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Immobilization of Gold-on-Carbon Catalysts Onto Perfluorocarbon Emulsion Droplets to Promote Oxygen Delivery in Aqueous Phase D-Glucose Oxidation

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The catalytic activity of metal nanoparticles (NPs) supported on porous supports can be controlled by various factors, such as NPs size, shape, or dispersivity, as well as their interaction with the support or the properties of the support material itself. However, these intrinsic properties are not solely responsible for the catalytic behavior of the overall reaction system, as the local environment and surface coverage of the catalyst with reactants, products, intermediates and other invloved species often play a crucial role in catalytic processes as well. Their contribution can be particularly critical in liquid-phase reactions with gaseous reactants that often suffer from low solubiltiy. One example is D-glucose oxidation with molecular oxygen over gold nanoparticles supported on porous carbons. The possibility to promote oxygen delivery in such aqueous phase oxidation reactions via the immobilization of heterogenous catalysts onto the interface of perfluorocarbon emulsion droplets is reported here. Gold-on-carbon catalyst particles can stabilize perfluorocarbon droplets in the aqueous phase and the local concentration of the oxidant in the surroundings of the gold nanoparticles accelerates the rate-limiting step of the reaction. Consequently, the reaction rate of a system with the optimal volume fraction of fluorocarbon is higher than a reference emulsion system without fluorocarbon, and the effect is observed even without additional oxygen supply.

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Main Text

In heterogeneous catalysis, scalable and quantum effects are the basis for the catalytic activity of nanoparticles (NPs), and even the chemically most inert metals like gold exhibit remarkable catalytic activities when their size is in the nanometer range and catalytically active surfaces are exposed.[1] In order to combine nanoscience with heterogeneous catalysis and to utilze the catalytic properties of NPs efficiently, it is necessary to control their size, shape, dispersity, and growth. This is often accomplished by deposition and stabilization of NPs onto the surface of porous materials.[2] In that way, the catalytic activity of these systems can be optimized via gaining control over the NP size and electronic state, strain effects, metal-support interactions, composition and porosity of the support, amongst others.[3]

The local concentration of reactants surrounding the active site of the catalyst also significantly impacts the catalytic performance. As an example, in catalytic transformations in the gas phase, an increase of the gas pressure and thus an increased surface coverage of the heterogenous catalyst surface considerably influences the turnover rates.[4] This is becoming even more relevant in liquid-phase reactions with gas reactants, such as catalytic oxidation of biomass compounds with oxygen.[5] Such catalytic transformations are in many cases diffusion limited, i.e. the transport of reactants towards the catalytically active sites and/or their dissolution in the solvent are rate-determining factors.[6] In any case, the local concentration of gaseous reactands in the proximity to the catalyst surface is crucial for the properties of the catalysts and the overall process. To address this possible bottleneck, methods to increase the local concentration of gas have been developed, for example by performing the catalytic reaction within confined architectures of porous materials such as metal oxides, zeolites, or metal-organic frameworks to ensure fast delivery kinetics.[7]

In an alternative approach, the gas solubility in the liquid phase can be increased by introducing a carrier with high gas solubility that at the same time retains the activity and desirable selectivity of the catalyst. In this context, perfluorocarbon solvents (PFCs), chemically omniphobic fluids, are attractive due to their capability to dissolve substantial volumes of gas.[8] PFCs are biologically inert and hydrophobic as well as lipophobic in character, which is associated with a high oxygen dissolving capacity and low water solubility. Consequently, the unique properties of this solvent class have been exploited in a number

