# Promising Applications of Polyethyleneimine as a Ligand in Rhodium-Catalyzed Tandem Hydroformylation/Hydrogenation of Olefins

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**Abstract**—Three rhodium-containing catalytic systems active in tandem hydroformylation/hydrogenation of unsaturated substrates were developed based on polyethyleneimine (PEI): a homogeneous system with distillation of the product; a biphasic system with segregation of the product and catalyst into a non-polar phase and a polar phase, respectively; and a solid catalyst prepared from PEI and (3-chloropropyl)triethoxysilane with its centrifugation from the product mixture. All the systems were shown to be reusable over multiple cycles in hydroformylation/hydrogenation, with the catalytic activity being partially sustained in both steps of the tandem process. Methylation of PEI (or its NH and $NH_2$ moieties in the case of solid material) was found to be critical for the catalytic activity in hydroformylation.

**Keywords**: hydroformylation, tandem reactions, reductive hydroformylation, olefins, alcohols, synthesis gas, rhodium complexes, polyethyleneimine, catalyst separation and recycle

Tandem hydroformylation/hydrogenation (also known as reductive hydroformylation or hydrohydroxymethylation) is a catalytic process to produce primary alcohols from olefins. A process design that provides for hydroformylation into intermediate aldehydes and their subsequent hydrogenation into alcohols without varying the reaction conditions or the catalyst is commonly referred to as a one-pot auto-tandem process (Scheme 1).

Although higher primary alcohols have been commercially produced from olefins over cobalt–phosphine catalysts [1], complexes of rhodium (the most active metal in hydroformylation) have not been used in single-step synthesis of alcohols. However, a number of rhodium catalysts are known to be active not only in hydroformylation but also in hydrogenation of aldehydes in the presence of synthesis gas (syngas) [2]. For this purpose, donor ligands that increase the electron density at the rhodium atom, such as aliphatic phosphines [3] and tertiary amines [4], have most commonly been used. Despite the high catalytic activity and selectivity in hydroformylation provided by phosphine ligands, they

are toxic and susceptible to oxidation in the presence of atmospheric oxygen. The latter drawback is more pronounced in aliphatic phosphines as donor ligands than in aromatic-substituted phosphines, a more common ligand type in catalysis. These issues predictably complicate both the process design and operation, thus increasing the cost of synthesis based on phosphine ligands. Tertiary amines are a more affordable and environmentally friendly alternative, though their rhodium complexes have not yet reached hydroformylation activity as high as that provided by their phosphorus-containing counterparts.

The ability of $Rh/NR_3$ systems to catalyze tandem hydroformylation/hydrogenation of olefins was first demonstrated in the 1970s [5, 6]. Over the next two decades, a number of solid polymer catalysts of this type were additionally developed [7–11]. Recent years have seen increasing interest in such systems [12]. Two years ago a German research team reported on their detailed study on the correlation between the structure of nitrogen-containing ligands and the activity of their complexes in tandem hydroformylation/hydrogenation

**Scheme 1.** Auto-tandem hydroformylation/hydrogenation of olefins.
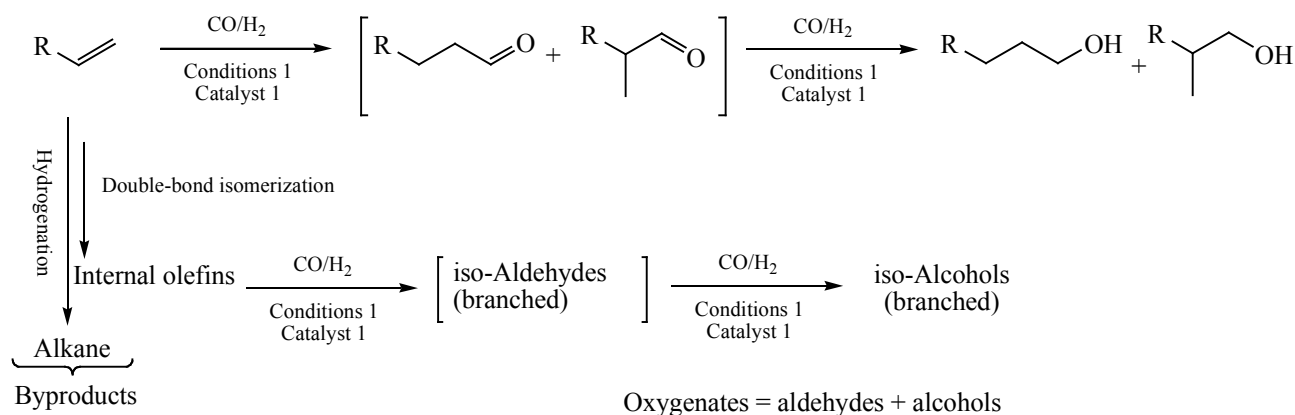


[13]. A research team headed by Prof. Monflier has published a series of studies focused on using Rh/NR$_3$ systems to modify complex unsaturated substrates such as unsaturated fatty acid esters [14–16]. Since 2021 a growing amount of developments has been devoted to biphasic systems of this kind for tandem hydroformylation/hydrogenation of oil-soluble substrates [17–19], including a study carried out in our laboratory [20]. Furthermore, in cooperation with U.S. researchers, we have synthesized a series of solid rhodium catalysts based on hybrid materials in which N-containing polymers such as polyallylamine and polyethyleneimine were grafted on the surface of a mesoporous silica [21]. In all the mentioned studies (except for [19], where the reaction was carried out in ionic liquids), high catalytic activity in hydroformylation/hydrogenation was achieved only if tertiary nitrogen atoms were in large excess compared to Rh atoms. This consideration reasonably serves as a guide for further developments of novel catalytic systems: a high concentration of NR$_3$ groups in the microenvironment of Rh must be of critical importance.

The present study was aimed at investigating the potential applicability of polyethyleneimine (PEI) in Rh systems for tandem hydroformylation/hydrogenation. PEI is a polymer produced on an industrial scale for various applications in products such as paper raw material,, surfactants, cosmetics, epoxy and polyurethane resins, etc. [22, 23]. PEI is distinguished by a high concentration of nitrogen sites, including those available for modification. The present work shows the feasibility of Rh/PEI catalytic systems for reductive hydroformylation under both homogeneous and biphasic catalytic conditions. Furthermore, the paper demonstrates the potential for preparing a novel PEI-based solid hybrid catalyst with high content of tertiary N atoms. The key factor in developing a catalytic system is to design an optimal technique for the separation and recycling of the catalyst, depending on the requirements governed by the molecular weights of the substrates [24]. For example, the optimal design for short-chain (<C$_5$) olefins is distillation of the product and recycling of heavy residues, whereas conversion in a biphasic system or over a heterogenized catalyst might prove to be the best choice for longer (>C$_5$) olefins (Scheme 2).

