually apply silica, alumina and MgCl<sub>2</sub> as supports. The former non-selective sorbents may destroy the metallocene catalyst, and that is the reason of pre-calcination of the supports at high temperatures, accompanied by a loss of specific surface area. In the

overwhelming majority of cases, the support has to be pre-treated with MAO-activator before the treatment with the transition metal catalyst [3]. In this case one deals with complexation of the transition metal to MAO and such system should be regarded as quasi-homogeneous.

We succeeded to avoid the above disadvantages using inorganic functional polymers possessing anion-exchange properties, layered double hydroxides of Al and Zn of hydrotalcite-type (Htlc), with the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2] [A^{n-}_{x/n} \cdot zH_2O]$ . The layer structure is similar to that of brucite, Mg(OH)<sub>2</sub>, and consists of M(OH)<sub>6</sub> octahedra that share edges to form a two-dimensional inorganic polymer. The layer are stacked one on the top of the other and the positive charges arising for the presence of the trivalent cations are compensated by anions accommodated in the interlayer region. These anions are exchangeable with other anions with desired properties and such intercalation provides new functionality to hydrotalcites. The

hydrotalcites have been widely used to obtain mixtures of oxides that are active catalysts of base-catalysed and oxidation reactions [4–6].

On traditional non-selective supports like  $\text{SiO}_2$ , and  $\text{MgCl}_2$  high catalyst concentrations may be reached only in the case of quasi-homogeneous system, *i. e.* when the support is pre-treated with MAO [3, 7]. In contrast to the conventional supports, the layered materials possess high polarity and are selective towards polar molecules like organometallic compounds [8]. In non-polar media the catalyst becomes immobilised on the surface due to dipole-dipole interactions with polar groups. On the other hand, one may also consider reactions between the molecules of the catalyst and functional groups of the sorbent. Finally, intercalation of the catalyst into the interlayer space is also possible.

Inorganic materials modified as above were used for norbornene polymerisation.

## Experimental Section

### *Synthesis of layered inorganic materials*

The crystalline inorganic layered materials of Htlc-type were synthesised using original procedures developed by U. Costantino *et al.* [9]. Solid urea was dissolved in 0.5 M solution of Zn and Al chlorides, having molar fraction  $[\text{Al}]/([\text{Al}]+[\text{Zn}]) = 0.33$ , until the molar ratio  $[\text{urea}]/([\text{Zn}]+[\text{Al}])$  reached the value 3.3. The clear solution was heated, with stirring at reflux temperature for 48 h. The solid, separated from the solution, was washed with distilled water up to a negative test for chloride ions. Finally, it was air-dried and stored in a desiccator with  $\text{P}_4\text{O}_{10}$  at room temperature. The material obtained as above was in the carbonate form. The chloride form of the material was obtained by titrating of the carbonate form, dispersed in a 0.1 M NaCl solution, with a 0.1 M HCl solution by means of an automatic titrator operating at pH stat mode and a pH value of 5 [9].

### *Preparation of heterogeneous catalysts*

Hydrotalcite-like layered double hydroxides of Al and Zn both in chloride and carbonate forms were dried in a vacuum for 8 h at 100 °C. Immobilisation of transition metal catalysts – bis-(acetylacetonato)nickel(II)  $\text{Ni}(\text{acac})_2$ , and dichloro(phthalocyaninato)zirconium(IV)  $\text{PcZrCl}_2$  – was realised by equilibrating 0.5 g of support with 0.1–0.15 M of transition metal catalyst in solution, at 50 °C for 72 h. Subsequently, the support was submitted to a series of extensive (3–5 times) washings with toluene, at room temperature. The heterogeneous catalysts were dried in a vacuum at 50–100 °C and stored in a desiccator under dry nitrogen atmosphere. The samples of the heterogeneous catalyst were analysed

for the transition metal by AAS or spectrophotometry. The amount of the supported catalysts, calculated as transition metal, were 38.25–436.6  $\mu\text{g-atom}$  per gram of the support.

### *Norbornene polymerisation*

Schlenk technique was used in all the polymerisations which were carried out at a constant temperature of 25 °C. Toluene was purified by distillation over Na-benzophenone. MAO (10 wt.% solution in toluene) from Witco GmbH was used without further purification.

