



A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions[☆]

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Abstract

This review considers cases in which a discrete transition-metal complex is used as a precatalyst for reductive catalysis; it focuses on the problem of determining if the true catalyst is a metal-complex homogeneous catalyst or if it is a soluble or other metal-particle heterogeneous catalyst. The various experiments that have been used to distinguish homogeneous and heterogeneous catalysis are outlined and critiqued. A more general method for making this distinction is then discussed. Next, the circumstances that make heterogeneous catalysis probable, and the telltale signs that a heterogeneous catalyst has formed, are outlined. Finally, catalytic systems requiring further study to determine if they are homogeneous or heterogeneous are listed. The major findings of this review are: (i) the in situ reduction of transition-metal complexes to form soluble-metal-particle heterogeneous catalysts is common; (ii) the formation of such a catalyst is easy to miss because colloidal solutions often appear homogeneous to the naked eye; (iii) a variety of experiments have been used to distinguish homogeneous catalysis from heterogeneous catalysis, but there is no single definitive experiment for making this distinction; (iv) experiments that provide kinetic information are key to the correct identification of the true catalyst; and (v) a more general approach for distinguishing homogeneous catalysis from heterogeneous catalysis has been developed. Additionally, (vi) the conditions under which a heterogeneous catalyst is likely to form include: (a) when easily reduced transition-metal complexes are used as precatalysts; (b) when forcing reaction conditions are employed; (c) when nanocluster stabilizers are present; and (d) when monocyclic arene hydrogenation is observed. Finally, (vii) the telltale signs of heterogeneous catalysis include the formation of dark reaction solutions, metallic precipitates, and the observation of induction periods and sigmoidal kinetics.

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1. Introduction

The use of transition-metal complexes for reductive catalysis is widespread. In general, the transition-metal complex added to the reaction is not the true catalyst. Rather, the added complex is a precursor, or precatalyst, from which the true catalyst forms in situ [1]. The true catalyst *can be colloidal metal that forms from*

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the precatalyst under reducing conditions, as well as bulk metal in the form of a film or powder. In fact, the literature indicates that in situ formation of such metal-particle heterogeneous catalysts is much more prevalent than currently appreciated. This fact is the primary motivation for writing this review.

It is important to be able to distinguish true homogeneous catalysis from soluble (i.e., dispersible) or other metal-particle catalysis because every important catalytic property is influenced differently for these two classes of catalysts: the catalyst's activity, selectivity, stability, lifetime, and recovery. In contrast to true homogeneous catalysts, which typically have a single type of active site, metal particles typically have multiple types of active sites on their metallic surface. Additionally, the types and abundance of active sites present on metal-particle catalysts may change with particle size, synthetic procedures and catalytic conditions. Hence, the *selectivity* of soluble-metal-particle catalysts is expected to be different (and typically worse unless ligand-modified) than that of true homogeneous catalysts. In order for a soluble-metal-particle catalyst to have a long *catalytic lifetime* it must be carefully stabilized against agglomeration, a factor that does not need to be considered for a metal-complex catalyst. Metal-particle catalysts also have an exaggerated sensitivity to poisons because only a fraction of the metal atoms are expected to be on the surface of the particle and active. Similarly, the *activity* of soluble or other metal-particle catalysts is influenced differently than for true homogeneous catalysts. For example, the activity of soluble-metal-particle catalysts depends not only on the relative abundance of different types of active sites, but also on the concentration and type of stabilizers present. In addition, practical considerations, such as catalyst solubility, depend on which class of catalyst is present. In short, if one is to rationally study or optimize a soluble catalyst, one must know if it is a true homogeneous catalyst or if it is, for example, a soluble-metal-particle catalyst.

Distinguishing metal-complex homogeneous catalysis from metal-particle heterogeneous catalysis is not trivial [1]; it is a task which has caused considerable consternation in the literature. This problem is most difficult when a soluble colloidal/nanocluster catalyst is involved, partly because colloidal solutions often appear homogeneous to the eye. Additionally, nanoclusters/colloids can be as small as ~ 1 nm in diam-

eter, which makes them difficult to detect by some methods (vide infra). The literature in this area dates back to about 1980 and includes contributions from Hamlin et al. [2], Whitesides et al. [3], Crabtree and co-workers [4–6], Collman et al. [1,7], Lewis and Lewis [8], Lewis [9] and our own group [10,11].