## EXPERIMENTAL

**Materials.** We used 1-hexene (98%, Merck); 1-octene (98%, Aldrich); cyclohexene (99%, Sigma-Aldrich); styrene (Merck); propylene trimers (an isomer mixture, Nizhnekamskneftekhim, Russia); branched PEI (number-average molecular weight 600 amu, weight-average molecular weight 800 amu, Sigma-Aldrich); formic acid (95%, Sigma-Aldrich); an aqueous formaldehyde solution (37%, Sigma-Aldrich); (3-chloropropyl)triethoxysilane (95%, Sigma-Aldrich), an aqueous ammonia solution (25%, AR grade, Komponent-Reaktiv, Russia); toluene (CP grade, Komponent-Reaktiv); dodecane (99%, Merck); sodium hydroxide (AR grade, Chimmed, Russia); *n*-heptane (pure, Komponent-Reaktiv); and methylene chloride (CP grade, Komponent-Reaktiv).

Solvents were prepared in accordance with standard procedures.

**Scheme 2.** Alternative approaches to development of PEI-based catalytic systems and techniques for their separation and recycle.
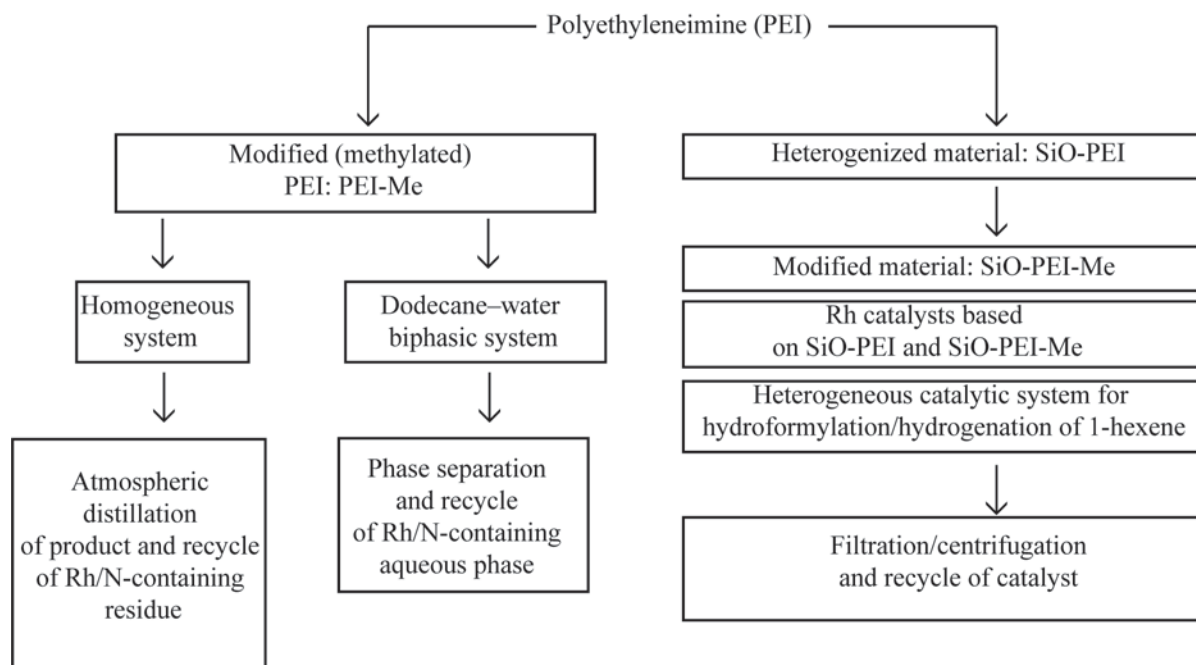


Rhodium acetylacetonate dicarbonyl, a compound with the formula $Rh(acac)(CO)_2$, was synthesized from rhodium(III) chloride hydrate, $RhCl_3 \cdot 4H_2O$ (Aurat, Russia), in accordance with the procedure described in [27].

**Synthesis of PEI-Me and Rh/PEI-Me.** Based on the procedure described in [28], we developed a technique for the methylation of PEI. Formaldehyde (20 mL of a 37% aqueous solution) and formic acid (20 mL) were added to 5 g of PEI-600. The mixture was stirred under refluxion for 8 h, then at room temperature for 16 h. When the reaction was completed, an excess aqueous NaOH solution was added. As the resultant mixture was turning orange, it was transferred to a separatory funnel and allowed to stand for 24 h to ensure segregation of the mixture. An upper phase (an orange viscous liquid that contained the reaction product) was separated from an aqueous phase. The yield of PEI-Me was 4.5 g.

To test the hydroformylation/hydrogenation of 1-hexene under biphasic conditions, as well as the hydroformylation/hydrogenation of other substrates, a solution of rhodium acetylacetonate dicarbonyl in methylated PEI was pre-prepared. For this purpose, 1.2 g of the PEI-Me was mixed with 10 mg of $Rh(acac)(CO)_2$ at 65°C for 2 h. As a result, the $Rh(acac)(CO)_2$ was completely dissolved to form a dark-orange viscous solution. In other experiments involving PEI and PEI-Me, the polymer and the $Rh(acac)(CO)_2$ were separately introduced into the reactor.

**Synthesis of SiO-PEI, SiO-PEI-Me, and related catalysts.** To synthesize SiO-PEI, the procedures described in [29] and [30] were adapted. PEI-600 (1.5 mg) and triethanolamine (1.15 g) were dissolved in 20 mL of ethanol. In another flask, 4 mL of (3-chloropropyl) triethoxysilane was dissolved in 25 mL of ethanol. This solution was added dropwise to the PEI-600 solution under stirring. The mixture was boiled for 12 h, then the ethanol was distilled using a rotary evaporator. To the remaining viscous mass, 15 mL of the 25% aqueous ammonia solution was added, stirred at room temperature for 1.5 h, and evaporated in the rotary evaporator. The resultant yellow solid was ground in a mortar and mixed with ethanol under heating (60°C) for 2 h, after which the washing solution was centrifuged, and the washing was repeated. Using a fresh portion of ethanol, the solid was transferred into a flask and dried, first in a rotary evaporator and then in a muffle furnace at 90°C for 6 h. After the double washing and double drying, 2.1 g of a pale-yellow free-flowing SiO-PEI powder was obtained.