In a 25  $\text{cm}^3$  glass flask with a magnetic stirrer, 1.0 g of norbornene and accurately weighed amount of dry immobilised catalyst containing 10  $\mu\text{mol}$  of the metal complex were placed into the reactor. Subsequently, a specified amount of toluene was introduced into the reactor under a stream of dry nitrogen, and co-catalyst solution was injected to initiate the polymerisation. The total volume of the reaction mixture was 10 ml. The polymerisation was stopped after 60 min by adding ethanol containing hydrochloric acid 5%. The obtained polynorbornene (PN) was washed with pure ethanol and vacuum dried at 60 °C for 12 h.

The data on activity of the new heterogeneous catalysts and the polymer properties are presented in Table 1. They correspond to mean values for 3 polymerisations.

### *Characterisation of layered materials and polymers*

The Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer 1720 spectrometer.

Molecular weights and polydispersity indices were determined by Gel Permeation Chromatography (GPC) using a Waters 150CV instrument at 135 °C, 1,2,4-trichlorobenzene as eluent, and a calibration curve prepared with monodisperse polystyrene standards.

Scanning electron microphotographs were taken on a Philips XL30 scanning electronic microscope fitted with a LaB<sub>6</sub> electron gun. Surface areas were determined by  $\text{N}_2$  adsorption-desorption isotherms at 77 K taken with a Micromeritics ASAP 2010 instrument after degassing the samples for 1 d at 393 K.

X-ray powder diffraction (XRPD) patterns of the samples were recorded with a Rigaku Miniflex+ diffractometer controlled by a PC running on a Windows platform and operating at 30 kV, 15 mA using a built-in goniometer with a variable ( $\theta$  compensating) divergence slit, and  $\text{Cu-K}\alpha$  radiation. Diffractograms were collected from  $2\theta = 2$  to  $90^\circ$  using steps of  $0.05^\circ$ .

## Results and Discussion

Chemical analyses of the  $\text{ZnAl-Htlc}$  gave the empirical formula  $[\text{Zn}_{0.65}\text{Al}_{0.35}(\text{OH})_2](\text{CO}_3)_{0.175} 0.5\text{H}_2\text{O}$ .

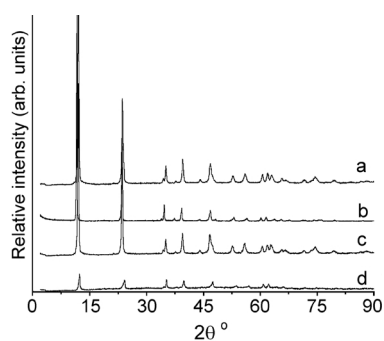


Fig. 1. XRPD of layered double hydroxide materials: Htlc-Cl (a); HtlcCO<sub>3</sub> (b); Htlc-Cl after Ni(acac)<sub>2</sub> treatment (c); partially exfoliated Htlc-Cl after Ni(acac)<sub>2</sub> treatment (d).

The weight-loss curve as a function of temperature indicates that the water of hydration is lost between 100 and 150 °C, while dehydroxylation and decarbonation reactions take place above 250 °C. The B.E.T. specific surface area, obtained from N<sub>2</sub> absorption isotherms, was of 27.4 m<sup>2</sup>/g. The Htlc in its chloride form has the empirical formula [Zn<sub>0.65</sub>Al<sub>0.35</sub>(OH)<sub>2</sub>]Cl<sub>0.35</sub> · 0.6H<sub>2</sub>O and the specific surface area was found to be 38.5 m<sup>2</sup>/g. Both materials have a high degree of crystallinity as is evident from their XRPD patterns reported in Figures 1a and 1b.

For the application as supports for heterogeneous catalytic systems, the hydrotalcite-like layered double hydroxides of Al and Zn were dried *in vacuo* for 8 h at 100 °C, to avoid dehydration accompanied by decomposition at higher temperatures. However, further research showed that such a treatment appeared to be quite sufficient for elimination of traces of water from the sorbent's phase and for the deactivation of Lewis-acidic centres. A widespread opinion states that the presence of hydroxyl and other groups possessing Lewis-acidity in the support material suppresses the activity of the heterogenised catalyst. As practice shows, this statement is true in the case of traditional supports [1, 3]. The results of the present study demonstrate the correctness of our assumption on the passivation of the acidic functionality of the above groups in absolute non-polar media [8]. Under such conditions they continue to be only polarisation sources. The above favours an exclusion of the decomposition of the transition metal active centre, when immobilised on the support not pre-treated with MAO.

