

Preparation, characterization, and catalytic testing of different Me-chitosan complexes for triglycerides transesterification

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Abstract A number of homogeneous and heterogenized chitosan complexes with different metals (Zn, Co, Ca, Ni, Sn, Pb) were synthesized and tested as catalysts in the reaction of transesterification of tributyrin simulating the process of biodiesel production from renewable natural feedstock (triglycerides, vegetable oils). It is found that chitosan complexes are effective catalysts for transformation of tributyrin into the corresponding esters. The comparative analysis of Me–chitosan (homogeneous), Me–chitosan (heterogeneous) and Me–chitosan/SiO₂ catalysts testify that the efficiency of three-component egg-shell systems is close to that of homogeneous catalysts.

Keywords Chitosan · Transesterification · Triglyceride

Introduction

Production of esters of long-chain acids from triglycerides by transesterification became a mature technology. Such esters are well known as biodiesel fuel [1, 2]. Usually methanol is used for transesterification under quite mild conditions (50–80 °C) using alkali (including NaOH or KOH) [3–6] or acid catalysts (H₂SO₄, HC1, H₃PO₄) [7, 8].The major part of biodiesel produced world wide is based on the use of homogeneous catalysts for transesterification [9].

However, the severe requirements to esters used in biodiesel (neutral pH, low content of alkaline metals, surfactants and other undesirable side products) stimulate

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the development of heterogeneous catalysts for the transesterification of vegetable oil.

Since the mechanisms of transesterification on acid and basic centers are different, the acid and basic heterogeneous catalysts are typically considered separately. A number of basic catalysts are described in the literature, some of them demonstrating a high activity in transesterification under mild conditions. Diverse oxides like hydrotalcites [10], MgO, MgO/Al₂O₃ [11], CaO [12, 13], catalysts based on zinc oxide, mixed oxides M–Al–O (M = Sr, Ba), M–Mg–O (M = Y, La) and M–La–O (M = Sr, Ba) [14] are known in the art.

The mechanism of transesterification on Broensted or Lewis acid sites includes the stage of formation of alcoholate species. The acid-type catalysts are widely used in biodiesel production and include basically homogeneous systems, such as Broensted acids (H₂SO₄, p-toluenesulfonic acid) [8] and Lewis acids (metal acetates, other metal complexes) [15, 16]. In studying transesterification of palm and coconut oil, it was shown that the solid oxide acid catalysts can be arranged in the following order with respect to their activity: sulfated $ZrO_2 >$ sulfated SnO₂ > ZnO > ZrO₂ [17].

The strength of acid sites should be optimal for the process to occur, because very strong Lewis acid sites do not demonstrate activity in transesterification as a result of very strong adsorption of products [18–20].

One of the most important problems is the development of a heterogeneous catalyst demonstrating a reasonably high activity under milder conditions compared to the conventional conditions used for heterogeneous catalysts (220–240 $^{\circ}$ C, 4.0–6.0 MPa), with the stability in aqueous solutions being another important factor.

Recently the interest is focused on the use of polymer matrices for immobilization of the active component (metal ions) for the transesterification reaction.

It was also reported that metal compounds of the type Me(3-hydroxy-2-methyl-4-pyrone)₂(H₂O)₂, where M = Sn, Zn, Pb and Hg, are active for soybean oil methanolysis [21, 22]. The activity diminishes in the order Sn²⁺ \gg Zn²⁺ > Pb²⁺ \approx Hg²⁺. It is worth to note that the complexes of Sn and Zn showed significant activities in this reaction, with the yield of the product approaching 90 % in 3 h at a molar ratio 400:100:1 (methanol:oil:catalyst). Thus, the complexes of this type, especially immobilized in a polymer matrix may show some promising results in the transesterification reaction.

Now, organic polymers including natural abundant and "green" materials (such as cellulose, chitin, and especially chitosan) are widely employed as carriers for immobilizing metal complexes that serve as catalysts in diverse processes. Chitosan (poly(1-4)-*N*-acetyl- β -D-glucosamine) is characterized by a high nitrogen content, which explains, in turn, its ability to concentrate metal ions and even neutral atoms of different metals via different mechanisms such as ion exchange or chelate formation, depending on the metal nature and pH of the solution.

