

CHEMISTRY A European Journal



Accepted Article Title: Supported Cobalt Nanoparticles for Hydroformylation Reactions Authors: Maximilian Franz Hertrich, Florian Korbinian Scharnagl, Anahit Pews-Davtyan, Carsten Krevenschulte, Henrik Lund, Stephan Bartling, Ralf Jackstell, and Matthias Beller This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201806282 Link to VoR: http://dx.doi.org/10.1002/chem.201806282

Supported by ACES



Supported Cobalt Nanoparticles for Hydroformylation Reactions

Maximilian Franz Hertrich,^{[a]+} Florian Korbinian Scharnagl,^{[a]+} Anahit Pews-Davtyan,^[a] Carsten Kreyenschulte,^[a] Henrik Lund,^[a] Stephan Bartling,^[a] Ralf Jackstell^[a] and Matthias Beller^{*[a]}

Abstract: Hydroformylation of olefins has been studied in the presence of specific heterogeneous cobalt nanoparticles. The catalytic materials were prepared by pyrolysis of preformed cobalt complexes deposited onto different inorganic supports. AAS-measurements indicate a correlation of catalyst activity and cobalt leaching as well as a strong influence of the heterogeneous support on the productivity. These novel, low-cost, easy to handle catalysts can substitute more toxic, unstable and volatile cobalt carbonyl complexes for hydroformylations on lab-scale.

Introduction

Regarding scale, hydroformylation of olefins constitutes the most important homogeneously catalysed methodology.^[1-2] The resulting aldehydes are easily transformed into esters, alcohols, carboxylic acids, and aliphatic amines, which are widely used as intermediates for plasticizers, solvents, detergents and fine chemicals. In industry, until to date only cobalt- and rhodium-based homogeneous catalysts are applied, even though alternative metals continue to attract significant attention.^[3] Since the 1970's, for lower olefins (<C₅) cobalt carbonyl complexes have been replaced by phosphine- or phosphitemodified rhodium systems, which possess superior activity and selectivity.^[4-5] On the other hand, cobalt catalysts are mainly applied for the conversion of mid- and long-chained olefins to alcohols due to their inherent high hydrogenation activity.

Notably, for both cases costs for metal/ligands or recycling are decisive. Hence, there is a growing interest to develop more economic technologies, which allow quantitative catalyst recycling.^[6] In this respect, many research groups investigated both heterogeneous and immobilised homogeneous catalysts for the title reaction, mainly using rhodium,^[7-14] but also cobalt systems^[15-17] as well as other metals.^[18-23] The main problem of all these catalysts is the leaching of active metal-species from the support in the presence of CO. Furthermore, both activity and selectivity of heterogenized catalysts are in general lower compared to their homogeneous counterparts.

To overcome these limitations, immobilisation of metal complexes, for instance, was introduced with supported ionic liquid-phase (SILPs) systems.^[24-28] Other methods attempted to build a bridge between homogeneous and heterogeneous catalysis by the formation of dispersed single metal atom catalysts (SACs)^[29-31] or small nanoparticles (NPs).^[32-33]

In past years, our group developed several nanoscale catalysts, especially based on N-doped carbon supported cobalt- and iron-species. Those catalysts are easily prepared by pyrolysis of a carbon source such as Vulcan[®] XC 72R, impregnated with *in situ* ligated Co^[34-35] and Fe,^[36-37] respectively. Similar materials containing nanoparticles supported on inorganic carriers^[38] and biomass-derived catalysts were studied, too.^[39-41] Based on these works, herein we describe the synthesis for cobalt-containing materials and studied their catalytic performance in hydroformylation reactions.

Results and Discussion

Preparation of and Structural Trends for the Materials

Initially, we prepared around 50 materials based on a general procedure developed by our group.^[34] For this purpose, different commercially available supports (e.g. carbon, titania, silica, ceria, alumina) were impregnated with cobalt(II) acetate in the presence of different N-containing organic ligands (2 eq.). Subsequent pyrolysis, in general at 800 °C, led to a library of catalysts named Co/Ligand@Support. Detailed descriptions the of preparation method, thermo-gravimetric analyses for the two mainly used ligands as well as for the preparation of Co/phen@C, the analytical methodologies, and the characterisation of selected materials are given in the supporting information.