The XRPD patterns of both compounds are shown in Figures 1a and 1b. The patterns indicate a good de-

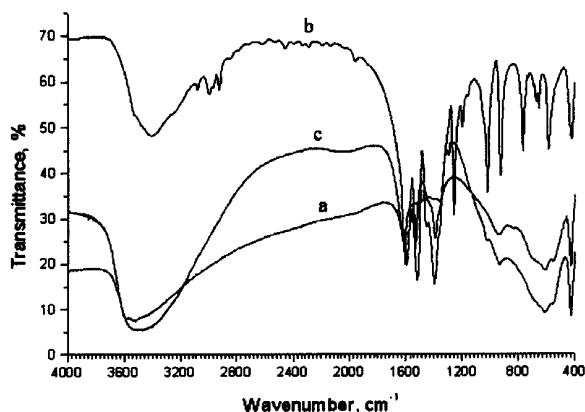


Fig. 2. FTIR spectra of the Htlc support (a); Ni(acac)<sub>2</sub> catalyst (b); and heterogenised catalyst (c).

gree of crystallinity degree of the materials and agree well with those already published and indexed on the basis of the R-3m space group and on hexagonal cell parameters  $a = 3.073$ ,  $c = 22.607$  and  $a = 3.073$ ,  $c = 23.205$  Å for the carbonate and chloride forms, respectively [10, 11]. The first maximum of each diffractogram corresponds to the 003 plane reflection and to an interlayer distance of 7.53 and 7.74 Å for the CO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup> forms, respectively. As a consequence of the dehydration of the samples at 100 °C under vacuum, the interlayer distance of the chloride form collapses to 7.30 Å, while that of the carbonate form remains practically unchanged. In both cases the dehydration process does not cause a change of the layer structure, but only a slight modification of the  $c$  parameter. The XRPD data reported in Fig. 1c and 1d did not show a detectable expansion of the original interlayer distance, indicating the absence of intercalation. Catalyst uptake mainly occurs on the surface of the microcrystals. In spite of repeated washings, the organometallic complex is firmly fixed on the surface of the layered material, possibly due to dipole-dipole interactions.

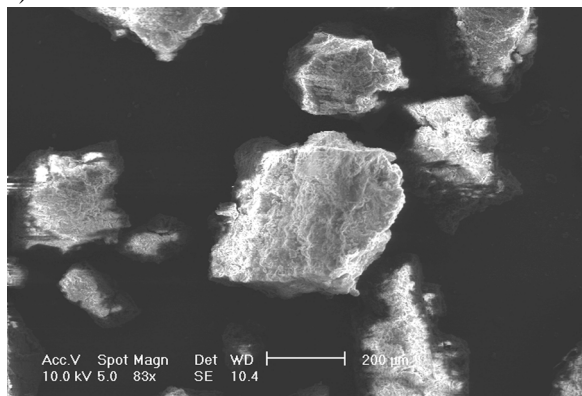
The heterogeneous catalysts were also studied by FTIR spectroscopy. Fig. 2 shows the reference spectra of conditioned Htlc and of the homogeneous catalyst Ni(acac)<sub>2</sub>, together with the target spectrum of the support containing the immobilised complex. The last spectrum contains new distinct absorption bands in the regions of C-H stretching and bending vibrations, C-C and C=O stretching vibrations, characteristic for the acetylacetonato-ligand in the nickel co-ordination compound. Analogous changes were also observed

Catalyst	Support	[M]:[Al]	Activity (kg pol./mol×h)	Mw×10 <sup>5</sup>	Mw×10 <sup>5</sup>	Mw/Mn
Ni(acac) <sub>2</sub>	Unsupported	1 / 750	7.32	1.05	0.54	1.92
Ni(acac) <sub>2</sub>	Htlc-Cl	1 / 500	15.15	3.13	1.49	2.11
Ni(acac) <sub>2</sub>	Htlc-CO <sub>3</sub> <sup>a</sup>	1 / 500	0.6	5.36	2.69	1.99
Ni(acac) <sub>2</sub>	Htlc-CO <sub>3</sub> <sup>b</sup>	1 / 500	21.0	5.39	2.63	2.05
PcZrCl <sub>2</sub>	Unsupported	1 / 1000	0.18	2.74	1.26	2.18
PcZrCl <sub>2</sub>	Htlc-Cl	1 / 500	0.59	1.30	0.61	2.14

Table 1. Norbornene polymerisation using supported and unsupported transition metal catalysts activated by MAO.