Metal-chitosan complexes are now widely used as catalysts in diverse reactions [23]: oxidation (Cu, Fe, Co) [24–27], hydrogenation (Pd, Pt, Ni, Cr, Zn) [28], allylic substitution [Trost–Tsuji reaction, Pd(II), Pd(0)], Suzuki and Heck reactions (Pd), polymerization (Cu, Co, Y, La, Pr, Nd, Er), olefins cyclopropanation (Cu),

carbonylation (Pd/Ni, Rh), asymmetric dihydroxylation of olefins (Os, Co), dechlorination (Pd/Fe) [29], alkynes hydroamination [30].

Thus, the goals of this study were to design heterogenized chitosan complexes with a representative set of non-noble metals, including basic (Ca) and acidic (Zn, Co, Ni, Sn, Pb) transesterification catalysts and to characterize their structure and catalytic performance.

Experimental

Materials

As-received chitosan powder (made from crab shells, molecular weight 100,000–150,000) was used without further purification. The deacetylation degree of amino groups was 70 %, the moisture content in the chitosan powder was 3 wt%. NiCl₂, Pb(OAc)₂, CaCl₂, ZnCl₂, SnCl₂, CoCl₂ were purchased from Fluka AG (Switzerland) as an analytical grade reagent, HCl and NaOH were also of the analytical grade purity. Glyceryl tributirate (tributyrine), 98 %, Aldrich product, was used without purification.

Complex preparation

Chitosan was modified with a number of metals [Ni(II), Pb(II), Ca(II), Zn(II), Sn(II), Co(II)] by different methods, described early in our previous works [6–9], such as adsorption of metal ions from water solutions on the surface of chitosan or coprecipitation of a soluble form of chitosan with divalent metal precursors. The metal content varied from 5 to 9 wt%.

Homogeneous metal–chitosan complex (starting material for the heterogenized complexes)

A calculated amount of metal chloride (or acetate in the case of Pb) was added to a 1.5 wt% solution of chitosan in 0.1 M HCl at room temperature, and the mixture was stirred until the formation of a transparent clear solution.

Coprecipitation method

A transparent clear solution of the homogeneous metal-chitosan complex was prepared as described above and added dropwise to a glass beaker with a 0.5 M NaOH solution, which led to immediate coagulation of the drops into spherical globules. The spherical particles formed (diameter, 2–3 mm) were filtered off after 10 min and repeatedly washed with distilled water until neutral pH. After this procedure, the globules of chitosan containing immobilized Lewis acid were filtered off and air-dried at room temperature for 48 h.

Impregnation (adsorption) method

A 1.5 wt% chitosan solution was added dropwise to a glass beaker with a 0.5 NaOH solution, with resulting immediate formation of spherical globules of pure chitosan. The particles were filtered off after 10 min, repeatedly washed with distilled water until neutral pH, filtered again and air-dried at room temperature for 48 h. A weighed amount of a metal chloride (or acetate in the case of Pb) was dissolved in 20 ml of distilled water and stirred with 1.0 g of dried chitosan particles for 1–3 h. Then the particles were removed by filtration, washed with distilled water and air-dried for 24 h.

Immobilization of the metal-chitosan complex on the surface of porous silica gel

One gram of amorphous SiO₂ (aerosil; fraction 0.25–1 mm; $S(BET) = 330 \text{ m}^2/\text{g}$; water adsorption capacity 1.2 ml/g) was impregnated with 1.2 ml of a solution of the homogeneous metal–chitosan complex prepared as mentioned above. Then complex-loaded silica was placed in a 0.5 M solution of NaOH for 15 min, filtered off and repeatedly washed by distilled water until neutral pH. The particles obtained were dried at room temperature in air for 24 h and then in a vacuum for 10 h.

Characterization

IR spectroscopy

Transmission FTIR spectra were recorded at 20 °C using a Nicolet Protege 460 spectrometer in the range of 4000–400 cm⁻¹ at a resolution of 8 cm⁻¹ and also with a Matteson Galaxy Series FTIR 5000 spectrometer in the range of 4000–600 cm⁻¹ at a resolution of 4 cm⁻¹. For the study of the homogeneous palladium–chitosan complex, some droplets of the solution were deposited on quartz plates and air-dried for 48 h. Dry globules of heterogeneous chitosan samples (adsorption and coprecipitation complexes) were ground in a mortar, the fine powder was mixed with KBr, pressed into a thin pellet, and placed in the sample holder.

