Colloids for Catalysts: A Concept for the Preparation of Superior Catalysts of Industrial Relevance

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Abstract: *Compared to conventional preparation methods for supported heterogeneous catalysts, the use of colloidal nanoparticles (NPs) allows for a precise control over size, size distribution, and distribution/location of the NPs on the support. However, common colloidal syntheses have restrictions that limit their applicability for industrial catalyst preparation. We present a simple, surfactant-free, and scalable preparation method for colloidal NPs to overcome these restrictions. We demonstrate how precious-metal NPs are prepared in alkaline methanol, how the particle size can be tuned, and how supported catalysts are obtained. The potential of these colloids in the preparation of improved catalysts is demonstrated by two examples from heterogeneous catalysis and electrocatalysis.*

Supported precious-metal nanoparticles (NPs) are among the industrially most relevant catalysts. They are applied in refinery, as exhaust gas catalysts, for bulk and fine chemicals production, and in electrocatalysis.[1] Owing to the high costs of precious metals, even small performance enhancements lead to significant ecologic and economic improvements. For this reason, novel but simple ways to prepare supported catalysts with improved properties are highly desirable.

For a given metal the performance of a supported catalyst depends mainly on the physical properties: 1) the NP size, 2) the size distribution, and 3) the distribution and location of the NPs on the support. As the surface to volume ratio increases with decreasing particle size, smaller NPs are usually beneficial in terms of activity per mass of metal. Depending on the reaction, selectivity can also strongly depend on the NP size. Thus accurate size control is highly desirable. In addition, supported NPs must be well accessible for the reactants to effectively utilize the expensive precious metal. This implies that they should be evenly distributed over the external surface of the support, but not be located inside small pores, where accessibility is hampered.

The typical industrial approach to prepare supported catalysts follows two steps. First, the active metal is spread onto the support by impregnation, adsorption, or incipient wetness, for example.[2] Second, calcination and reduction treatments are applied that lead to the formation of active NPs. The fact that the NPs form on the support leads to various limitations regarding the control and optimization of the catalyst's physical properties. Owing to capillary forces, NPs are formed inside small pores of the support, which reduces their accessibility.[3] Furthermore, the chemical and physical properties of the support surface strongly influence the distribution of the NPs on the support. This is a particular problem when higher loadings are required because the formation of aggregates and the probability of sintering increase (see also Figure S1 and the discussion in the Supporting Information), lowering the precious-metal-related activity.[2]

The use of colloids is an approach that overcomes these limits of conventional catalyst preparation methods. NPs are formed in a solvent by reduction of dissolved metal precursors and are subsequently deposited onto the desired support. Alternatively, they may be used directly without a support to prepare bulk catalysts. The separation of NP preparation and deposition into individual steps diminishes any contribution of the support on the NP formation. This allows for optimized control over NP size.[4] NPs cannot form in small support pores, but particle deposition occurs preferably at the external surface, which improves their accessibility to reactants. As a result, the physical properties of supported catalysts can be optimized to achieve a more efficient use of the expensive precious metal.

However, colloidal methods also bear challenges, as recently highlighted by BASF,[5] that hamper their use for

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industrial catalyst preparation. These are 1) the need for surfactants, 2) the use of high-boiling-point solvents,[6] and 3) restrictions to low metal concentrations.

In most colloidal approaches, sintering of precious-metal NPs is a fundamental problem. For this reason, often surfactants (e.g., PVP) are used that cover the NP surface to prevent sintering. However, surfactants are detrimental for catalytic applications as they block the NP surface. Their removal after NP deposition on the support is hence an essential step.[7] Several surfactant removal procedures have been demonstrated on laboratory scale, but their technological feasibility has not been proven to date.

For the synthesis of precious-metal colloids, usually solvents with high boiling points such as ethylene glycol (EG) or oleylamine are applied. Alkaline EG functions as a solvent and reducing agent, and the reaction products stabilize the NPs,[8] whereas water as the solvent requires surfactants, for example, glucose, to stabilize the NPs.[9] To deposit the NPs onto a support, ideally one may add only the support to a surfactant-free colloidal NP dispersion and then remove the solvent at reduced pressure. Certainly, this is not feasible with a solvent such as EG owing to its high boiling point. Therefore, the NPs must be precipitated, cleaned from EG, and redispersed in a low-boiling-point solvent prior to deposition. This complicates the preparation and additional chemicals such as HCl may be needed,[10] which could poison the final catalysts.

The use of low metal concentrations bears another technological challenge. Reaction volumes should be as small as possible to minimize waste and equipment costs.[5] In other words, high metal concentrations are required. This is often not possible without suffering from significant metal losses that are due to sintering and precipitation.