<sup>a</sup> The supported catalyst was exposed to natural humidity at room temperature for 3 d before use; <sup>b</sup> the catalyst was immobilised on partially exfoliated support.

a)



b)

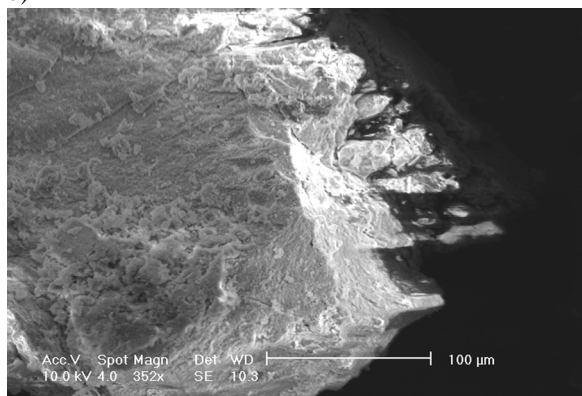


Fig. 3. SEM microimages of polynorbornene samples obtained by homogeneous polymerisation with Ni(acac)<sub>2</sub>/MAO.

for the spectrum of hydrotalcite treated with the dichloro(phthalocyaninato)zirconium(IV) complex.

Table 1 reports the data obtained for homo- and heterogeneous polymerisations. The results indicate that no catalyst desorption takes place during the polymerisation process.

The polymers obtained on heterogeneous catalysts differ from those obtained on homogeneous systems by higher molecular weight values, since hetero-

genisation hinders a majority of chain-transfer and chain-termination reactions. The polymerisation needs smaller excesses of expensive MAO co-catalyst [1, 3]. These facts are reaffirmed by our investigation (see Table 1). Polynorbornene synthesis on heterogeneous catalytic systems is of particular interest, especially because the activity of the heterogeneous system was found to be higher with respect to the homogeneous one. A narrow molecular weight distribution (MWD) of the polymers obtained indicates the presence of a single type of catalytic centres. It was also of interest to determine the activity of a macrocyclic phthalocyanine catalyst both in homo- and in heterogeneous systems for olefin polymerisation.

The FTIR spectra of the polynorbornenes obtained are similar to those known from the literature, and clearly indicate a realisation of the vinyl-polymerisation mechanism, as the vibration bands in the region of 1620–1680 cm<sup>-1</sup> corresponding to carbon-carbon double bond stretching disappear [12].

SEM microimaging was used for morphological observations of the samples of polynorbornene obtained. According to the literature data, one may expect the polymers to be amorphous [13, 14]. Indeed, a lamellar structure has not been observed in any of the polynorbornene sample microphotographs. However, the differences in the polymer appearance are clearly distinguishable for the samples obtained in homo- and heterogeneous polymerisations. In the first case, the polymer consists of quite dense and compact particles well-developed in all directions, which sometimes have small cracks (Fig. 3). The polynorbornenes obtained with heterogenised catalysts have a different appearance. Their morphology is more crumbly with a clearly visible layered flake structure, evidently originating from that of the hydrotalcite support. Their surface contains well-developed sub-structures of ~10–20 μm possessing a well-defined layered-flake character (Fig. 4a, b). This image is consistent with a double grain model proposed by Skomorokhov *et al.* [15], who suggest that solid olefin polymerisation catalysts