To synthesize SiO-PEI-Me, 300 mg of SiO-PEI, 3 mL of the 37% aqueous formaldehyde solution, and

a mixture of 3 mL of formic acid and 0.3 mL of water were introduced into a round-bottom flask. The mixture was boiled for 7 h, then stirred without heating for 12 h. The solid was centrifuged, washed with methanol under heating (60°C, twice for 2 h), topped up with methylene chloride, transferred into the round-bottom flask, and dried using a rotary evaporator. The resultant SiO-PEI-Me white powder weighed 295 mg. The composition and structure of SiO-PEI and SiO-PEI-Me were examined by IR spectroscopy and elemental analysis.

To load rhodium on SiO-PEI and SiO-PEI-Me, the following procedure was used: 250 mg of the material, 25 mg of Rh(acac)(CO)$_2$, and 5 mL of methylene chloride were loaded into a round-bottom flask; the mixture was stirred at room temperature for 24 h, washed twice with toluene (2 mL each), and dried in a rotary evaporator. The SiO-PEI and SiO-PEI-Me powders turned pale green and bright yellow, respectively. The powders weighed 237 and 245 mg, respectively.

**Catalytic test.** The catalytic tests of hydroformylation/hydrogenation of liquid substrates were performed in quartz test tubes, into which the required reactants and a magnetic stir bar were introduced. The tubes were then placed in an autoclave, and the autoclave was closed. In the ethylene hydroformylation/hydrogenation experiments, the solvent, the Rh/PEI phase, and the magnetic stir bar were introduced directly into the autoclave. The autoclave was purged with syngas, then the required amount of syngas was injected (as well as ethylene, if needed, with the difference in the autoclave weight before and after the ethylene was loaded being measured), and the reaction was conducted under stirring (700 rpm) at a specific temperature. When the autoclave was cooled and depressurized, an internal standard (unless otherwise specified) was added to the reaction mixture, and the mixture was stirred for about 30 s. *n*-Heptane (to identify 1-propanol, propanal, and C$_6$ hydrocarbons) and *n*-dodecane (for C$_7$ alcohols and aldehydes) were used as internal standards. The mixture was then analyzed by gas chromatography (GC).

In catalyst stability tests, the reaction conditions varied depending on the catalytic system type. After the hydroformylation/hydrogenation of ethylene, the homogeneous mixture was allowed to remain in the autoclave connected to a thermostat filled with silicone oil. The autoclave was subsequently connected to a reflux condenser tied to a direct cooler. The distillation was carried out in an argon flow at 130°C until about 20% of the initial liquid volume remained in the autoclave. The liquid residue and the distillate were GC-analyzed. Subsequently, toluene was added to the residue to a total volume of 10 mL, and the autoclave was closed and purged with syngas, after which new portions of syngas and ethylene were injected. In the case of *n*-dodecane–water/PEI biphasic system, the mixture was allowed to settle in a quartz test tube until the foam subsided and the mixture was completely segregated (for about 1 h). The upper (organic) phase was separated, and new portions of *n*-dodecane and 1-hexene were added, after which the test tube was placed in the autoclave to run the next reaction cycle.

When testing solid catalysts, the reaction mixture was centrifuged, and the liquid was decanted, after which the catalyst was washed with toluene (2 mL), centrifuged again, and decanted. This was followed by adding new portions of toluene and 1-hexene to run the next reaction cycle.

**Instrumentation.** Liquid products were analyzed by GC using a Chromos chromatograph equipped with a flame ionization detector and a 50 m capillary column (DB-5 phase, programmed heating from 60 to 230°C, with helium as a carrier gas).

$^1$H NMR spectra were recorded on a Varian XL-400 spectrometer with an operating frequency of 400 MHz. To measure the N, H, and C concentrations in SiO-PEI and SiO-PEI-Me, a Vario MICRO Cube CHNOS universal elemental analyzer was used. For this purpose, a 0.8–1.0 mg sample was burned at 950°C in helium as a transport gas. At the time when the sample in the tin boat was ignited, the oxygen temperature reached 1800°C.

The gaseous decomposition products (nitrogen, carbon dioxide, and water) were separated using a thermal desorption column of the analyzer in a helium flow and detected using a thermal conductivity detector (TCD). The concentrations of C, H, and N were computed automatically using the analyzer's software taking into account the calibration coefficients pre-calculated for reference samples.

The silicon content was measured spectrophotometrically in the form of a blue silicon–molybdenum complex using a Cary-100 instrument. The surface areas were determined on a Micromeritics Gemini VII 2390 (V1.02t) in accordance with the standard procedure. Before the measurement, the sample was degassed at 120°C and $3 \times 10^{-4}$ MPa for 12 h.

**Scheme 3.** Modification of $NH_2$ groups in PEI-600 to produce a methylated derivative (PEI-Me).



PEI

$CH_2O/HCOOH/H_2O$    Stirring, $T$(°C), 24 h

PEI-Me
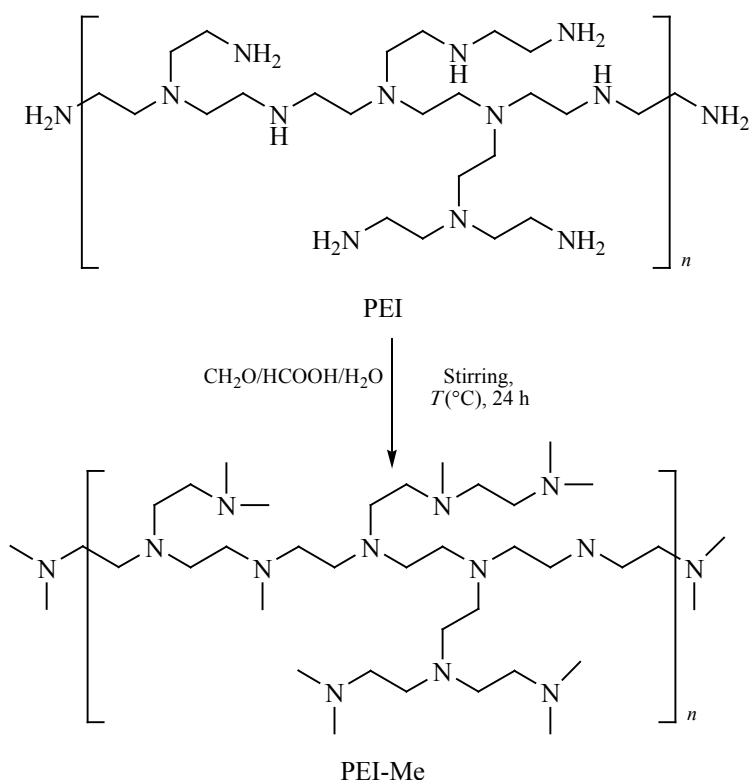
Adsorption and desorption isotherms were recorded at 77 K. The calculations were performed using standard software. The specific surface area was evaluated using a Brunauer–Emmett–Teller (BET) model at a relative partial pressure ($P/P_0$) of 0.2.