X-ray absorption spectroscopy

XAS measurements were carried out at HASYLAB (DESY in Hamburg, Germany) on the beamline X1 (Pb L₃-edge, 13035 eV) using a double-crystal Si(311) monochromator, which was detuned to 50 % of the maximum intensity to exclude higher harmonics in the X-ray beam. Ni *K* edge X-ray absorption spectra at 8333 eV were measured at HASYLAB on the beamline E4 using a Si(111) double crystal monochromator, which was detuned to 30 % of the maximum intensity to exclude higher harmonics. Samples were pressed into wafers (with polyethylene as a binding agent) in a standard 13-mm die, using the optimum weight to maximize the signal-to-noise ratio. The spectra were recorded in the transmission mode at a low temperature (T = 80 K) in order to decrease the Debye–Waller factors. All spectra were measured simultaneously with the reference spectrum of Pb or Ni foil placed

between the 2nd and 3nd ionisation chambers for energy calibration. The spectra of Pb or Ni foils, PbO and Pb(OAc)₂, NiO, Ni(NO₃)₂, Ni₂(OH)₂CO₃ and NiCl₂ were used as references and were collected under the same conditions.

Analysis of the EXAFS spectra was performed with the software VIPER for Windows [31, 32]. In the spectra of the absorption coefficient μ , a Victorian polynomial was fitted to the pre-edge region for background subtraction. A smooth atomic background μ_0 was evaluated using a smoothing cubic spline. The Fourier analysis of the k^2 -weighted experimental function $\chi = (\mu - \mu_0)/\mu_0$ was performed with a Kaiser window. The required scattering amplitudes and phase shifts were calculated by the ab initio FEFF8.10 code for PbO and NiO. The fitting was done in the *k*- and *r*-spaces. The shell radius *r*, coordination number *N*, Debye–Waller factor σ^2 and adjustable "muffin-tin zero" ΔE were determined as fitting parameters. The errors of the fitting parameters were found by decomposition of the statistical χ^2 function near its minimum, taking into account maximal pair correlations.

SEM

Micrographs of sample surfaces were taken by scanning electron microscopy (JSM-5300LV JEOL). Before measurement samples surface was decorated by fine Au layer using JFC-1100E set-up.

Catalytic experiments

Catalytic experiments on tributyrine transesterification were performed in a batch reactor. Ttributyrine—1,3-di(butanoyloxy)propan-2-yl butanoate—is a triglyceride naturally present in butter. It is an ester composed of butyric acid and glycerol. The reaction temperature was t = 65 °C, the reaction time, 3–6 h, catalyst/tributyrine = 1/20, a threefold excess of CH₃OH, the stirring rate—750 rpm. The reaction was carried out without any solvents. Ester formation was controlled by the GC method (capillary column PONA Dimethylpolysiloxane, Length: 50 m, Inner Diameter: 0.20 mm, Film Thickness: 0.50 mm).

Results and discussion

Catalytic tests

Tributyrine was chosen as a model substrate to estimate the catalytic activity of metal-chitosan complexes in the transesterification reaction (Fig. 1).

Homogeneous complexes of chitosan with different metals demonstrated the activity as indicated in Table 1 and Fig. 2. The most active were the Pb- and Ni-containing samples.

When we switched from homogeneous to heterogenized systems, we found that their activity as catalysts of the tributyrine transesterification reaction depended on the method of preparation. The Me–chitosan complexes prepared by adsorption were virtually inactive in the reaction. When these complexes were tested, the



Fig. 1 Transesterification of tributyrin. Reaction conditions: t = 65 °C, catalyst/substrate = 1/20, a threefold excess of CH₃OH, the reaction time—3 h

| Table 1 Catalytic performance of homogeneous complexes Me-chitosan | τ (h) Ester concentration (g/ml) | | | | | | |
|--|---------------------------------------|------|------|------|------|------|------|
| | _ | Pb | Ni | Sn | Zn | Ca | Co |
| | 1.00 | 0.34 | 0.07 | 0.12 | 0.12 | 0.04 | 0.05 |
| | 2.00 | 0.50 | 0.40 | 0.17 | 0.17 | 0.08 | 0.06 |
| | 3.00 | 0.53 | 0.48 | 0.23 | 0.30 | 0.21 | 0.09 |



Fig. 2 Conversion of tributyrin on homogeneous metal(II)-chitosan complexes

reaction solutions were colored, which is an evidence for the leaching of the metal ions.

