



Rhodium nanoparticles as catalysts in the hydroformylation of 1-dodecene and their recycling in thermomorphic solvent systems

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ABSTRACT

Rhodium nanoparticles of about 3 nm in size were provided in stabilizing polar solvents. These nanoparticles were used in hydroformylation reactions of higher alkenes; 1-dodecene was used as a model substance. With a metal/substrate ratio of 1:1000, a 97% yield of aldehydes was achieved and an *n/iso* ratio of 72:28 was obtained. The addition of the ligand biphephos decelerated the reaction, but high *n/iso* ratios of up to 96:4 were achieved.

For the first time, an effective catalyst recycling of these long-term stable nanoparticles in a thermomorphic multicomponent solvent (TMS) system was performed. The catalyst phase was recycled for three runs without any evident loss in activity. TEM images proved that after the recycling runs rhodium nanoparticles were still the active catalyst.

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Rhodium-based catalysts are frequently used in homogeneous transition metal catalysis and therefore play an important role in chemical industry. Rhodium complexes can be used as catalysts, for example, in hydroformylation of alkenes for the production of aldehydes. In the hydroformylation of long-chained alkenes, efficient catalyst recycling is still a big challenge. In recent years, the use of nanoparticles as catalysts has gained importance, especially when expensive noble metals are used. Common uses of rhodium nanoparticles are hydrogenation reactions.¹ Their application in hydroformylation reactions has also been described.²

For the stabilization of rhodium nanoparticles, the use of ligands is possible. In the hydroformylation of 1-hexene, the particles can be stabilized by poly(ethylenimin)amide yielding aldehydes with an *n/iso* ratio of about 1:1.³ Also, stabilization of rhodium nanoparticles with diphosphite ligands has been described by Claver et al. in the hydroformylation of styrene.⁴ They assume that during the reaction the colloidal Rh(0) nanoparticles undergo a transformation to a catalytically active Rh(I) complex. Thus the nanoparticle can be regarded as a reservoir of the molecular catalyst.

In the literature, there have been some methods described for catalyst recycling of rhodium nanoparticles in the hydroformylation of higher olefins. The separation of products and the catalyst can be done by decantation or filtration of the nanoparticles, if the nanoparticles are immobilized on a solid surface, for example,

charcoal.⁵ However, in industry large-scale filtration is a comparatively complicate operation, which usually causes some catalyst losses.

Bruss⁶ described the hydroformylation of 1-alkenes with ligand-modified or unmodified Rh(0) nanoparticles with a size of about 5 nm and supposed, too, that the nanoparticles attend to work as a catalyst precursor. With the addition of the ligand xantphos, it is possible to generate a high *n/iso* ratio of 25:1. The methods of analysis used in this study assume that Rh(0) nanoparticles decomposed under the reaction conditions and merged into soluble mononuclear Rh species, which then catalyze the hydroformylation. During the reaction the nanoparticles build a black solid and can thereby be recycled by filtration. Unfortunately an induction period of up to 4 h was detected, presumably for generating the catalytic active species out of the solid powder, which would be a disadvantage considering industrial application.

Furthermore, rhodium-based nanocatalysts can be immobilized on different carriers like, for example, silica and subsequently used in hydroformylation reactions.⁷ In all these cases, separation can be carried out by filtration or decantation.

Recently, supported aqueous-phase catalysis (SAPC) has increased in importance, and also the use of SAPC in hydroformylation was investigated.⁸ Fumed-silica particles are used as carrier material for aqueous phosphine–rhodium complexes. In this case, the separation of the solid catalyst and the liquid reaction phase can be done by phase separation. Conversions of up to 73% can be achieved for the hydroformylation of 1-hexene in toluene, with about 0.4 mol % Rh and an *n/iso* ratio of 3:1–6:1.

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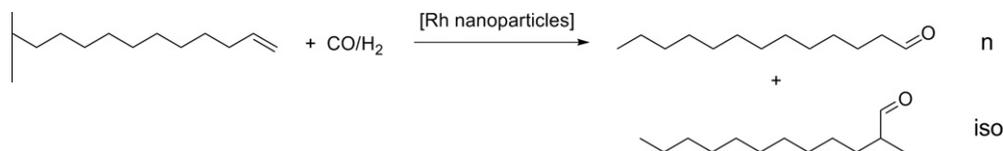


Figure 1. Rhodium nanoparticle-catalyzed hydroformylation of 1-dodecene to aldehydes.