The supports were examined by Fourier-transform infrared spectroscopy (FTIR) using a Thermo Scientific Nicolet IR2000 instrument using multiple distortions of the total internal reflection method with multi-reflection HATR accessories, containing a 45° ZnSe crystal for different wavelengths with a resolution of 4 cm$^{-1}$. The rhodium content in the SiO-PEI/Rh and SiO-PEI-Me/Rh samples was quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a SHIMADZU ICPE-9000 instrument.

## RESULTS AND DISCUSSION

The initial PEI with an average molecular weight of 600 Da was a moderately viscous liquid. Knowing that the blanched polymer contains a number of tertiary nitrogen atoms, we reasonably assumed that the PEI could act as a ligand in tandem hydroformylation/hydrogenation. However, after 3 h treatment of 1-hexene (0.5 mL) with syngas (CO : H$_2$ = 1 : 1, 5.0 MPa) in the presence of 5 mg of PEI-600 and 2 mg of rhodium acetylacetonate dicarbonyl (100°C, with toluene as a solvent), only trace amounts of aldehydes and internal hexenes were detected by GC, whereas the bulk of 1-hexene was found to remain unreacted. Under similar conditions but without PEI, the hydroformylation and isomerization reactions occurred with fairly high intensity, such that after three hours of reaction the yield of aldehydes reached 98% with an *n*/*iso* ratio of 0.9 (the *n*/*iso* ratio hereinafter specifically indicates the ratio of the total yield of 1-heptanol and heptanal to the total yield of branched alcohols and aldehydes). These data show that PEI, even in amounts as small as 5 mg, likely created bonds with rhodium too strong to form, under these reaction conditions, hydride–carbonyl complexes active in hydroformylation. Based on available reports [6, 13], as well as on our previous laboratory experience with nitrogen-containing materials [21], we decided to activate the catalytic system by modifying PEI with methyl groups, thus increasing the
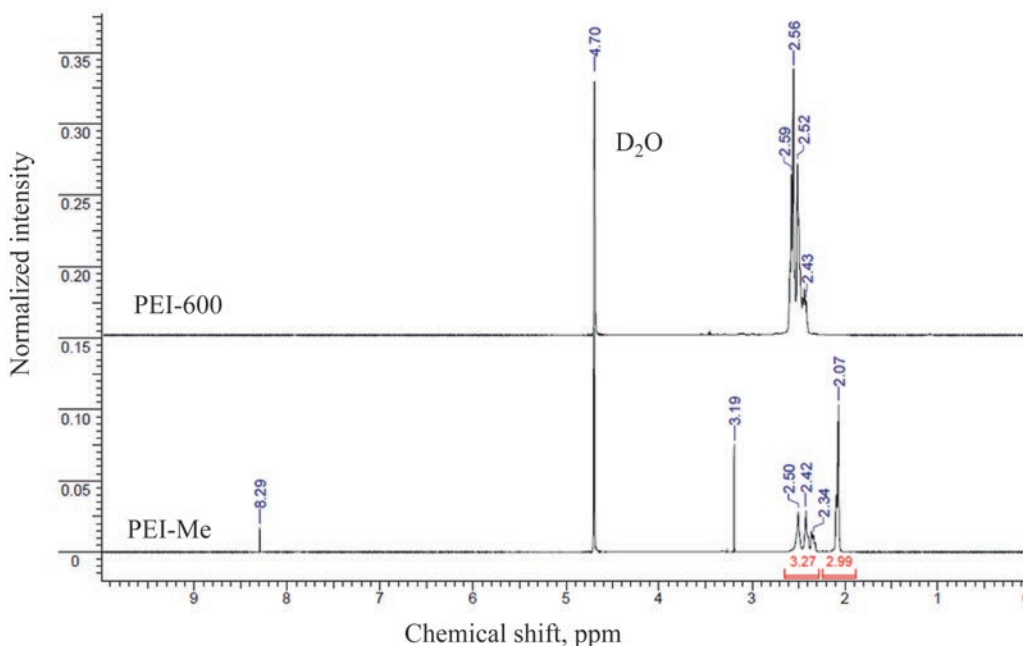
**Fig. 1.** $^1$H NMR spectra in $D_2O$ for PEI-600 before and after methylation.

number of tertiary nitrogen atoms and changing the spatial environment of rhodium in the system.

The PEI was modified via interaction of the polymer with a mixture of formaldehyde and formic acid (i.e., the Eschweiler–Clarke reaction, Scheme 3).

The separated product was examined by NMR spectroscopy. The spectra both of the initial PEI-600 and the produced PEI-Me are given in Fig. 1.

In the PEI-600 spectrum, protons of amino groups do not appear due to their strong interaction with the solvent. The PEI-Me spectrum is essentially different: a number of peaks attributable to protons of methyl groups bound to nitrogen atoms appear near 2.07 ppm. The ratio between the integrated intensities of the peaks corresponding to methyl and methylene groups in the macromolecule, equal to about 1 : 1, confirms the successful PEI modification. Furthermore, the PEI-Me spectrum contains peaks at 8.29 and 3.19 ppm. To further validate our assumptions on the identity of these peaks, $^{13}$C NMR spectra of PEI and PEI-Me in $D_2O$ were recorded. After the methylation, a new peak (170.37 ppm) appeared in the $^{13}$C spectrum. This peak, as well as the peak at 8.29 ppm in the $^1$H spectrum, are known to be typical of formate anions [25]. Therefore, it would be reasonable to

attribute the 3.19 ppm peak to protons at the carbon atoms adjacent to the protonated nitrogen atoms in the polymer (R–C$\underline{H}_2$–NH$^+$R$_2$). Presumably, despite the treatment with excess alkali, some amino groups in the methylated polymer remained in the form of formate. The 1 : 125 ratio between the integrated intensities of formate protons and other protons indicates a relatively small proportion of protonated amino groups: given the irregular structure of branched PEI, the lower limit of this ratio in the case that all nitrogen atoms were bound to formic acid can roughly be estimated as 1 : 8 to 1 : 9. Nonetheless, the presence of ionic moieties in the polymer molecule likely contributed to the fairly high water solubility of PEI-Me needed for the experiments under biphasic catalytic conditions (as described below). In particular, when the alkaline solution in $D_2O$ was added to the NMR ampoule containing the PEI-Me solution in $D_2O$, we observed that the polymer was partially segregated into a separate phase. Thus, it is desirable to partially retain formate anions in the macromolecule to ensure that a stable biphasic system is produced.

The PEI-Me was tested in the tandem hydroformylation/ hydrogenation of 1-hexene under conditions similar to those imposed in the PEI test. The test data are presented in Table 1.