The herein presented colloidal synthesis approach, which is referred to as Co4Cat (colloids for catalysts), addresses the drawbacks of colloidal syntheses for catalyst preparation. It is 1) free of surfactants, 2) proceeds in a low-boiling-point solvent, and 3) is scalable to high metal concentrations (ca. 5 g precious metal per liter). In the following, we first discuss an example based on Pt NPs, but the general concept is also applicable to Ir, Ru, Pd, and bimetallic NPs (see Figures S2–S5 and Table S1).

The Pt NPs were prepared by heating a mixture of the Pt precursor salt with alkaline methanol (see the Supporting Information and Tables S2 and S3 for details). The NPs have a narrow size distribution, and the size can be controlled in the range of 2 nm to 6 nm (Figure 1 and Figure S6) by adding water to the reaction mixture. The dispersions are stable for at least 12 hours. If kept for prolonged periods, some particles sediment, but these NPs are not sintered and can be redispersed without changes in the particle size by vigorous stirring (Figures S7 and S8). The NPs can also be isolated as dry powders by solvent removal through distillation. These dried NPs are redispersible and can be further processed[8a] without changes in particle size (Figured S9 and S10).

Owing to the low boiling point of mono-alcohols, the Co4Cat NPs can be easily deposited onto a support by adding the desired support material and removing the solvent, for example, under reduced pressure. The solvent can be fully
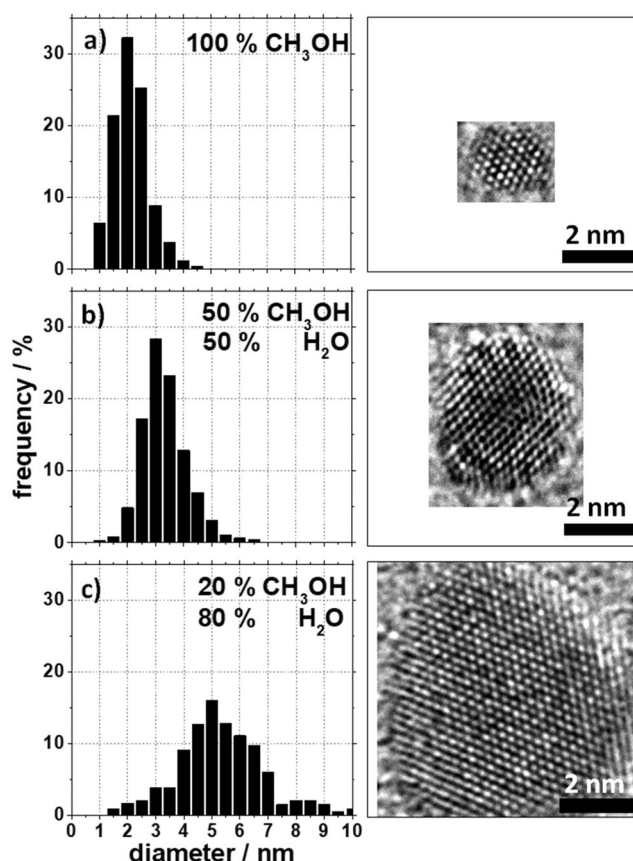

Figure 1. Left: Size distribution estimated from TEM images for Pt NPs synthesized using an alkaline mixture of methanol with a volume percentage of a) 0, b) 50, or c) 80% water. Right: HRTEM images of individual NPs obtained by the indicated syntheses.

recycled and reused for the synthesis of new NPs without changes in the NP properties (Figure S11).

In the following, catalytic reactions performed with supported Pt catalysts prepared by the Co4Cat technology are compared to those of industrial catalysts prepared by conventional methods. We used the hydrogenation of 2-butanone as a test reaction to compare Co4Cat catalysts with industrial standards provided by Clariant. Three different metal loadings were investigated: 1, 5, and 10 wt% Pt on γ-Al_2O_3. Kinetic tests confirmed the absence of external diffusion limitations. To evaluate the performance of the different catalysts, the reaction time needed to obtain 100% conversion was determined for the same total catalyst masses (Pt + support, see Figure 2). It was found that all catalysts prepared from the colloidal approach were more active than the respective industrial benchmarks. Particularly interesting is the behavior of the catalysts with increased Pt loading. The aim of increasing the Pt loading is to increase the catalyst-mass-related activity. This allows for achieving higher space–time yields in a reactor of a given size. Such behavior was indeed observed for the colloid-based catalyst. By comparison, for the industrial benchmark, the reaction time required to obtain 100% conversion significantly increased with metal loading, that is, the mass-related activity decreases.
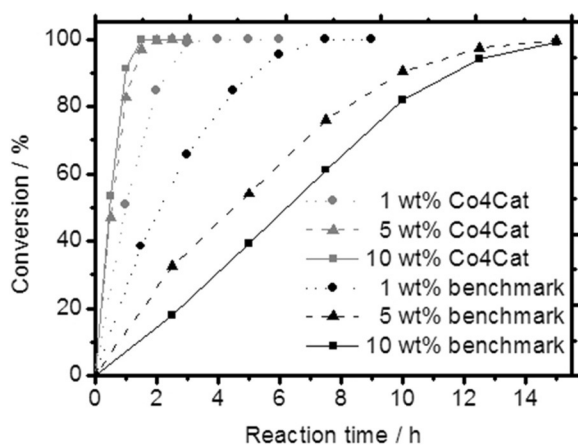
Figure 2. Catalyst-mass-related activities expressed as the reaction time required to obtain full conversion of butanone into 2-butanol. Three loadings were tested for catalysts prepared by the Co4Cat technology (gray) and industrial standards (black). For the industrial catalysts, mass-related activities decrease with increasing metal loading, a typical limitation of conventional catalyst preparation methods. In contrast, for Co4Cat catalysts, the mass-related activities increase with metal loading.