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of applications, including their use as artificial blood,[9] for the generation of superhydrophobic coatings,[10] as ultrasound contrast agents,[11] as an inert solvent in chemical transformations,[12] and in magnetic resonance imaging.[13] The solubility of oxygen in PFCs is up to one order of magnitude higher than that in water, making them a highly potent oxygen carrier.[14]
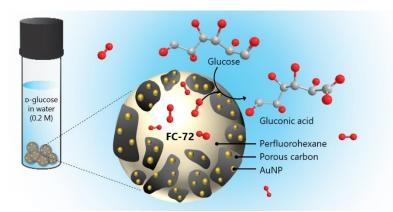
A reaction that can be used as a model system to investigate the effect of such an oxygen carrier in a relevant liquid-phase catalytic transformation due to its high selectivity under mild conditions and relatively simple hardware is the aqueous phase $_D$-glucose oxidation to gluconic acid with molecular oxygen. Gluconic acid and its salts serve as important biodegradable chelating agents and intermediates in the food, pharmaceutical, and concrete industry. 100.000 tonnes are industrially produced per year by fermentation and the current applications of gluconic acid continue to expand.[15] An alternative way towards gluconic acid would be the use of supported heterogeneous oxidation catalysts. Gluconic acid is the major product formed in this reaction which is usually carried out at moderate temperature (40–50 °C) and mild alkaline conditions (pH = 9–10). The oxidation product of glucose gets deprotonated and the conversion vs. time curve for such a reaction can be easily recorded by titration with an alkaline solution. Gold NPs supported on porous carbon materials (Au—C) have proven to be active catalysts for the oxidation of alcohols and carbohydrates, and particularly selective towards gluconic acid in the mentioned reaction.[5a,16] For this reaction, we have recently postulated a significant influence of the environment surrounding gold NPs supported on porous carbon materials on the local concentration of the reactants and by that on the "apparent activity" of the catalysts.[17]

To link the beneficial properties of PFCs to heterogeneously catalyzed $_D$-glucose oxidation with molecular oxygen, we postulated that the provision of PFCs would be associated with a higher local O_2 concentration in the proximity of the active catalytic reaction centers. This, in turn, can accelerate the rate of O_2 delivery and the oxygen coverage of the catalyst surface and thereby alleviate throughput constraints. To utilize the exceptional gas-dissolving properties of PFCs and to achieve a homogeneous mixture with the aqueous reaction media, it is beneficial to increase their interfacial area, while bringing both liquids into close contact with the catalyst. This can be achieved by the use of Pickering-type emulsions, in which oil or water are dispersed into the other phase in the form of micrometer-sized droplets that are stabilized by solid catalyst particles instead of molecular amphiphiles. With the catalyst confined at the liquid–liquid interface with two reactants confined in either the oil or water phase, traditional biphasic reactions in which the reactants are soluble in opposing liquids can be converted to a macroscopically homogeneous emulsion phase.

To increase the local concentration of oxygen next to the active phase of the catalyst, PFCs stabilized by Au—C (Au—C—PFC) were prepared, and the oxidation of $_D$-glucose was used to test their activity (Scheme 1). The introduction of 2% (v/v) dispersed fluorocarbon phase increased the rate of the oxidation reaction and significantly increased the reaction kinetics. Compared to catalysts immobilized at the interface of hydrocarbons with lower O_2 carrier capabilities, the introduction of emulsion droplets increased the rate of the oxidation reaction by a 5-fold. A comparison with the Au—C catalyst, as well as with Pickering emulsion comprised of a hydrocarbon instead of perfluorocarbon oil (Au—C—HC) is discussed.

Ordered mesoporous carbon (CMK-3) was recently used as a support material for the synthesis of a supported AuNP catalyst that shows remarkable activity in $_D$-glucose oxidation.[17] The carbon material was synthesized by nanocasting, through impregnation of ordered mesoporous silica hard template (SBA-15) with sucrose, followed by carbonization.[18] After the removal of the silica template, CMK-3 was obtained.[19] Before the deposition of active species, CMK-3 has been treated under a reducing atmosphere, to remove surface functional groups and ensure hydrophobic surface structure. This is an effective strategy for stabilization of small catalytically active AuNPs and avoiding their growth upon deposition.[20] The Au—C catalyst was obtained by deposition of 1 wt% of AuNPs on the porous surface of the carbon support. Resulting Au—C catalysts still show a uniform particle morphology that is typical for

Scheme 1. Structure of the Au—C—PFC emulsion consisting of perfluorohexane stabilized by particles of Au—C catalyst in an aqueous solution of $_D$-glucose.

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hexagonally ordered mesoporous materials (Figure S1, Supporting Information).