**Table 1.** PEI-Me in hydroformylation/hydrogenation of 1-hexene under homogeneous conditions[a]

| $m$(PEI-Me), mg | 1-Hexene conversion, % | Yield of oxygenates, % | Yield of $C_7$ alcohols, % | $n : iso$[b] |
|---|---|---|---|---|
| – | 99 | 98 | 0 | 0.9 |
| 5 | 95 | 62 | 2 | 1.5 |
| 50 | 95 | 50 | 5 | 2.1 |
| 150 | 99 | 59 | 13 | 1.9 |
| 250 | 97 | 59 | 28 | 1.6 |

[a] Reaction conditions: Rh(acac)(CO)$_2$ 2.0 mg, toluene 2.5 mL, 1-hexene 0.5 mL; 100°C, syngas pressure 5.0 MPa, CO : H$_2$ = 1 : 1; 3 h.
[b] The ratio of the total yield of 1-heptanol and heptanal to the total yield of branched alcohols and aldehydes.

Interestingly, the addition of PEI-Me, even in 50-fold larger amounts, did not decrease the 1-hexene conversion as dramatically as in the case of PEI addition. The mass of the added PEI-Me had almost no effect on the conversion of 1-hexene. Likewise, the PEI-Me loading had a negligible effect on the oxygenate yield (i.e., on the catalytic performance in hydroformylation): this yield varied between 50 and 62% without noticeable regularity. On the other hand, the amount of PEI-Me clearly correlated with the yield of $C_7$ alcohols: within the tested range, this yield almost linearly rose with the polymer amount. A finely dispersed dark precipitate was found in the mixture after the reaction. At high PEI-Me loads (150–200 mg), the polymer also tended to form a separate viscous phase, which proved to be water-soluble. This finding motivated us to test a Rh/PEI-Me catalytic system under biphasic catalytic conditions, as discussed below.

**Hydroformylation/hydrogenation of ethylene under homogeneous conditions with product distillation and catalyst recycling.** When compared to low-molecular-weight amine ligands, PEI has an obvious major advantage for the purposes of tandem hydroformylation/hydrogenation and, specifically, for the separation of reaction products from the catalyst through distillation: the non-volatility of the polymer prevents the ligand from entering the oxygenate product mixture. Therefore, we found it potentially promising to use the non-volatile polymeric nitrogen-containing ligand for hydroformylation/hydrogenation of ethylene followed by the distillation of $C_3$ oxygenates. In addition to the fact that distillation is obviously the simplest technique for separating this oxygenate group, the regioselectivity of Rh/tertiary amine catalytic systems (which is currently their weak point) is of no importance for hydroformylation of ethylene due to its molecular symmetry.

To test this application of Rh/PEI-Me catalytic systems, we carried out a series of experiments on the hydroformylation/hydrogenation of ethylene with the reaction products being distilled and the rhodium complex being reused.

Figure 2 provides a photo of the distillation setup and a diagram illustrating the results of three successive experiments.

The total yield of oxygenates was stable (at about 10 mmol). Taking into account the material losses of light volatiles typical of the equipment included in this setup as well as the high ethylene weight measurement error, this yield corresponds to the almost complete (about 90–99%) conversion of ethylene to oxygenates. Thus, the hydroformylation activity of the system expressed in turnover frequency (TOF) can be estimated as at least 200 h$^{-1}$. Although the yield of 1-propanol in Cycle 2 was lower than in Cycle 1, it remained stable between Cycles 2 and 3, specifically about 3 mmol over a period of 3 h, which corresponds to a TOF of about 60 h$^{-1}$.

The chromatograms both of the distillate and of the residual liquid in the autoclave show that the oxo synthesis products and the internal standard were completely distilled off prior to each successive cycle, thus preventing the products from building up from cycle to cycle. Moreover, the heating initiated no new reactions such as aldol condensation of propanal, because no heavy products were detected in either liquid. Despite some decline in the yield of 1-propanol after Cycle 1, the study convincingly demonstrated the reusability (and partially sustaining catalytic activity) of the Rh/PEI-Me system in hydroformylation/hydrogenation of ethylene by distillation of the product.

**Other substrates.** Table 2 provides the chromatographic data for experiments with other substrates. These data are presented as a distribution of the chromatogram
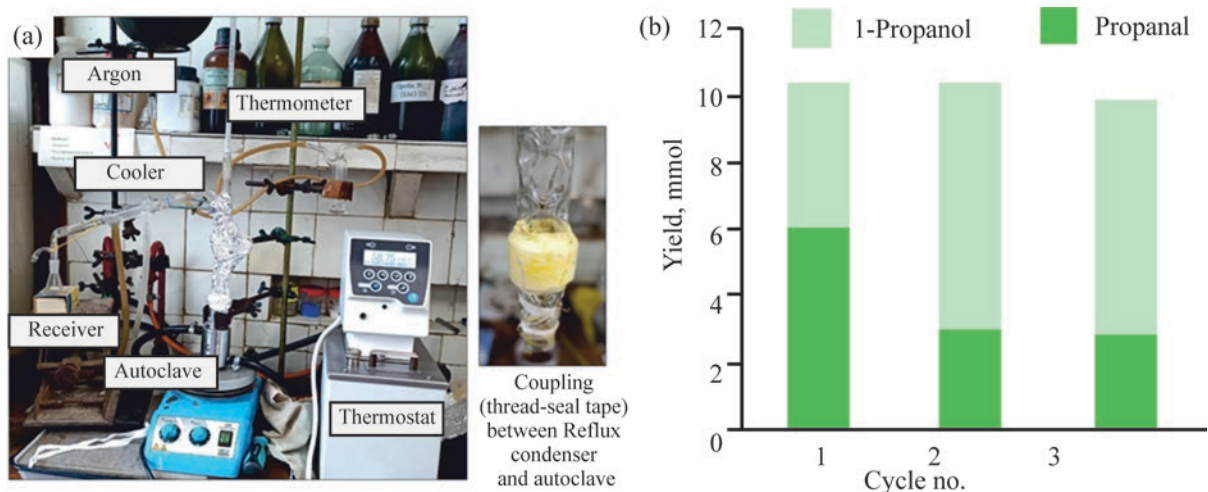
**Fig. 2.** Hydroformylation/hydrogenation of ethylene with product separation via distillation: (a) a setup for distillation of reductive hydroformylation products; and (b) catalytic test data for Rh/PEI-Me reuse after distillation. Reaction conditions: 500 mg Rh/PEI-Me solution, 9.5 mL toluene, 0.55 MPa ethylene (0.3 g, 0.0107 mol), 100°C, 5.45 MPa syngas, $CO : H_2 = 1 : 1$, 6.0 MPa overall, 3 h.

peak areas because no calibration curves were made for each substrate relative to the internal standard. The data suggest, on a qualitative level, that all the tested substrates, including aromatic and internal olefins, were suitable for producing corresponding alcohols. In all likelihood, the hydroformylation of the internal double bonds of cyclohexene occurred more slowly than that of its terminal bonds. For 1-octene, like in the case of 1-hexene, the formation and hydroformylation of *iso*-octenes was observed. Under harsh conditions and extended reaction times, we were able to produce alcohols even from a complex substrate such as a commercial propylene trimer mixture consisting of a variety of $C_9$ hydrocarbons, including branched and internalized components. Accordingly, the tandem reaction produced complex mixtures of various aldehydes and alcohols.