Table 1
Rhodium nanoparticle-catalyzed homogeneous hydroformylation of 1-dodecene

Entry	Solvent	M/L ^a	Conversion (%)	Y _{aldehydes} (%)	<i>n</i> / <i>iso</i> (aldehydes)	Y _{iso-alkenes} (%)	Y _{alkane} (%)
1 ^{**}	PC	—	>99	11	68:32	85	4
2	PC	—	>99	25	52:48	71	4
3 ^{***}	DMF	—	>99	61	45:55	37	2
4 ^{**}	DMF	—	>99	8	73:27	90	2
5	DMF	—	>99	97	70:30	2	1
6 ^a	DMF	1:5	>99	91	66:34	8	1
7 ^a	DMF	1:20	>99	84	68:32	12	4
8 ^a	DMF	1:50	>99	36	49:51	62	2
9 ^b	DMF	1:5	>99	85	96:4	11	4

Reaction conditions: 20 bar CO/H₂ (1:1), 20 h, *T* = 110 °C, Rh-precursor = dicarbonyl-acetylacetonato-rhodium, *c*(cat) = 0.1 mol %.

^a M/L = metal to ligand ratio.

^{**} Rh-precursor = rhodium acetate.

^{***} Reaction without nanoparticles.

^a Ligand = triphenylphosphine.

^b Ligand = biphephos.

Li^{2a} described the hydroformylation of higher olefins (such as 1-decene, 1-dodecene, or cyclohexene) in an aqueous two-phase-system (water/1-butanol) by the application of thermo regulated phase-transfer catalysis with ligand-stabilized rhodium nanoparticles. Recycling was easily performed by phase separation. Above temperatures of 60 °C, nearly complete conversion of the substrates occurred. This temperature was necessary because under these conditions, enough of the aqueous phase-dissolved catalyst switched into the organic phase. With this technique, *n*/*iso* ratios of 1.3:1–2.4:1 were achieved. However after every catalyst recycling run, the Rh nanoparticles increased in size as shown in TEM images.

In the literature, there are some examples of a very convenient method of stabilizing nanoparticles using solvents only (studies by Behr,⁹ Reetz,¹⁰ Bönnenmann,¹¹ van Leeuwen¹²). This easy method of nanocatalyst preparation is predestinated for thermomorphic multicomponent solvent (TMS) systems. TMS systems have been developed using solvents of variable polarity, with homogeneous reaction processes at reaction temperatures and the formation of a two-phase system after cooling. Therefore, a simple separation of the catalysts and products can be performed and the catalyst phase can be easily recycled.¹³

The solvent-stabilized nanoparticles generate the catalyst phase without any additives, and products are separated (at room temperature) in a second phase. By the selection of a compatible solvent, it is possible to create a very simple and variable TMS system. Behr and Lux¹⁴ have shown that there is a broad band width of possible metals (including Rh) and various solvents of different polarity, enabling to find a matching Rh/solvent system for TMS.

To the best of our knowledge, catalyst recycling in TMS systems for the hydroformylation of higher olefins with rhodium nanoparticles has not been described yet. The concept of TMS systems combines classical homogeneous transition metal catalysis with highly efficient catalyst recycling by easy phase separation.¹⁵ This concept was successfully transferred to the hydroformylation of long-chain olefins.^{13a,c,d} Kinetic investigation of the hydroformylation of

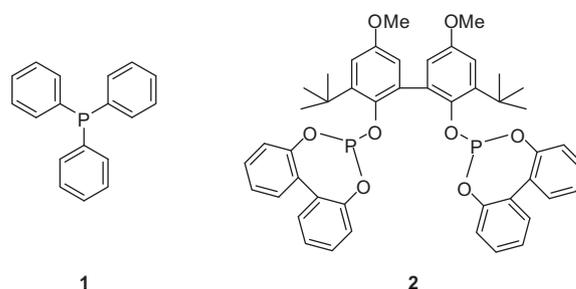


Figure 2. Triphenylphosphine (1) and biphephos (2).

octene in the TMS system propylene carbonate/dodecane/1,4-dioxane has been done.^{15c}

In polar solvents, stabilized rhodium nanoparticles can be used as homogeneous catalysts in the hydroformylation of the long-chain terminal alkene 1-dodecene (Fig. 1). The first successful application of catalyst recycling via TMS systems herein is described.