The general compositions of selected catalysts were studied by powder X-ray diffraction (XRD) experiments and elementary analysis (EA) while the surface structures for some supported nanoparticles were characterised in more detail by X-ray photoelectron spectroscopy (XPS) or transmission electron microscopy (TEM). All supported cobalt nanoparticles are either core shell structured with a cobalt core and a closed cobalt oxide shell or a pure cobalt oxide or metallic cobalt phase, respectively. In some cases graphene layers covering big particles were observed. Remarkably, no clear correlation between cobalt content or oxidation state of the cobalt species at the surface and catalytic activity of the materials could be ascertained.

[[]a] Maximilian Franz Hertrich, Florian Korbinian Scharnagl, Anahit Pews-Davtyan, Carsten Kreyenschulte, Henrik Lund, Stephan Bartling, Ralf Jackstell and Matthias Beller Leibniz-Institut für Katalyse e.V. an der Universität Rostock Albert-Einstein-Straße 29a, D-18059 Rostock, Germany.

⁺ These authors contributed equally to this work. * Corresponding E-Mail-adress: matthias.beller@catalysis.de Supporting Information (SI): General experimental procedures, characterisation data and NMR spectra are available. See DOI: 10.1039/x0xx00000x

As ligands, inexpensive compounds such as urea, typical pyridine derivatives, but also biologically relevant nucleobases, amino acids, and even biopolymers (chitosan and chitin)^[42] were used. Notably, chitosan is produced via deacetylation of chitin, simply obtained from shrimp or crab shells.^[43-45] It is known to form stable complexes with metal ions^[46-47] and it was found to be an excellent precursor for *N*-doped graphene.^[48-49] Previously, both chitosan- and phenanthrolin-based materials exhibited good performance in catalytic hydrogenation reactions;^[39-41] thus, we focused especially on these systems.

Catalytic Activity

We started to explore the activity of the cobalt catalysts in two hydroformylation reactions (Table 1). Neohexene (*tert*-butyl ethylene) and *n*-butyl acrylate were chosen as model substrates. In the first case, the hydroformylation was expected to yield regioselectively the linear aldehyde **2** as product due to the steric demand of the *tert*-butyl group.

 Table 1. Hydroformylation of neohexene and *n*-butyl acrylate catalyzed by cobalt nanoparticles on different supports.



Standard reaction conditions: neohexene (1) (193 μ L, 1.5 mmol) or nbutyl acrylate (3) (214 μ l, 1.5 mmol), catalyst (29.5 mg), toluene (1.5 mL), 40 bar CO/H₂ (1:1), 100 °C, 18 h. ^aConversions and yields represent the mean value of three experiments and were calculated by GC using hexadecane as internal standard. ^bLinearity represents the amount of **4a** with respect to the total amount of linear and branched aldehyde (**4a** + **4b**).

As an example of an electronically activated olefin, *n*-butyl acrylate was selected to study the n/iso selectivity. In both cases unwanted isomerization reactions cannot take place. We decided to perform the reaction under a pressure of 40 bar

syngas (CO : $H_2 = 1 : 1$) at 100 °C for 18 hours. To compare the activity of our systems with the "corresponding" homogeneous one, we carried out experiments with dicobalt octacarbonyl as pre-catalyst, as well (Table 1, entry 1).

In general, the conversion of *n*-butyl acrylate in hydroformylation should be faster than the conversion of neohexene. Indeed, when dicobalt octacarbonyl was used as pre-catalyst this prediction was confirmed (Table 1, entry 1). The reason for that is the steric demand of the *tert*-butyl group in neohexene on the one hand and the electronic activation of the double bond by the ester group in *n*-butyl acrylate on the other hand. Following this trend, all catalysts based on the phenanthroline precursor were less active in neohexene hydroformylation than for the reaction of *n*-butyl acrylate (Table 1, entries 2, 4, 6, 8). Conversely, the catalysts prepared with the chitosan precursor showed the opposite behaviour (Table 1, entries 3, 5, 7). This finding is remarkable and contrary to general expectations. Obviously, the support of the catalyst as well as the ligand has an important influence on the activity.