**Hydroformylation/hydrogenation in Rh/PEI-Me system under biphasic catalytic conditions.** As noted above, at some compositions of reaction mixtures (generally at large amounts of PEI-Me and in the absence of more polar lower alcohols and aldehydes such as 1-propanol and propanal), after the reaction the polymer tends to aggregate into a separate viscous phase with almost no detriment to the yield of target products. Therefore, it may be advantageous to develop a high-performance biphasic catalytic system based on methylated PEI. A biphasic system with a phosphine ligand, specifically the sodium salt of triphenylphosphine-3,3′,3″-trisulfonic acid, has been successfully applied in commercial hydroformylation of propylene [26]. This type of system is distinguished by easy separation of the catalyst from the reaction products, where the simple segregation of the two liquid phases after stirring
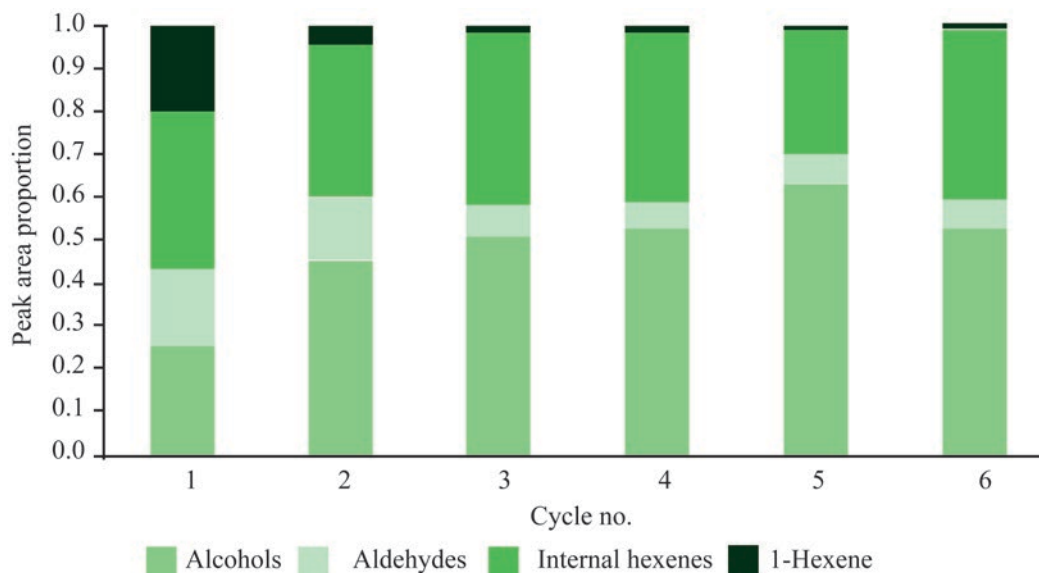
**Table 2.** Hydroformylation/hydrogenation of unsaturated substrates over Rh/PEI-Me[a]

| Substrate | Proportion | | | $n : iso$ |
|---|---|---|---|---|
| | substrate | oxygenates | alcohols | |
| 1-Octene | <0.1 | 0.77 | 0.11 | 1.5 |
| Styrene | 0.39 | 0.61 | 0.11 | 0.5 |
| Cyclohexene | 0.85 | 0.15 | 0.02 | – |
| Propylene trimers[b] | 0.61 | 0.39 | 0.09 | NA |

[a] Reaction conditions: 50 mg Rh/PEI-Me solution, 2 mL toluene, 1.9 mmol substrate, 100°C, 5.0 MPa syngas, $CO : H_2 = 1 : 1$, 4 h.
[b] 100 mg Rh/PEI solution, 0.5 mL propylene trimers, 3.5 mL toluene, 125°C, 7.0 MPa, $CO : H_2 = 1 : 1$, 24 h, 20 mL autoclave.
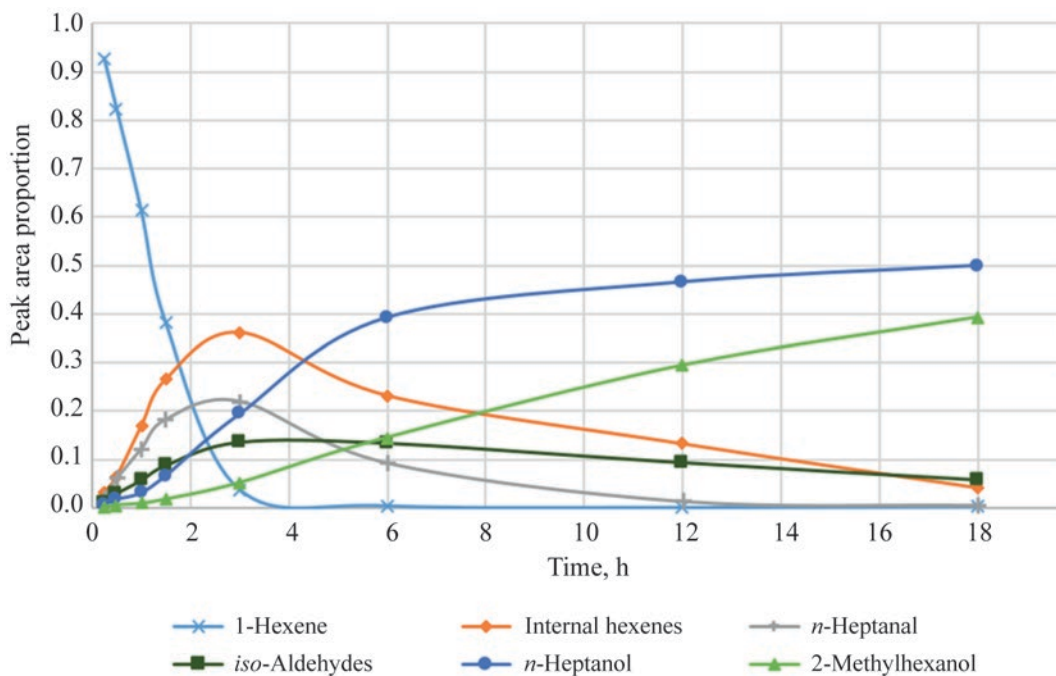
**Fig. 3.** Hydroformylation/hydrogenation of 1-hexene in dodecane–water biphasic system with recycle of the Rh-containing aqueous phase. Reaction conditions: 250 mg Rh/PEI-Me solution, 1.25 mL water, 0.3 mL 1-hexene, 1.5 mL dodecane, 100°C, 5.0 MPa syngas, CO : $H_2$ = 1 : 1, 3 h.