The synthesis of the rhodium nanoparticles was performed under hydrogen pressure (*p* = 10 bar) and increased temperature (*T* = 80 °C), after dissolving a rhodium precursor in a polar solvent such as dimethylformamide (DMF) or propylene carbonate (PC).¹⁶ For use in the hydroformylation of 1-dodecene, the precursor dicarbonyl-acetylacetonato-rhodium was more capable than rhodium acetate and produced a higher yield of aldehydes (cf. entries 1 and 2 vs 4 and 5 in Table 1). When the reaction was done with Rh nanoparticles prepared from dicarbonyl-acetylacetonato-rhodium in DMF, a yield of 97% aldehydes with an *n*/*iso* ratio of 70:30 was achieved.¹⁷

It should be stressed that in this reaction, no ligand with a regioselective influence was added. In complex-catalyzed hydroformylation reactions, with unmodified rhodium species, an *n*/*iso* ratio of merely 45:55 was obtained (entry 3 in Table 1). Thus the use of Rh nanoparticles provided a certain selectivity control for the hydroformylation reaction to the *n*-isomer. As side-products

Table 2
Catalyst recycling in a TMS system for the hydroformylation of 1-dodecene with rhodium nanoparticles

Run	Conversion (%)	$Y_{\text{aldehydes}}$ (%)	n/iso (aldehydes)	$Y_{\text{iso-alkenes}}$ (%)	Y_{alkane} (%)	Rh-losses (product phase) (ppm)
1-1*	59	27	51:49	29	3	3
1-2*	62	36	47:53	23	3	6
1-3*	66	40	46:54	24	2	4
2-1**	92	60	53:47	29	3	6
2-2**	92	64	51:49	26	2	2
2-3**	95	66	49:51	26	3	3

* Reaction conditions: 30 bar CO/H₂ (1:1), 3 h, $T = 110$ °C, Rh-precursor = dicarbonyl-acetylacetonato-rhodium, $c(\text{cat.}) = 0.1$ mol %, TMS-system: DMF/*n*-decane (wt.-50%/wt.-50%), without ligand.

** Reaction conditions: 30 bar CO/H₂ (1:1), 20 h, $T = 110$ °C, Rh-precursor = dicarbonyl-acetylacetonato-rhodium, $c(\text{cat.}) = 0.1$ mol %, TMS-system: DMF/*n*-decane (wt.-50%/wt.-50%), without ligand.

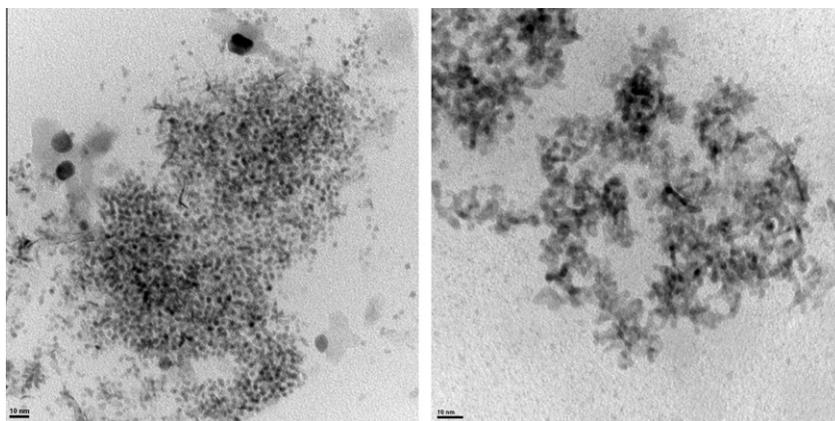


Figure 3. TEM images of Rh nanoparticles before reaction (left) and after three recycling runs (right).

iso-alkenes from isomerization and the alkane from hydrogenation of the substrate were detected.

If the ligands triphenylphosphine (1) or biphosphos (2) (see Fig. 2) were used, which are typical ligands in hydroformylation, the yield of the aldehyde decreased. It seems that the hydroformylation with nano catalyst is inhibited by the addition of ligands. The use of ligand 1 led to a lower n/iso ratio, in contrast to the use of ligand 2 which resulted in a very high n/iso ratio of 96:4.

Next, we attempted to investigate the application of these nanoparticles to recycling concepts with TMS systems. For this, a TMS system of two solvent components with different polarity was chosen (DMF/*n*-decane). Even with the addition of a non-polar solvent component like *n*-decane, the reaction proceeded. Therefore we did several recycling runs.

The catalyst recycling experiments with nanoparticles proved to be quite effective (see Table 2). After 3 h (entries 1-1 to 1-3 in Table 2), there was incomplete conversion, but with a longer reaction time of 20 h (entries 2-1 to 2-3 in Table 2), it is possible to generate higher conversions up to 95%. The yield is increasing during the recycling runs up to 66%.