As a general trend for the hydroformylation of neohexene we found that the ceria supported catalysts Co/phen@CeO2 and Co/Chitosan@CeO₂ (Table 1, entries 2 and 3) showed the lowest activity compared to the other materials based on the respective precursor. The phenanthroline derived catalyst supported on silicon dioxide Co/phen@SiO2 was slightly more productive in neohexene hydroformylation (Table 1, entry 4). Best activity for the phenanthroline based materials was reached with Co/phen@C, followed by Co/phen@TiO₂ (Table 1, entries 6 and 8). However, the conversion rates for that type of catalysts were not higher than 55% (Table 1, entry 6) and product yields did not exceed 45% (Table 1, entry 8). Comparing materials resulting from the pyrolysis of chitosan, we found that the silicon dioxide support led to the best performance (52% conversion and 46% yield; Table 1, entry 5), comparable to that of Co/phen@C. The corresponding material based on titania Co/Chitosan@TiO₂ was less active (Table 1, entry 7).

While the phenanthroline based catalysts are more active in the hydroformylation of *n*-butyl acrylate compared to the corresponding chitosan derived materials, there is no clear trend observed for neohexene hydroformylation. Among the different supports, cobalt on ceria gave the lowest conversions and yields (Table 1, entries 2 and 3). In fact, the two ceria supported catalysts are almost inactive. Most suitable for catalysing *n*-butyl acrylate hydroformylation are Co/phen@TiO₂ and Co/phen@C (Table 1, entries 6 and 8). Both showed full conversion of *n*-butyl acrylate and over 80% yield. In the case of the chitosan catalysts Co/Chitosan@SiO₂ gave the highest conversion rate (47%) and a yield of 33% (Table 1, entry 5), followed by the titania supported Co/Chitosan@TiO₂ (Table 1, entry 7).

As by-products, we observed in all reactions the corresponding alkanes. In the case of *n*-butyl acrylate we could also detect some dimerisation by-product.

In addition, we tested all catalysts of our library. In general, the catalysts based on other ligands than chitosan or phenanthroline did not show an improved activity. Furthermore, the reaction conditions were varied to study the influence of temperature, pressure, and solvent amount in the presence of the most active catalysts. An overview of these experiments is given in the

supporting information (Table S 3). At 85 °C the rate of hydroformylation of both olefins was significantly declined. The performance for hydroformylation of neohexene could be improved by increasing the reaction temperature to 120 °C or 140 °C, respectively. Solvent concentration had only minor influence on the catalysis, however, under neat conditions the selectivity was rather low. Using butyl acrylate the reaction was also scaled up by a factor of 10 leading to similar results (see supporting information experimental methods).

To proof the general suitability of Co/phen@C for other hydroformylations, we investigated reactions of 1-octene (5) and cyclohexene (10) as linear and cyclic aliphatic compounds, styrene (8) as an aromatic compound, *N*-vinyl phthalimid (9) and diisobutene (7) as industrial relevant substrates, and 1,1-diphenyl ethylene (6) as a sterically hindered one. The results of this substrate scope are summarised in Scheme 1.



Scheme 1. Standard reaction conditions: substrate (1.5 mmol), catalyst (29.5 mg), toluene (1.5 mL), 40 bar CO/H_2 (1:1), 100 °C, 18 h. Conversion of **5-10**, the yielded products and the linearity represent the mean value of two experiments and were calculated by GC using hexadecane as internal standard *or calculated by 1 H NMR measurements using 1,4-dimethoxybenzene as internal standard.

Except for the sterically hindered **6**, we observed mediocre to good yields for the generated aldehydes. The hydrogenation of the olefins to the corresponding alkanes is a competitive pathway in some cases. In fact, for **6** and **8** 1,1-diphenyl ethane and ethyl benzene were detected as major products.

Kinetic Behaviour and Leaching

For a better understanding for the activity of the catalytic materials, we investigated the kinetic behaviour of our systems as well as the metal leaching of the catalysts for hydroformylation of n-butyl acrylate under the standard conditions. Therefore, we determined the conversion rates and yields after different reaction times from six hours up to 24 hours. The results of these experiments are summarised in Figure 1. We chose three catalysts one with low graphs), (Co/phen@CeO₂, blue one with moderate (Co/chitosan@TiO₂, green graphs) and one with hiah productivity (Co/phen@TiO2, red graphs). For Co/phen@TiO2 we saw a growing activity until the twelfth hour of the reaction. After that point the activity declined due to saturation effects.