obviates the need for either heating or additional reactants. Previously, our team developed a biphasic Rh/tertiary amine system active in tandem hydroformylation/hydrogenation of unsaturated substrates [20]. In the most efficient and stable embodiment, the non-polar phase (the one that contained the substrate and the reaction products) was prepared from dodecane, and the polar phase from triethanolamine, in which a Rh precursor was pre-dissolved. The embodiment with methylated PEI was less preferable because of the physical properties of the polymer phase, in particular its propensity to deposit on the reactor walls after the reaction and to aggregate as separate clusters. Therefore, for the purposes of the present study we chose a *n*-dodecane–water/PEI-Me system. For biphasic reactions, we used the same Rh(acac)(CO)$_2$ solution in PEI-Me as in the homogeneous reactions with ethylene.

A series of experiments were carried out to test the reusability of the polar (rhodium-containing) phase in the dodecane–water/PEI-Me system. Figure 3 illustrates the chromatographic data on the non-polar reaction phases. In this series of experiments, the distribution of chromatographic peak areas of reaction products was evaluated without the addition of an internal standard. After the last cycle, a GC analysis with the addition of internal standards (heptane to identify hexenes and

1-octanol to identify oxygenates) revealed that hexenes and $C_7$ oxygenates were present in the upper phase in an amount of about 75% of the initial content of 1-hexene. About 10% of the reaction products were further detected by extracting the products from the aqueous phase with 2.5 mL of pure dodecane, with alcohols accounting for more than 95% of these products. The remaining percentage was represented by mechanical losses and, likely, by some portion still retained by the polymer-containing aqueous phase. Nonetheless, the major portion of the reaction products (and of the unreacted substrate) was found in the non-polar phase; hence, the peak area distribution can serve as an adequate basis for the rough estimation of the system stability.

The biphasic system exhibited fairly high activity both in hydroformylation and hydrogenation, the yields in both steps increasing from Cycle 1 to Cycle 2 of reusing the Rh-containing phase. In all probability, the active Rh form was generated during Cycle 1, and this form remained, at least partially, while the autoclave was cooled and depressurized before the next reaction. Over the subsequent cycles, only minor variations in the concentrations of both alcohols and aldehydes in the product mixture were observed. Similar trends were reported in our study on the triethanolamine-based system [20].

**Fig. 4.** Conversion of 1-hexene and yield of products in hydroformylation/hydrogenation over time. Reaction conditions: 250 mg Rh/PEI-Me solution + 1.25 mL water (the phase was previously used in one reaction cycle under the conditions noted in Fig. 3), 0.5 mL 1-hexene, 1.5 mL dodecane, 100°C, 5.0 MPa syngas, CO : $H_2$ = 1 : 1. At each point marked along the time axis, the reaction was suspended, and the contents were sampled for GC, after which the reaction was resumed.

To evaluate the degree of rhodium leaching, 0.5 mL of 1-octene was added to the organic phase separated after Cycle 5, followed by stirring under the reaction conditions (5.0 MPa syngas and 100°C) for 0.5 h. The 1-octene conversion and the yield of aldehydes were as low as 4% and about 1%, respectively. For comparison purposes, a similar experiment was conducted with a solution of 0.25 mg of Rh(acac)(CO)$_2$ in 1.8 mL of dodecane, which corresponded to 12% of the Rh amount initially contained in the polar phase of the biphasic system. In this case, the 1-octene conversion and the aldehyde yield reached 98 and 58%, respectively. This finding suggests that only small amounts of rhodium leached into the non-polar phase, markedly below 10% per cycle. This is consistent with the sustaining catalytic activity observed over the multiple reuse cycles.

Figure 4 illustrates the chromatographic data (also expressed in proportions to the total peak area) that describe the reaction progress over time. Bearing in mind that the previous series of experiments demonstrated the difference in the system's activity in Cycle 1 compared to that in the subsequent cycles, the temporal trend of

the mixture's composition was investigated for Cycle 2 of reusing the aqueous phase in hydroformylation/hydrogenation.

Aldehydes and their alcohol derivatives were formed from the first hour of the reaction. The content of aldehydes in the mixture reached its maximum after 3 h. Among them, heptanal and 2-methylhexanal were predominant. They further entered into the hydrogenation reaction, where heptanal transformed into the respective alcohol more rapidly than 2-methylhexanal, a more sterically hindered aldehyde. Furthermore, a small amount of 2-ethylpentanal was produced from 2-hexene, a compound that barely entered into hydrogenation and remained in the mixture until the end of the 18-hour experiment.

**Use of PEI to synthesize novel solid catalysts for hydroformylation/hydrogenation.** Previously we prepared a rhodium catalyst based on WP-1, a hybrid material synthesized by our colleagues from Montana State University [21]. Although this catalyst proved to be active in tandem hydroformylation/hydrogenation of olefins, it rapidly lost its hydrogenation activity. WP-1
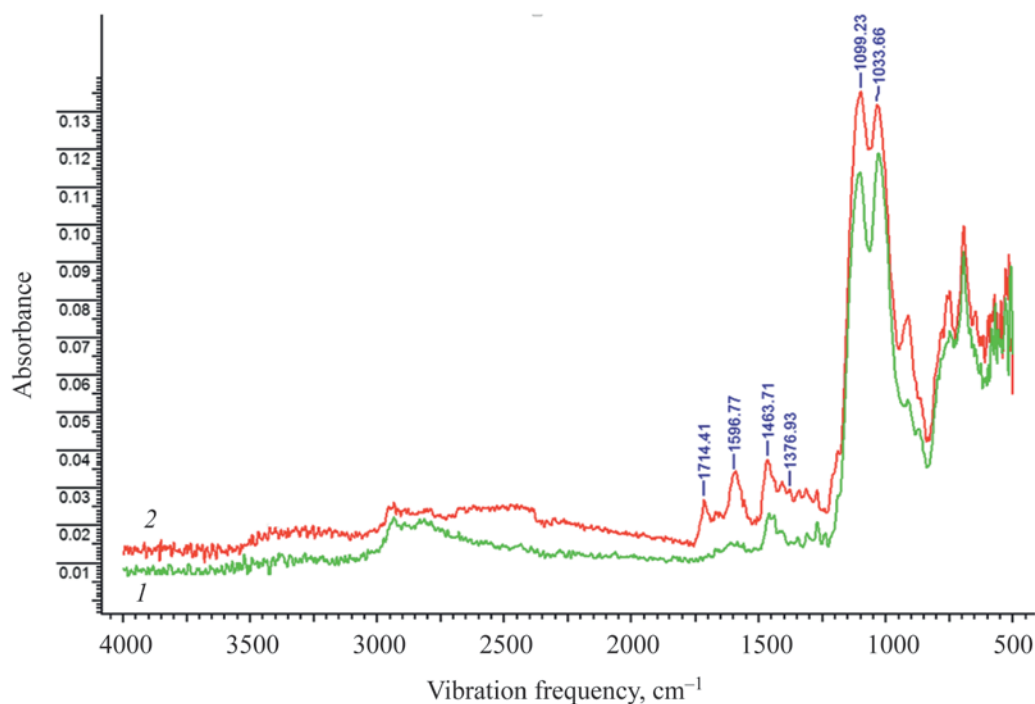
**Fig. 5.** IR spectra of SiO-PEI and SiO-PEI-Me: (*1*) SIO-PEI and (*2*) SIO-PEI-Me.