N_2 physisorption experiments ($-196\,°C$) were conducted to investigate the pore structure of the Au–C catalyst. The catalyst displayed a type IV(a) isotherm with a type H2(a) hysteresis loop (Figure 1a), according to the IUPAC classification.[21] The hysteresis loop is present in the relative pressure range of 0.4–0.75, which suggested an ordered mesoporous structure of the carbon support. The pore size distribution (PSD) was analyzed using the quenched-solid density functional theory (QSDFT, adso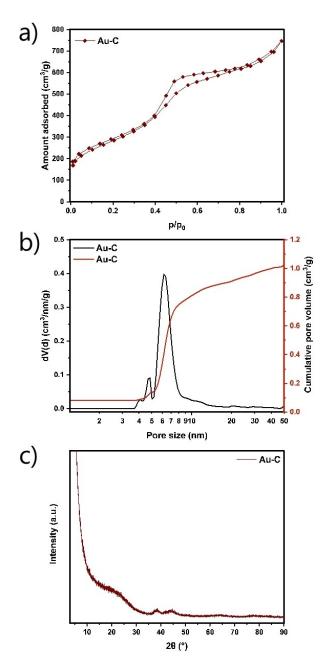rption branch kernel) for N_2 adsorbed on carbon with slit/cylindrical/spherical pore shape (Figure 1b). Au–C has a narrow PSD centered around a diameter of 6 nm, because of its ordered nature originating from synthesis with a hard silica template. Its porous system is dominated by mesopores (mesopore volume $1.00\ cm^3\,g^{-1}$), with a low micropore volume of $0.08\ cm^3\,g^{-1}$. The catalyst exhibits a high (multi-point) Brunauer-Emmett-Teller specific surface area (SSA_{BET}) of $1016.8\ m^2\,g^{-1}$.

X-ray powder diffraction (XRD) measurements of the catalyst reveal typical amorphous carbon patterns, with four broad peaks corresponding to Bragg reflections of the (111), (200), (220), and (311) planes of the face-centered cubic lattice of gold (Figure 1c). The peaks originating from gold appear rather broad, indicating that the active species of the catalyst was deposited on the carbon support in the form of nanoparticles. Transmission electron microscopy (TEM) images of the Au–C show the ordered nanorods of carbon with AuNPs dispersed on the external surface of the support (Figure 2a). Particle size distribution is rather narrow, with the AuNP sizes in the range from 1–7.5 nm, and an average particle size of 3.0 nm (Figure 2b).

To explore the feasibility of using oxygen-loaded PFC microcontainers for increasing the O_2 delivery to the active phase of the catalyst and thus improving the rate of $_D$-glucose conversion, small volumes of PFCs (1–10 vol.% dispersed phase) were emulsified inside aqueous dispersions of the Au–C catalyst (concentration of dispersion was $0.2\ mg\,mL^{-1}$). We opted for the perfluorohexane oil FC-72 as the dispersed phase and observed that the particles acted as potent Pickering emulsifiers preferentially residing at the oil/water interface (Figure 2c). This particular PFC is chosen for its outstanding oxygen-dissolving capability even amongst other perfluorinated compounds.[22] The particles uniformly cover the entire surface of the emulsion droplets, and once formed, no coalescence of droplets was observed over a month. A series of particle-stabilized PFC emulsions were prepared by vortex mixing of small volumes of PFC in an aqueous dispersion of Au–C. In emulsions formed at high volumes of the dispersed phase, the coverage of the emulsion surface was incomplete and droplet coalescence occurred, thus resulting in large droplets, decreasing the effective surface area. Lowering the injected volume of the dispersed oil phase to an ideal concentration of 2% v/v led to stable emulsion droplets with an average diameter of $244\pm46\ \mu$m. Further decreasing the dispersed phase volume resulted in densely jammed Au–C particle stacks at the droplet interfaces (Figure S2 a–c, Supporting Information). A series of reference emulsions based on bromohexane stabilized by Au–C (Au–C–HC) with lower oxygen solubility but similar structure as compared to the PFCs has been prepared for comparison (Figure S2 d–f, Supporting Information).