Actually, after 18 hours the substrate is completely converted and the yield of aldehydes remained stable at a level of about 85%. In contrast, for the two least productive catalysts Co/phen@CeO₂ and Co/chitosan@TiO₂ we found out that there is an induction period of at least six hours where the systems are not active. Even after twelve hours the conversion rates and yields are not higher than 10% for both materials.



Figure 1. Conversion rates (dark colours) and yields (bright colours) for hydroformylation of n-butyl acrylate after a certain reaction time with three different catalysts. Standard reaction conditions: n-butyl acrylate (1.5 mmol), catalyst (29.5 mg), toluene (1.5 mL), 40 bar CO/H₂ (1:1), 100 °C. Conversions and yields were calculated by GC using hexadecane as internal standard. Key: dark red/red graphs represent conversion/yield with catalyst Co/phen@TiO₂, dark green/green graphs represent conversion/yield with catalyst Co/chitosan@TiO₂ and dark blue/blue graphs represent conversion/yield with catalyst Co/phen@CeO₂.

Although the activity of Co/chitosan@TiO₂ and the yield and conversions were rising after this induction period, the productivity of the catalysts decreased again after 18 hours and no higher yields than 32% were detected after 24 hours reaction time. Co/phen@CeO₂ showed a slightly different behaviour: For the whole investigated period there seemed to be the same activity after the induction period. However, the overall productivity of Co/phen@CeO₂ was very low (5% yield after 24 h).

It is well known in literature that heterogeneous metal catalysts are leaching under typical condition of hydroformylation. In those cases the active species – usually a metal carbonyl – is formed *in situ*.^[50-53] Since the reaction solutions were normally coloured after stopping the reaction, we presumed that this colour originated from leached cobalt carbonyl species. Indeed, recycling of the catalyst Co/phen@C *via* filtration and washing resulted in a significant drop of the productivity. For example, only 8% product yield was detected after the third run compared to 58% after the first cycle (see supporting information Table S 4).

Consequently, we decided to study the amount of cobalt in the reaction solutions after stopping the hydroformylation at certain times (6, 12, 18, and 24 hours). For this purpose, the reaction mixtures were filtered immediately after opening the reactor. All volatile components were removed and the residues were dissolved in *aqua regia*. Afterwards, the cobalt content of these

10.1002/chem.201806282

aqueous solutions was determined *via* AAS. The results of this analysis for Co/phen@TiO₂ (red graph), Co/phen@C (orange graph), Co/chitosan@TiO₂, (green graph) and Co/phen@CeO₂ (blue graph) are shown in Figure 2.



Figure 2. Amount of leached cobalt after a certain time with four different catalysts. Standard reaction conditions: n-butyl acrylate (1.5 mmol), catalyst (29.5 mg), toluene (1.5 mL), 40 bar CO/H_2 (1:1), 100 °C. Cobalt mass was calculated based on AAS-analysis of the fused reaction solutions. Key: red graph represents cobalt in solution with catalyst Co/phen@TiO₂, orange graph represents cobalt in solution with catalyst Co/phen@C, green graph represents cobalt in solution with catalyst Co/chitosan@TiO₂ and blue graph represents cobalt in solution with catalyst co/chitosan@TiO₂ and blue graph represents cobalt in solution with catalyst Co/phen@CO₂.

Obviously, the amount of cobalt in solution correlates to some degree with the productivity of the catalysts. Independent of the reaction time, the leaching of Co/phen@CeO2 remains on a low level as well as the activity of this catalyst. The amount of cobalt deliberated from the other investigated catalysts Co/phen@TiO₂, Co/phen@C and Co/chitosan@TiO2 is increasing with the reaction time and seemed to be saturated after 18 hours. For these three materials no clear correlation between leaching and productivity could be ascertained. On the one hand, Co/phen@C and Co/phen@TiO₂ showed almost same results for conversion and yield after 18 hours (see Table 1). In contrast to that, the amount of leached cobalt is twofold higher for Co/phen@TiO2 as for Co/phen@C. On the other hand, the detected values for cobalt in solution for the reaction with Co/phen@C and Co/chitosan@TiO₂ are at the same level, whereas the activity of both materials for hydroformylation differs not proportionally. Interestingly, there is no correlation between cobalt content at the surface and amount of leached cobalt, as well (see supporting information).