was obtained by grafting PEI onto a prefabricated silicate matrix. In the present study, we synthesized a novel hybrid material using a different stepwise procedure. Initially PEI reacted with $(EtO)_3Si(CH_2)_3Cl$ to fix the silicon-containing moiety with the polymer. Then, via hydrolysis and subsequent dewatering in a rotary evaporator, Si–O–Si bonds were generated, thus producing a solid hybrid material denoted as SiO-PEI. This procedure provided a higher concentration of the polymer phase in the material (compared to the post-synthetic immobilization of PEI) to form a more stable microenvironment of rhodium atoms. The elemental analysis confirmed the presence both of nitrogen (8.85 wt %) and silicon (16.12 wt %) in SiO-PEI. The nitrogen to silicon ratio was approximately 1.1, or almost half that in the PEI and $(EtO)_3Si(CH_2)_3Cl$ taken for the synthesis. Nonetheless, the nitrogen content in SiO-PEI was twice that in WP-1, thus indicating the appropriateness of the chosen synthesis strategy. The concentrations of carbon and hydrogen were 31.03 and 6.65 wt %, respectively. Based on our previous experience with WP-1 and with PEI under homogeneous conditions, we methylated the synthesized material by the Eschweiler-Clarke reaction to produce SiO-PEI-Me. Figure 5 illustrates the IR spectra of SiO-PEI and SiO-PEI-Me.

The peaks in the region of 1000–1100 cm$^{-1}$ correspond to Si–O–Si vibrations, and the peaks near 2500–3000 and 1400 cm$^{-1}$ are attributable to C–H bonds in polymer moieties. After methylation, the minor peak in the 1370–1380 cm$^{-1}$ region indicates the appearance of new methyl groups. Another group of new peaks appeared near 1600–1700 cm$^{-1}$, a region typical of carbonyl compounds. Their presence is likely associated with the residues of formaldehyde and formate anions remaining after the $CH_2O$/HCOOH-induced methylation.

To prepare SiO-PEI/Rh and SiO-PEI-Me/Rh catalysts, rhodium was loaded on SiO-PEI and SiO-PEI-Me from the $Rh(acac)(CO)_2$ solution in methylene chloride. However, the ICP-AES examination showed that the weight concentrations of rhodium differed more than 10-fold between the resultant catalysts: 0.37 and 3.86 wt % for the catalysts based on SiO-PEI and SiO-PEI-Me, respectively. This led to a difference in their catalytic activity (Table 3). For SiO-PEI/Rh, the 1-hexene conversion after 4 h of reaction was about 3% and was no enhanced during the catalyst reuse cycle; SiO-PEI-Me/Rh was fairly active both in 1-hexene isomerization and tandem hydroformylation/ hydrogenation. Taking into account the data on the PEI-based homogeneous catalysis at the identical rhodium

**Table 3.** Hydroformylation/hydrogenation of 1-hexene over heterogeneous catalysts SiO-PEI/Rh and SiO-PEI-Me/Rh[a]

| Catalyst (cycle no.) | 1-Hexene conversion, % | Yield of oxygenates, % | Yield of alcohols, % | *n : iso* |
|---|---|---|---|---|
| SiO–PEI/Rh (1) | 3 | 1 | 0 | |
| SiO–PEI/Rh (2) | 2 | < 1 | 0 | |
| SiO–PEI–Me/Rh (1) | 99 | 64 | 7 | 1.5 |
| SiO–PEI–Me/Rh (2) | 99 | 71 | 9 | 1.1 |
| SiO–PEI–Me/Rh (3) | 99 | 80 | 4 | 1.1 |
| SiO–PEI–Me/Rh (4) | 99 | 88 | 1 | 0.9 |

[a] Reaction conditions: 30 mg catalyst, 2.5 mL toluene, 0.5 mL 1-hexene, 100°C, 5.0 MPa syngas, $CO : H_2 = 1 : 1$, 4 h.

load, it is fair to posit that in the case of solid catalysts, likewise, both the content and microenvironment of Rh make a major contribution to the significant difference in their catalytic activities.

Table 3 clearly shows an increase in the hydroformylation activity of SiO-PEI-Me/Rh over four successive cycles, reaching a TOF of 77 $h^{-1}$ in the last cycle; nonetheless, the yield of alcohols gradually decreased. Although no specialized studies have been carried out to make it clear, this was most likely associated with rhodium leaching.

To identify pathways for further improvement of the performance and stability of solid catalysts of this type, the SiO-PEI surface was examined by nitrogen adsorption/desorption. The surface was found to be fairly undeveloped, with an area of 1.08 $m^2$/g. Further systematic research is needed to reveal whether seeking to increase the surface area of the material would be consistent with efforts to retain a high concentration of polymer moieties.

## CONCLUSIONS

The basic feasibility of the multiple reuse of methylated-PEI-based catalytic systems in hydroformylation/hydrogenation was demonstrated under homogeneous and biphasic catalytic conditions. Furthermore, a novel heterogeneous catalyst was synthesized from polyethyleneimine, (3-chloropropyl)triotoxysilane, and a rhodium precursor. This catalyst proved to be active in hydroformylation/hydrogenation and separable from the reaction products by centrifugation. These catalytic systems can be separated from the reaction products and recycled for multiple reuse. The study definitely shows the potential promise of relevant follow-up research.

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## CONFLICT OF INTEREST

E.A. Karakhanov, a co-author, is an Editorial Board member at the Neftekhimiya (Petroleum Chemistry) Journal. The other co-authors declare no conflict of interest requiring disclosure in this article.

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