Catalytic testing of heterogenized Me–chitosan complexes prepared by the coprecipitation method revealed a good performance of all the catalysts for the reaction of transesterification. The Pb- and Ni–chitosan complexes demonstrated the best catalytic activity, Sn and Ca-complexes exhibited the activity comparable with that of the leading metals (Pb, Ni). The tributyrin conversion reached 65 % for the Pb-containing catalysts and 50 % for the Ni-sample, with the selectivity of 98 %. Consequently, the catalytic activity order found for the homogeneous chitosan complexes is reproduced for the heterogenized catalysts obtained by the coprecipitation method.

As we found earlier, metal-chitosan complexes immobilized on the surface of macroporous silica to produce the egg-shell catalysts possess a more developed



Fig. 3 Activity of Pb-containing catalysts

surface area ($\sim 300 \text{ m}^2/\text{g}$) and a higher mechanical stability as compared with bulky heterogenized chitosan complexes [25, 26].

The efficiency of the heterogenized egg-shell Me–chitosan/SiO₂ catalysts was compared with the activity of heterogenized Me–chitosan complexes and homogeneous samples. It was shown that the activity of the egg-shell systems is close to the activity of the homogeneous catalysts.

The results obtained for the most active system, Pb-chitosan, are displayed in Fig. 3.

Catalyst stability was confirmed by SEM and XAS methods. SEM data testify that the polymer complex film covering the surface of Pb-containing catalyst is not changing during the catalytic operations (Table 1). All the catalysts are stable during four cycles of operations. SEM images and XAS results for catalysts after catalysis are given after the 4-th cycle of operations (Fig. 4).

IR spectroscopy experiments as well provide information about the polymer complex structure being saved during the catalysis (Fig. 5).

The IR spectra of all samples studied are characterized by the absorption bands of chitosan and its derivatives (Fig. 5, lower curve): (1) a broad unstructured absorption between 3700 and 3100 cm⁻¹ related to the superposition of OH and NH group stretching vibrations; (2) narrow bands of CH group stretching vibrations at 2800–3000 cm⁻¹, assigned to CH₂ (2860 and 2930 cm⁻¹) and CH (\sim 2900 cm⁻¹) fragments; and (3) bands of bending NH group vibrations in the 1660–1530 cm⁻¹ range. Additionally, the IR spectra of Pb–chitosan complexes as prepared and after catalysis exhibit an intense set of bands in the low-frequency region (800–400 cm⁻¹). Presumably, these bands are ascribed to stretching vibrations of Pb–N, Pb–O bonds.

This set of bands is observed as a broad feature peaking at 657 cm^{-1} . Furthermore, there is also a change in relative intensities in the region of bending NH group vibrations (1500–1680 cm⁻¹). The spectra of Pb-complexes before and after catalysis are similar.

Figure 6 shows Pb L₃ XANES spectra of the samples with the reference compounds: Pb foil, PbO and Pb(OAc)₂. The spectra of Pb samples are quite different from those of Pb foil and PbO and resemble the spectrum of $Pb(OAc)_2$.



Fig. 4 SEM images of catalyst/carrier particles and catalyst/carrier surface. **a** SiO₂ ($S_{BET} = 330 \text{ m}^2/\text{g}$); **b** egg-shell system Pb–chitosan/SiO₂ before catalysis ($S_{BET} = 275 \text{ m}^2/\text{g}$); **c** egg-shell system Pb–chitosan/SiO₂ after catalysis ($S_{BET} = 270 \text{ m}^2/\text{g}$)

The Fourier transformations of EXAFS oscillations of Pb samples and references are presented in Fig. 7. In the spectrum of Pb foil, two main peaks correspond to the first coordination shell containing 12 Pb atoms at 3.500 Å real distances from the central Pb atom. In the spectrum of PbO, the first peak corresponds to the first coordination shell containing 4 O atoms at 2.308 Å real distances from the central Pb atom.

The FT EXAFS spectra of Pb–chitosan samples are different from those of three references. Two peaks between 1.5 and 2.5 Å uncorrected distances are developed in these spectra.