These results demonstrate that both precursor and support of the catalyst have an influence on metal leaching. Notably, adding the commercial support material silica or titania to the active homogeneous catalyst, resulted in a strong decline of the catalyst activity, whereas addition of carbon or ceria did not show any influence on the performance (see supporting information Table S 4).

Conclusions

In summary, we prepared several Co-containing materials by pyrolysis and demonstrated their performance in several hydroformylation reactions. The kinetic behaviour and the rate of leaching of the catalysts depend strongly on the support and *in situ* generated cobalt complex. As a result of these investigations, we assume that the presented hydroformylation reactions take place mainly in solution. Nevertheless, active centres on the surface are productive to a limited extent, too. In general, both Co/phen@TiO₂ and Co/phen@C represent stable, non-volatile and easy to handle reservoirs for active homogeneous cobalt species, and thus can conveniently substitute the common but toxic dicobalt octacarbonyl complex in hydroformylations on small scale. Further investigations to find more stable heterogeneous catalysts for hydroformylation are ongoing in our group.

Experimental Section

Catalytic Experiments

Typically, the catalytic experiments were carried out in 4 mL glass vials. The vials were filled with 1.5 mL toluene, 193 µL neohexene (1.5 mmol) or 214 µL n-butyl acrylate, 29.5 mg of the catalyst (corresponding to 1 mol% of Co) and a glass-coated stirring bar and closed with a septum cap. In order to allow gas exchange, a needle was pierced through the septum. The vials were placed on a steel plate in a 300 mL steel autoclave. The closed reactor was washed three times with syngas and filled with 40 bar syngas ($H_2:CO = 1:1$). The reaction was performed for 18 hours at 100 °C while stirring (700 rpm to 800 rpm) the reaction mixtures. After stopping the reaction via cooling of the autoclave, the gas was released. The vials were moved out of the autoclave and hexadecane as standard was added to the reaction solution. After diluting with acetone, ethyl acetate or toluene the grey to black suspension was filtered through a syringe filter. Yields and conversion rates were calculated by GC analysis with hexadecane as internal standard.

Proof of Leaching

For proof of leaching, the filtered reaction solution (hydroformylation of n-butyl acrylate) was transferred into a pressure tube. All volatile components of the solution were removed under reduced pressure and 6 mL of *aqua regia* (HNO₃:HCI = 1:3) were added to the residue. The pale yellow mixture was heated up to 140 °C for 4 hours in the closed pressure tube. The resulting red-brownish solution was cooled down to room temperature and then diluted with 6 mL of water. After that, air was funnelled through the solution to remove all nitrogen oxides, the solution was filled with water up to 25 mL and was analysed by AAS.

Kinetic Experiments

For the kinetic experiments, the reaction protocol was the same as for the catalytic experiments. The reaction time was

decreased to 6 or 12 hours or increased to 24 h, respectively. The work-up and the analytic procedure were the same as described before.

Acknowledgements

This work was part of the KataPlasma project (MatRessources program) funded by the German Federal Ministry of Education and Research (BMBF). NoNaCat program and the federal state Mecklenburg Western Pomerania are gratefully of acknowledged for financial funding. We thank Dr. Annette-Enrica Surkus for fruitful discussions and her useful advice for the preparation of heterogeneous catalysts. Dr. Giovanni Agostini is acknowledged for his XPS measurements. We thank Alexander Wotzka for conducting TGA measurements. The support of the analytical department of the LIKAT and the University of Rostock especially for the elementary analysis is recognised with thanks.

Keywords: hydroformylation • cobalt • heterogeneous catalysis • aldehydes • carbonylation • leaching