application bears significant advantages over conventional preparation methods and the potential to economically and ecologically optimize processes.

As a second test reaction for our colloidal catalyst preparation approach, the oxygen evolution reaction (OER) was investigated. The OER is the anode reaction in water-based electrolysis processes. Electrolysis is essential for regenerative energy concepts, for example, the generation of hydrogen from water using wind or solar power. Under acidic conditions, state-of-the-art OER catalysts are oxidized Ir or Ir alloy NPs used without supports (IrO_2 black) or coated as thick films onto non-conducting supports.[11] As described above for Pt, colloidal Ir NPs were prepared in alkaline methanol, but then directly spray-coated onto a glassy carbon electrode (GC) of a rotating disk electrode (RDE) setup. This method generated thin homogenous coatings (Figure E1) of the Ir NPs on the GC surface. In Table 1 (and Table S7), the mass-related OER activity determined by RDE is compared to data from the literature. It is seen that the colloidal Ir NPs exhibit significantly improved OER performances; depending on the chosen benchmark, improvement factors of 3 up to 10 and higher were achieved. As all catalysts are composed of IrO_2, which forms at the applied electrode potentials, the

Based on a careful characterization of the physical properties of the different catalysts, we relate these findings to the smaller NP size of the colloid-based catalysts, but also to the more uniform distribution of the NPs over the support surface, which reduces internal diffusion limitations (see also the Supporting Information). In the commercial benchmark, larger aggregates are formed on the support at higher Pt loadings. This is typical for conventional preparation methods but can be avoided by the Co4Cat approach as TEM and EDX analysis revealed (Figures S12 and S14). Large aggregates significantly lower the active metal surface area. Furthermore, areas with high particle densities increase the probability of internal diffusion limitations. In contrast, small NPs that are evenly distributed over the support lead to high metal surface areas and reduce the probability of internal diffusion limitations. The benefit of such optimized physical properties can be further highlighted when comparing Pt-mass-related activities (Figure S14 and Table S4). Even though the particle density on the 5 wt% catalyst prepared with the colloidal NPs is significantly higher than that of the industrial 1 wt% catalyst, the Pt-mass-related activities are similar. However, not only the catalyst activity is improved. Additional investigations show that the optimized physical properties of the colloidal catalysts also lead to improved recyclability and slower deactivation as compared to the commercial benchmark (Figure S15 and Tables S4–S6). Considering that an industrial process is always a compromise between costs for the reactor (that increase with increasing reactor size), catalyst costs, and the resulting space–time yield, the possibility to optimize the physical catalyst properties according to the needs of a specific

Table 1: Mass-related OER activities of colloidal Ir NPs prepared in alkaline methanol as compared to different literature values.

		Mass activity [$A\,g_{Ir}^{-1}$]	Potential of measurement [V_{RHE}]	Ref.
Ir Co4Cat[a]	**Ir**	**205**	**1.5**	
Ir Co4Cat[a]	**Ir**	**1130**	**1.55**	
Ir-ND[b]	Ir	65	1.51	[12]
Ir-ND/C[b]	Ir	68	1.51	[12]
Ir-ND/ATO[b]	Ir	70	1.51	[12]
IrO$_2$-TiO$_2$ (UMICORE)[c]	IrO$_2$/TiO$_2$	2	1.5	[11]
IrO$_2$-TiO$_2$-245[c]	IrO$_2$/TiO$_2$	20	1.5	[11]
JM-Iridium Black[d]	Ir	300	1.55	[13]
AA[d]	IrO$_2$	140	1.55	[13]
AA-Iridium Black[d]	Ir	240	1.55	[13]
PR-Iridium Black[d]	Ir	270	1.55	[13]
PR[d]	Ir/Vulcan	460	1.55	[13]
UM-Iridium Black[d]	Ir	140	1.55	[13]
UM[d]	Ir/TiO$_2$	70	1.55	[13]