Fig. 5 IR-spectra of initial chitosan and chitosan modified with lead (coprecipitation complex) before and after catalysis



Fig. 6 Pb L₃ XANES spectra of Pb–chitozan samples and references: *1* Pb foil, 2 PbO, *3* Pb(OAc)₂, *4* Pb–chitosan before catalysis, 5 Pb–chitosan after catalysis

The Pb L_3 EXAFS spectra of the samples may be readily fitted in both r- and k-spaces with a double-shell model—first: an oxygen shell around the central absorbing lead atom and second: an oxygen and/or nitrogen shell around the central absorbing lead atom. Because the atoms (O and N) are similar in the atomic weight and atomic size, the X-ray scattering amplitudes and phases for these atoms are similar, so, they are practically indistinguishable as scattering atoms in EXAFS spectroscopy. The results of the model fits of the EXAFS spectra are given in Table 2.



Fig. 7 Fourier transforms of Pb L_3 EXAFS spectra of Pb–chitozan samples and references: *1* Pb foil, 2 PbO, 3 Pb(OAc)₂, 4 Pb–chitosan before catalysis, 5 Pb–chitosan after catalysis

| Table 2 EXAFS results for Pb-chitosan samples | Sample | Path | <i>r</i> (Å) | Coordination number | |
|--|------------------|--------|-----------------|---------------------|--|
| | Before catalysis | Pb–O | 2.267 ± 0.009 | 0.6 ± 0.1 | |
| | | Pb-O/N | 3.116 ± 0.006 | 2.2 ± 0.1 | |
| | After catalysis | Pb–O | 2.267 ± 0.012 | 0.7 ± 0.1 | |
| | | Pb-O/N | 3.116 ± 0.012 | 1.9 ± 0.2 | |

XAS (XANES and EXAFS) spectra show that Pb in the samples under study exists as Pb^{2+} and nearest-neighbors are oxygen and nitrogen atoms. Both the electronic and coordination states of lead species anchored in the chitosan matrix did not change during the catalytic reaction.

Because the Pb-polymer complex could not be considered as a good candidate for "green catalysis", we have investigated the Ni-polymer complex as well.

The Ni *K*-edge XANES spectra of the catalysts and the reference samples are depicted in Fig. 8. The positions of the Ni K-edge energy in the spectra of samples are different from that of Ni-foil and close to those of NiO, Ni(NO₃)₂, Ni₂(OH)₂CO₃ and NiCl₂·6 H₂O, thus indicating that the Ni species in Ni–chitosan samples prepared by different methods are Ni²⁺ ions. The intensity of the white line in the spectra of the Ni–chitosan samples are the same for both samples, and after catalysis it does not change. Noteworthy that the intensity of the white line in the spectra of catalysts is different from those observed for references.

The Fourier transformation of EXAFS oscillations of the Ni–chitosan samples and Ni references are presented in Fig. 9. In the spectrum of NiO, the first two peaks correspond to the first and second coordination shells containing 6 O atoms at 2.084 Å and 12 Ni atoms at 2.947 Å real distances from the central Ni atom. In the spectrum of Ni(NO₃)₂ a single peak observed corresponds to the first coordination



Fig. 8 Normalized XANES spectra of Ni–chitosan catalysts and reference compounds: *1* Ni foil, 2 NiO, 3 Ni(NO₃)₂, 4 Ni₂(OH)₂CO₃, 5 NiCl₂, 6 Ni–chitosan, co-precipitated, before catalysis, 7 Ni–chitosan, co-precipitated, after catalysis, 8 Ni–chitosan, impregnated, before catalysis, 9 Ni–chitosan, impregnated, after catalysis



Fig. 9 Fourier transforms of Ni K-edge EXAFS spectra of Ni–chitosan catalysts and references: *1* Ni foil, 2 NiO, 3 Ni(NO₃)₂, 4 Ni₂(OH)₂CO₃, 5 NiCl₂, 6 Ni–chitosan, co-precipitated, before catalysis, 7 Ni–chitosan, co-precipitated, after catalysis, 8 Ni–chitosan, impregnated, before catalysis, 9 Ni–chitosan, impregnated, after catalysis

shell containing 6 O atoms at 2.419 Å. In the spectrum of NiCl₂·6 H₂O, one can observe one peak corresponding to the first and second coordination shells containing 2 O atoms at 1.783 Å and 2 O atoms at 2.273 Å.