References

- R. Franke, D. Selent, A. Börner, *Chem. Rev.* 2012, *112*, 5675-5732.
- [2] A. Börner, R. Franke, Hydroformylation: Fundamentals, Processes, and Applications in Organic Synthesis, Wiley-VCH, Weinheim, 2016.
- [3] J. Pospech, I. Fleischer, R. Franke, S. Buchholz, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 2852-2872.
- [4] R. Tudor, M. Ashley, Platinum Met. Rev. 2007, 51, 116.
- [5] K.-D. Wiese, D. Obst, in *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Berlin-Heidelberg, **2006**, pp. 1-33.
- [6] F. Hebrard, P. Kalck, *Chem. Rev.* **2009**, *109*, 4272-4282.
- [7] L. Alvarado Rupflin, J. Mormul, M. Lejkowski, S. Titlbach, R. Papp, R. Gläser, M. Dimitrakopoulou, X. Huang, A. Trunschke, M. G. Willinger, R. Schlögl, F. Rosowski, S. A. Schunk, ACS *Catal.* 2017, 3584-3590.
- [8] C. Li, L. Yan, L. Lu, K. Xiong, W. Wang, M. Jiang, J. Liu, X. Song, Z. Zhan, Z. Jiang, Y. Ding, *Green Chem.* 2016, 18, 2995-3005.
- [9] R. Lang, T. Li, D. Matsumura, S. Miao, Y. Ren, Y.-T. Cui, Y. Tan, B. Qiao, L. Li, A. Wang, X. Wang, T. Zhang, *Angew. Chem. Int. Ed.* **2016**, 16054-16058.
- [10] Q. Sun, Z. Dai, X. Liu, N. Sheng, F. Deng, X. Meng, F.-S. Xiao, J. Am. Chem. Soc. 2015, 137, 5204-5209.
- [11] T. T. Adint, C. R. Landis, J. Am. Chem. Soc. 2014, 136, 7943-7953.
- M. Jakuttis, A. Schönweiz, S. Werner, R. Franke, K. D. Wiese, M. Haumann, P. Wasserscheid, *Angew. Chem. Int. Ed.* 2011, 50, 4492-4495.

- [13] C. Li, W. Wang, L. Yan, Y. Ding, Front. Chem. Sci. Eng. 2018, 12, 113-123.
- [14] D. Gorbunov, D. Safronova, Y. Kardasheva, A. Maximov, E. Rosenberg, E. Karakhanov, ACS Appl. Mater. Interfaces 2018, 10, 26566-26575.
- [15] X. Song, Y. Ding, W. Chen, W. Dong, Y. Pei, J. Zang, L. Yan, Y. Lu, *Appl. Catal.*, A **2013**, 452, 155-162.
- [16] Z. Cai, H. Wang, C. Xiao, M. Zhong, D. Ma, Y. Kou, J. Mol. Catal. A: Chem. 2010, 330, 94-98.
- [17] Y. Zhang, K. Nagasaka, X. Qiu, N. Tsubaki, *Catal. Today* 2005, 104, 48-54.
- [18] G. Parrinello, J. K. Stille, J. Am. Chem. Soc. 1987, 109, 7122-7127.
- [19] J. Su, C. Xie, C. Chen, Y. Yu, G. Kennedy, G. A. Somorjai, P. Yang, J. Am. Chem. Soc. 2016, 138, 11568-11574.
- [20] D. G. Hanna, S. Shylesh, P. A. Parada, A. T. Bell, J. Catal. 2014, 311, 52-58.
- [21] L. Oresmaa, M. A. Moreno, M. Jakonen, S. Suvanto, M. Haukka, *Appl. Catal.*, A **2009**, 353, 113-116.
- [22] A. E. Marteel, T. T. Tack, S. Bektesevic, J. A. Davies, M. R. Mason, M. A. Abraham, *Environ. Sci. Technol.* **2003**, 37, 5424-5431.
- [23] L. Alvila, J. Pursiainen, J. Kiviaho, T. A. Pakkanen, O. Krause, J. Mol. Catal. **1994**, *91*, 335-342.
- [24] M. Haumann, A. Riisager, Chem. Rev. 2008, 108, 1474-1497.
- [25] A. Riisager, R. Fehrmann, M. Haumann, P. Wasserscheid, *Eur. J. Inorg. Chem.* 2006, 2006, 695-706.
- [26] A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, J. Catal. 2003, 219, 452-455.
- [27] A. Riisager, R. Fehrmann, S. Flicker, R. van Hal, M. Haumann, P. Wasserscheid, *Angew. Chem. Int. Ed.* 2005, 44, 815-819.
- [28] C. Van Doorslaer, J. Wahlen, P. Mertens, K. Binnemans, D. De Vos, *Dalton Trans.* 2010, *39*, 8377-8390.
- [29] J. Liu, ACS Catal. 2017, 7, 34-59.
- [30] X.-F. Yang, A. Wang, B. Qiao, J. Li, J. Liu, T. Zhang, Acc. Chem. Res. 2013, 46, 1740-1748.
- [31] X. Cui, K. Junge, X. Dai, C. Kreyenschulte, M.-M. Pohl, S. Wohlrab, F. Shi, A. Brückner, M. Beller, ACS Cent. Sci. 2017, 3, 580-585.
- [32] D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. Int. Ed. 2005, 44, 7852-7872.
- [33] L. Liu, A. Corma, *Chem. Rev.* **2018**, *118*, 4981-5079.
- [34] F. A. Westerhaus, R. V. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner, M. Beller, *Nat. Chem.* **2013**, *5*, 537-543.
- [35] D. Formenti, C. Topf, K. Junge, F. Ragaini, M. Beller, Catal. Sci. Technol. 2016, 6, 4473-4477.
- [36] R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science* **2013**, *342*, 1073-1076.
- [37] M. Lefèvre, E. Proietti, F. Jaouen, J.-P. Dodelet, Science 2009, 324, 71-74.
- [38] F. Chen, C. Kreyenschulte, J. Radnik, H. Lund, A.-E. Surkus, K. Junge, M. Beller, ACS Catal. 2017, 1526-1532.