We have checked the Rh-losses through the product phase by ICP-OES measurements. All values are equal or under 6 ppm, which is also the limit of quantification in our measurements, so we can say that in our experiments only a very low loss of Rh over the product phase has appeared. The Rh concentration in the solution before experiments is measured as 86 ppm. With this performance a recycling is possible and three runs without charge new catalyst are easy and practicable.

Our demonstration of the fundamental function of the TMS concept with nanoparticles in the hydroformylation of long chain alkenes proved to be successful. The TEM images (see Fig. 3) show that even after three recycling runs, nanoparticles of about 3 nm

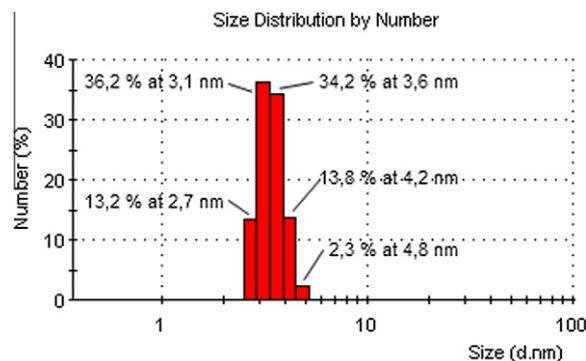


Figure 4. Size distribution histogram of DLS measurement of the Rh nanoparticles in DMF.

in diameter remained in the catalyst solution, and there was no significant enlargement or agglomeration of the particles. However, it is also possible that there was equilibrium between nanoparticles and dissolved rhodium. In this case, these rhodium particles served as a catalyst reservoir for the polar catalyst phase as previously described in the literature.⁴

Likewise DLS measurements (see Fig. 4) indicate, that there are nanoparticles of a small size distribution from 2.7 nm up to 4.8 nm (for 99.7% of the particles).

In conclusion, stable Rh nanoparticles in polar solvents were synthesized and successfully used for the hydroformylation of 1-dodecene. Beyond this, the influence of regioselective ligands was analyzed. It was shown that the addition of the ligand biphosphos slightly decreased the conversion to aldehyde, but increased the n/iso ratio up to 96:4.

The best system (without any addition of a ligand) was a solution of nanoparticles derived from Rh(acac)(CO)₂ in DMF, with a yield of 97% aldehyde and a relatively high *n*/*iso* ratio of 70:30 in comparison with the use of the rhodium complex Rh(acac)(CO)₂, as homogeneous catalyst, with a *n*/*iso* ratio of 45:55.

Furthermore, for the first time, catalyst recycling of nanoparticles in a hydroformylation reaction using a TMS system was shown.

Acknowledgments

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- The nanoparticles were synthesised by dissolving the rhodium precursor into the polar solvent with stirring for 2 h at 80 °C and 20 bar hydrogen pressure. All experiments were carried out under argon atmosphere. Chemicals were purchased from VWR, Acros Organics and Messer Industriegase. The rhodium precursor was received as a donation from Umicore. Rhodium particle synthesis and recycling in the TMS system were performed in a 300 mL stainless steel Parr autoclave.
- The hydroformylation reaction was performed in a 10 mL self-developed reactor (for more information over this reactor see Behr, A.; Henze, G.; Johnen, L.; Reyer, S. *J. Mol. Catal. A: Chem.* **2008**, *287*, 95–101) In a typical hydroformylation experiment, 1-dodecene (1.14 g, 6.8 × 10⁻³ mol) was dissolved in the rhodium nanoparticle solution prepared from the rhodium precursor Rh(acac)(CO)₂ (6.8 × 10⁻⁶ mol, metal/substrate ratio = 1:1000) and the polar solvent DMF (8.5 mL). In the recycling experiments, the non-polar solvent *n*-decane was added to create the TMS system (50 wt % polar and 50 wt % non-polar solvent). The vessel was closed and the reaction solution was placed in the reactor under an inert gas atmosphere. The pressure of the synthesis gas was adjusted to 20 bar or 30 bar, respectively. The stirrer was adjusted to 650 rpm in the multiplex or 800 rpm in the 300 mL autoclave. The autoclave was heated to 110 °C. After the reaction time, the reactor was cooled to room temperature within a few minutes by cooling with an ice bath. The reactor was depressurized and flushed with argon. In the recycling experiments, the catalyst phase was separated and used in the next reaction. The reaction solutions were analyzed with a gas chromatograph (Hewlett-Packard) equipped with a capillary column (HP 5) and a FID detector. 1-Decanol was used as internal standard.