Considering that the strength of interaction of Au–C with the hydrophobic phase is comparable in both Au–C–PFC and Au–C–HC systems and given the comparable droplet diameters in both a cases (Figure S3, Supporting Information), it can be expected that the amount of catalyst exposed to the aqueous phase is also comparable for a given volume ratio. Thus, their corresponding catalytic activities will be mainly affected by the gas-dissolving nature of the non-aqueous phase.

Figure 1. a) N_2 physisorption isotherm (at $-196\,°C$) with the corresponding b) differential and cumulative pore size distribution plots calculated with QSDFT (N_2 on carbons with slit/cylindrical/spherical pores at 77 K, adsorption branch kernel), and c) powder XRD pattern of Au–C.

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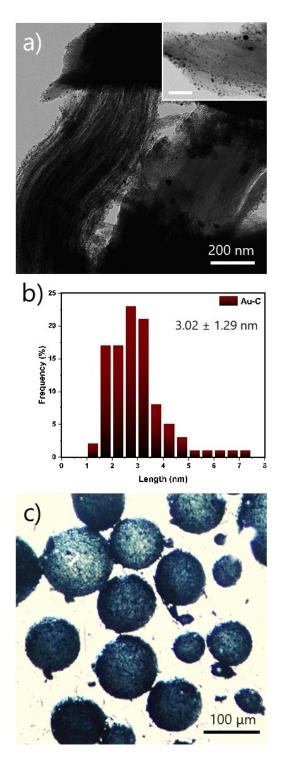European Chemical
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Figure 2. a) TEM images of the Au–C catalyst (length of scale bar in the insert is 50 nm), b) AuNP size distribution with the average NP size in Au–C catalyst, and c) microscopy image of Au–C–PFC Pickering emulsion with 2 vol.% PFC in water.

In order to test the anticipated increased oxygen delivery by provision of PFCs to the aqueous dispersions, we colorimetrically tracked the catalytic activities of the Au–C catalyst with and without PFC emulsions in the liquid phase $_D$-glucose oxiditiaon reaction without additional oxygen supply. The reactions were conducted for three systems, including Au–C catalyst in aqueous solution, Au–C–HC, and Au–C–PFC with different volume fractions of PFC (Figure 3). All systems had a molar ratio of $_D$-glucose to Au of ≈ 20000. The reaction progress was monitored by the universal pH indicator, which was added to the $_D$-glucose solution before the reaction. The starting pH value was adjusted to 9, catalysts were added, and the vials were closed. After 4 h, the pH values lowered only in systems with PFC, whereas Au–C and Au–C–HC showed no significant change in pH. In the series from 2.5 to 10 vol.% PFC, an increasing amount of PFC led to a more notable decrease in pH, thus more gluconic acid was formed when a higher fraction of PFC was present in the system. The experiments reported here prove that with the addition of PFC and the Au–C catalyst to the solution of $_D$-glucose, it is possible to obtain the oxidation product even without the additional supply of oxidant. Such an emulsion is stable for several weeks (Figure S4, Supporting Information)

Catalytic activities of the reported emulsion systems were further investigated in the oxidation of $_D$-glucose with the addition of molecular oxygen. The reactions were operated in aqueous solution at pH = 9 and 30 °C, with the same molar ratio of $_D$-glucose to Au as in the previous experiments. The basic conditions were maintained by titration with NaOH, and the volume of the added base can be directly correlated with the conversion of $_D$-glucose to gluconic acid (Figures S5 and S6, Supporting Information). The Au–C catalyst dispersed in the aqueous solution of $_D$-glucose achieves a $_D$-glucose conversion of 6.8%, while the same amount of catalyst in the Au–C–HC system has no detectable catalytic activity (Figure 4a). On the other hand, Au–C–PFC shows distinctly higher catalytic activity than the Au–C catalyst alone, with a conversion of 9.8%. This can be ascribed to the ability of PFCs to dissolve gases exceptionally well, behaving like nearly ideal gas-like fluids. In the Au–C–PFC system, the described property of PFCs leads to an increase in the local concentration of oxygen in the proximity of the catalyst. In this way, the oxidation of $_D$-glucose on the surface of AuNPs is promoted by increasing the concentration of the oxidant. However, this effect is competing with the opposite influence that the creation of a Pickering emulsion has on the activity of Au–C. A volcano-like dependence of $_D$-glucose conversion after 60 minutes on the volume fraction of PFC in the Au–C–PFC system can be seen (Figure 4b). It can be observed that the highest conversion is obtained with 2 vol.% of PFC, whereas both less and more PFC lead to a decrease in the activity of the catalytic system. In that sense, the opposite effect that the creation of an emulsion has is blocking one part of the catalyst, leaving a lower amount of catalytically active material in contact with reactants. When the PFC content is lower than the optimal volume, part of the Au–C is trapped in the bulk PFC, and such a low fraction of PFC has less capability to deliver oxygen. On the other hand, when the PFC content is too high, the Pickering emulsion becomes unstable, which negatively influences the catalytic activity. Notably, under the conditions applied, the overall conversion after 170 minutes of $_D$-glucose oxidation is lower than typically