10.1002/chem.201806282

WILEY-VCH

- [39] F. K. Scharnagl, M. F. Hertrich, F. Ferretti, C. Kreyenschulte, H. Lund, R. Jackstell, M. Beller, *Sci. Adv.* 2018, *4*, 1-9.
- [40] B. Sahoo, A.-E. Surkus, M.-M. Pohl, J. Radnik, M. Schneider, S. Bachmann, M. Scalone, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* 2017, *56*, 11242-11247.
- [41] B. Sahoo, D. Formenti, C. Topf, S. Bachmann, M. Scalone, K. Junge, M. Beller, *ChemSusChem* **2017**, *10*, 3035-3039.
- [42] T. X. Wu, G. Z. Wang, X. Zhang, C. Chen, Y. X. Zhang, H. J. Zhao, Chem. Commun. 2015, 51, 1334-1337.
- [43] K. Kurita, Mar. Biotechnol. 2006, 8, 203.
- [44] X. Chen, H. Yang, N. Yan, Chem. Eur. J. 2016, 22, 13402-13421.
- [45] N. Yan, X. Chen, Nature 2015, 524, 155-157.
- [46] E. Guibal, Sep. Purif. Technol. 2004, 38, 43-74.
- [47] E. Taboada, G. Cabrera, R. Jimenez, G. Cardenas, J. Appl. Polym. Sci. 2009, 114, 2043-2052.
- [48] A. Primo, P. Atienzar, E. Sanchez, J. M. Delgado, H. Garcia, *Chem. Commun.* **2012**, *48*, 9254-9256.
- [49] L. Zhao, N. Baccile, S. Gross, Y. Zhang, W. Wei, Y. Sun, M. Antonietti, M.-M. Titirici, *Carbon* **2010**, *48*, 3778-3787.
- [50] D. F. Taylor, B. E. Hanson, M. E. Davis, *Inorg. Chim. Acta* 1987, 128, 55-60.
- [51] M. Lenarda, L. Storaro, R. Ganzerla, J. Mol. Catal. A: Chem. 1996, 111, 203-237.
- [52] J. A. Díaz-Auñón, M. C. Román-Martínez, C. Salinas-Martínez de Lecea, J. Mol. Catal. A: Chem. 2001, 170, 81-93.
- [53] M. C. Román-Martínez, J. A. Díaz-Auñón, C. Salinas-Martínez de Lecea, H. Alper, *J. Mol. Catal. A: Chem.* 2004, 213, 177-182.

WILEY-VCH

Entry for the Table of Contents

FULL PAPER

FULL PAPER

We report a new class of low-cost, easy to handle materials for labscale hydroformylation. The pyrolysis of preformed Co complexes deposited onto inorganic supports resulted in immobilized cobalt nanoparticles for oxo synthesis. The most active materials Co/phen@TiO₂ and Co/phen@C represent convenient reservoirs for active homogeneous cobalt species, and thus can substitute the common but toxic dicobaltoctacarbonyl complex.



Maximilian Franz Hertrich, Florian Korbinian Scharnagl, Anahit Pews-Davtyan, Carsten Kreyenschulte, Henrik Lund, Stephan Bartling, Ralf Jackstell and Matthias Beller*



Supported Cobalt Nanoparticles for Hydroformylation Reactions