[a] 0.1 M $HClO_4$, 10 mV s^{-1}. [b] 0.05 M H_2SO_4, 5 mV s^{-1}. [c] 0.1 M $HClO_4$, steady state. [d] 0.1 M $HClO_4$, 20 mV s^{-1}. Additional information, including the electrochemical surface areas, can be found in the Supporting Information.

improved performance is related to an improved dispersion of the Ir NPs, as determination of the electrochemically available surface area (Table S7) confirmed.

In conclusion, the presented colloidal approach, "Co4Cat", offers significant benefits over state-of-the-art catalysts preparation techniques, which are summarized in Scheme S1. The synthesis is simple, fast (< 1 h), and can be performed at low temperatures (< 70°C) without the need for any surfactants. No inert gas atmosphere is required, and the synthesis is robust towards increasing the metal precursor concentration (up to ca. 5 g Pt L^{-1}) and changes in the reaction volume and reaction time (Tables S2 and S3). Perhaps most importantly, the introduced technology enables

the true design of the physical catalyst properties according to the needs of a specific process, which paves the way to enhanced performances and a more efficient utilization of the expensive precious metal. These advantages were demonstrated with catalysts based on colloidal Pt and Ir NPs, but the method is also applicable to other metal catalysts and even bimetallic NPs.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

[1] R. Schlögl, *Angew. Chem. Int. Ed.* **2015**, *54*, 3465–3520; *Angew. Chem.* **2015**, *127*, 3531–3589.

[2] O. Deutschmann, H. Knözinger, K. Kochloefl, T. Turek in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, New York, **2009**.

[3] a) R. Strobel, W. J. Stark, L. Mädler, S. E. Pratsinis, A. Baiker, *J. Catal.* **2003**, *213*, 296–304; b) Y. C. Park, H. Tokiwa, K. Kakinuma, M. Watanabe, M. Uchida, *J. Power Sources* **2016**, *315*, 179–191.

[4] J. Quinson, M. Inaba, S. Neumann, A. A. Swane, J. Bucher, S. B. Simonsen, L. Theil Kuhn, J. J. K. Kirkensgaard, K. M. Ø. Jensen, M. Oezaslan, S. Kunz, M. Arenz, *ACS Catal.* **2018**, *8*, 6627–6635.

[5] P. T. Witte, P. H. Berben, S. Boland, E. H. Boymans, D. Vogt, J. W. Geus, J. G. Donkervoort, *Top. Catal.* **2012**, *55*, 505–511.

[6] S. S. Mao, G. Mao, US Patent 6,686,308, **2004**.

[7] M. Cargnello, C. Chen, B. T. Diroll, V. V. T. Doan-Nguyen, R. J. Gorte, C. B. Murray, *J. Am. Chem. Soc.* **2015**, *137*, 6906–6911.

[8] a) S. Neumann, S. Grotheer, J. Tielke, I. Schrader, J. Quinson, A. Zana, M. Oezaslan, M. Arenz, S. Kunz, *J. Mater. Chem. A* **2017**, *5*, 6140; b) Y. Wang, J. W. Ren, K. Deng, L. L. Gui, Y. Q. Tang, *Chem. Mater.* **2000**, *12*, 1622–1627.

[9] C. Massimiliano, D. P. Cristina, M. Roberto, R. Michele, *Angew. Chem. Int. Ed.* **2004**, *43*, 5812–5815; *Angew. Chem.* **2004**, *116*, 5936–5939.

[10] X. Wang, P. Sonström, D. Arndt, J. Stöver, V. Zielasek, H. Borchert, K. Thiel, K. Al-Shamery, M. Bäumer, *J. Catal.* **2011**, *278*, 143–152.

[11] E. Oakton, D. Lebedev, M. Povia, D. F. Abbott, E. Fabbri, A. Fedorov, M. Nachtegaal, C. Coperet, T. J. Schmidt, *Acs Catal.* **2017**, *7*, 2346–2352.

[12] H. S. Oh, H. N. Nong, T. Reier, M. Gliech, P. Strasser, *Chem. Sci.* **2015**, *6*, 3321–3328.

[13] S. M. Alia, B. Rasimick, C. Ngo, K. C. Neyerlin, S. S. Kocha, S. Pylypenko, H. Xu, B. S. Pivovar, *J. Electrochem. Soc.* **2016**, *163*, F3105–F3112.