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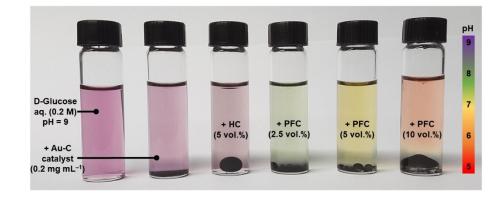Chemistry
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Figure 3. Progress of D-glucose oxidation after 4 h without additional oxygen supply, comparing Au–C catalyst in water, as well as Au–C–PFC and Au–C–HC systems by using universal indicator.

reported for this reaction. For example, in our recent work the fastest full conversion of D-glucose was accomplished after 53 minutes, with the oxygen flow of ≈ 250 mL min^{-1}, at pH = 9 and 45 °C, and a D-glucose to Au ration of 2000. The major reasons for that are the lower temperature and the higher molar ratio between D-glucose and gold applied in the present work. Besides, the possibility of lower availability of D-glucose, which will remain dissolved in the aqueous phase has to be considered as well but is still not the limiting factor under the conditions applied as the yield in the Au–C–PFC system is higher than in the purely aqueous solution.

Conclusion

A Pickering emulsion of perfluorocarbon in the aqueous phase, stabilized by a porous carbon material with 1 wt% of gold nanoparticles was prepared. The remarkable capability of perfluorocarbon to dissolve gases was employed to enhance the catalytic oxidation of D-glucose oxidation with molecular oxygen. It was shown that it is indeed possible to increase the local concentration of the oxidant in the surroundings of the gold nanoparticles and thus to improve the rate-limiting step of the reaction. Consequently, the catalytic activity of a system with the optimal volume fraction of fluorocarbon rises, in comparison to the system without fluorocarbon. The effect of enhanced oxygen delivery was observed even without additional oxygen supply during the reaction. Moreover, a control system with hydrocarbon Pickering emulsion has shown a complete absence of catalytic activity. The present work is a case example of how catalytic activity can be optimized by increasing the local concentration of reactants around the active phase, and that the unique nature of fluorocarbons can be utilized for this purpose. This strategy offers a possibility to overcome the limited solubility of gases in aqueous reaction media which is often the rate-limiting step. While the present work has to be seen as a proof-of-concept study, there is still room for improvement by optimizing the emulsion composition and the reaction conditions. One other promising way to further improve the catalytic properties of such a system would be the application of smaller and more defined solid catalyst particles.
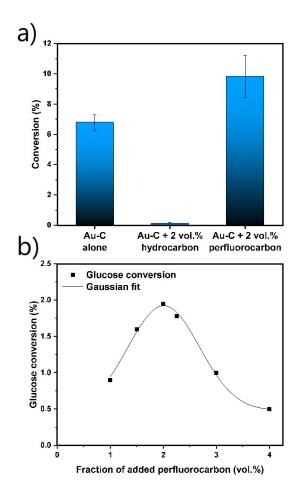

Figure 4. a) Comparison of the conversions of three catalytic systems after 170 minutes: Au–C catalyst alone, with 2 vol.% added hydrocarbon, and with 2 vol.% added perfluorocarbon. b) Dependence of D-glucose conversion after 60 minutes on the volume fraction of added perfluorocarbon.

Experimental Section

The details of experimental procedures are available in the electronic supporting information.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

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