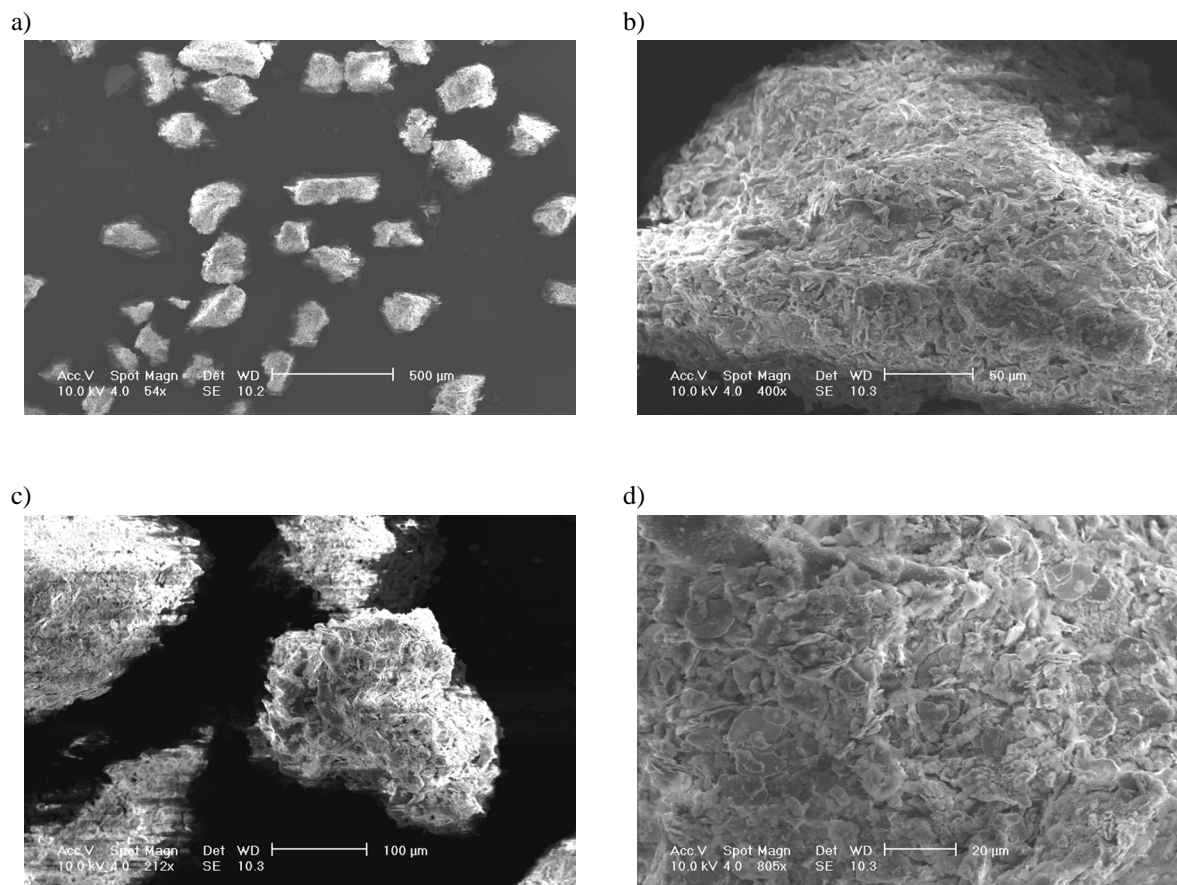


Fig. 4. SEM microimages of polynorbornene samples obtained by heterogeneous polymerisation with  $\text{Ni}(\text{acac})_2/\text{Htlc}/\text{MAO}$ .

possess a well-developed surface to produce polymer macroparticles of 100–500  $\mu\text{m}$ , which consist of sub-particle (10–50  $\mu\text{m}$ ) aggregates, which in turn consist of closely packed aggregates of non-porous microparticles (0.2–0.5  $\mu\text{m}$ ) bearing active catalytic centres on their surface. Since the authors have used a microgranulated  $\text{TiCl}_3$ , they succeeded to obtain electron microscopy images of micro-, sub-, and macroglobules of a polyolefin supporting the model proposed. In the case of hydrotalcites, the material applied by us possesses hexagonal symmetry. It is reasonable to assume that a growing polymer particle would replicate the shape of the sub-particles of the support during the macromolecule growth. Hence, the polymer particles are produced in a form of flakes that subsequently aggregate in conglomerates of larger dimensions (Fig. 4c, d). The formation of dense polymer particles by the homoge-

neous catalytic system, *i.e.* in the absence of the solid phase of the support of a certain symmetry and shape, also underpins the above presumption. In the case of heterogenised catalysts, the support's morphology may influence the shape, density and dimensions of the resulting polymer particles.

## Conclusions

Synthetic tailor made inorganic polymers, crystalline layered double hydroxides of hydrotalcite type, were first used successfully as supports for catalysts in  $\alpha$ -olefin polymerisation. Intercalation of the transition metal catalyst into the interlayer space of the hydrotalcites was not observed, but the surface uptake occurs instead. The activity of immobilised nickel catalysts was found to be higher than that of the

homogeneous ones, preserving traditional advantages of heterogeneous single-site catalysts like higher MW of the resulting polymer, suitability for drop-in technological applications *etc.* A certain catalytic activity was also found for group 4 phthalocyanines. Polynorbornenes, advanced functional plastics, were first obtained using heterogenised transition metal catalytic systems activated by MAO. Dispersity and morphology of the layered material support influence the growth of polymer chain aggregates, and open the

possibility to obtain functional polymers with tailored particle shapes and dimensions.

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