The FT EXAFS spectra of Ni–chitosan samples are different from those of NiO. Two peaks near 1.5 and 2.5 Å uncorrected distances are developed in the spectra of the Ni–chitosan samples prepared by the co-precipitated method. The FT EXAFS

| Sample | Treatment | Atomic pair | <i>r</i> (Å) | CN | $\sigma^2 \; (10^{-3} \; {\rm \AA}^2)$ | $\Delta E (eV)$ |
|---|------------------|-----------------|-------------------|---------------|--|-----------------|
| Co-precipitated | Before catalysis | Ni-Cl | 2.170 ± 0.009 | 5.6 ± 0.5 | 12 ± 1 | -3 ± 1 |
| | | Ni–O | 2.057 ± 0.006 | 6.2 ± 0.3 | 9 ± 1 | 14 ± 1 |
| | After catalysis | Ni-Cl | 2.170 ± 0.009 | 6.0 ± 0.5 | 13 ± 1 | -3 ± 1 |
| | | Ni-O | 2.059 ± 0.006 | 6.4 ± 0.3 | 9 ± 1 | 15 ± 1 |
| Impregnated | Before catalysis | Ni–O | 2.087 ± 0.005 | 6.7 ± 0.3 | 12 ± 1 | 16 ± 1 |
| | After catalysis | Ni–O | 2.089 ± 0.005 | 6.6 ± 0.2 | 12 ± 1 | 16 ± 1 |
| Ni-foil | | Ni–Ni | 2.485 ± 0.001 | 11.6 ± 0.2 | 4 ± 0.1 | 10 ± 0.2 |
| NiO | Ni–O | 2.092 ± 0.008 | 5.9 ± 0.4 | 11 ± 2 | 3 ± 0.8 | |
| | | Ni–Ni | 2.944 ± 0.003 | 11.9 ± 0.4 | 7 ± 0.3 | 0.1 ± 0.4 |
| Ni(NO ₃) ₂ | | Ni–O | 2.043 ± 0.003 | 4.9 ± 0.2 | 6 ± 0.5 | -1 ± 0.4 |
| Ni ₂ (OH) ₂ CO ₃ | Ni–O | 2.046 ± 0.004 | 4.9 ± 0.2 | 8 ± 0.7 | 0.1 ± 0.4 | |
| | | Ni–Ni | 3.112 ± 0.004 | 6.1 ± 0.3 | 9 ± 0.5 | 0.4 ± 0.5 |
| NiCl ₂ | | Ni-Cl | 2.251 ± 0.006 | 6.0 ± 0.3 | 16 ± 1 | 2 ± 1 |

Table 3 EXAFS data for 5 % Ni/chitosan catalysts and references

spectra of the Ni–chitosan samples prepared by impregnation are different. A single peak near 1.5 Å uncorrected distance is observed.

Table 3 presents apparent coordination number (CN) and distance obtained by fitting coordination shells with the amplitude and phase functions extracted from the data for NiO and NiCl₂.

The fitting revealed that the Ni–O coordination number is around 6 for the samples prepared by the co-precipitation method and about 7 for the samples prepared by impregnation. The Ni–O real distance is about 2.06 Å in the co-precipitated samples and about 2.09 Å in the impregnated samples The first coordination shell of Ni in the samples prepared by the co-precipitation method contains about 6 Cl atoms at the 2.17 Å real distance. No changes were found between the Ni–chitosan samples before and after catalysis.

Earlier we have found for the Pd–chitosan complexes that the method of preparation of the complex (co-precipitation or adsorption) determines the way of the metal coordination [24]. The monodentate coordination predominates in the complexes prepared by adsorption, whereas chelated coordination complexes are formed in the case of the complexes prepared by co-precipitation. The data obtained by the EXAFS method for the Ni–chitosan complexes prepared by different methods are consistent with the results found for Pd–chitosan complexes.

Conclusions

The proposed chitosan-supported metal complexes with different metals (Pb, Sn, Ni, Ca, Zn, and Co) belong to the hybrid nanomaterials [33], especially the heterogenized systems on an oxide support. They were synthesized and characterized by IR and XAS methods. All the complexes catalyze the transesterification of triglycerides. It was found that the most active catalysts are Pb-, and Ni-containing

polymer complexes. With the example of Pb-containing complexes, it was shown that the efficiency of egg-shell systems Me–chitosan/SiO₂ is close to that of homogeneous Me–chitosan catalysts.

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