Although clear and useful distinctions between “colloids” and “nanoclusters” have been made [12], for the purposes of this review it will suffice to use both words synonymously herein to refer to soluble metal particles [13–19]. Conventionally, the criterion of solubility was used to categorize “homogeneous” and “heterogeneous” catalysts; however, we will follow Schwartz's modern definitions for homogeneous and heterogeneous catalysis [20]. Specifically, heterogeneous catalysts have multiple types of active sites and homogeneous catalysts have a single type of active site. Therefore, soluble (i.e., dispersible) nanoclusters will be referred to as “soluble heterogeneous catalysts”.

This review considers cases in which a transition-metal complex is added as a precatalyst for reductive catalysis (primarily hydrogenation catalysis); it focuses on the problem of determining if the true catalyst is a metal-complex homogeneous catalyst or if it is a soluble-metal-particle heterogeneous catalyst. First, the various experiments that have been used to distinguish homogeneous and heterogeneous catalysis will be outlined and critiqued. Then, a more general method for making this distinction will be discussed. Next, we discuss the circumstances that make heterogeneous catalysis probable, as well as the telltale signs that a heterogeneous catalyst has formed. Finally, we list literature catalyst systems that require further study to determine if their true catalysts are homogeneous or heterogeneous (see [Appendix A](#)).

2. Description of the various experiments used to distinguish true homogeneous catalysis from soluble-metal-particle catalysis

A variety of experiments have been used to distinguish homogeneous catalysis from heterogeneous catalysis. However, it must be emphasized that *there is no single definitive experiment for making this distinction*. The most convincing studies [4,8,10,21–24] use a combination of experiments before arriving at

a compelling conclusion. Additionally, some experiments cannot be used with certain catalyst systems; therefore, it is important to be aware of the experimental “toolkit” available and to know the strengths and weaknesses of each experimental “tool”. A perusal of these experiments illustrates a few important points: first, experiments that provide information about kinetics are crucial for determining the identity of the true catalyst;¹ second, control experiments using authentic heterogeneous catalysts (e.g., nanoclusters) or authentic homogeneous catalysts are quite important where possible [10]; and third, the detection of small, soluble, nanocluster catalysts by some of the experimental techniques below is problematic.

2.1. Reaction kinetics

Because catalysis is a wholly kinetic phenomenon [25,26], the most compelling evidence for the identity of the true catalyst will always be kinetic in nature.¹ Three observables related to reaction kinetics will be discussed in terms of how they help distinguish homogeneous from heterogeneous catalysis: (i) kinetic reproducibility; (ii) the observation of sigmoidal kinetics for the catalytic reaction; and (iii) comparison of the kinetics of the catalytic reaction with the kinetics of precatalyst decomposition.

It has been suggested that one can distinguish homogeneous from heterogeneous catalysis by whether or not the kinetics are reproducible—that is, homogeneous catalysis exhibits reproducible kinetics and heterogeneous catalysis exhibits irreproducible kinetics [27,28].² However, the recent discovery of highly

reproducible catalytic systems involving nanocluster catalysts shows that such a distinction is not absolute [10,29]. In short, the observation of irreproducible kinetics is consistent with the in situ formation of a heterogeneous catalyst, but reproducible kinetics cannot be used to rule out a heterogeneous catalyst since soluble heterogeneous catalysts with $\pm 15\%$ kinetic reproducibility are now known [10].

The observation of a sigmoidal kinetic curve³ for the hydrogenation of substrate is powerful *prima facie* evidence for the in situ formation of a heterogeneous catalyst [10,21,24,30–35], assuming that the reaction products—the first step of reliable mechanistic studies—have already been established to be nanoclusters (e.g., by TEM)⁴ or a bulk-metal precipitate (e.g., by visual observation). Sigmoidal kinetics results from an apparently general⁵ mechanism for the formation of either soluble or insoluble [24] metal particles from transition-metal salts under H₂ [30,31]. This mechanism involves a pseudo-elementary [30,31,36–38] nanocluster nucleation step ($A \rightarrow B$, rate constant k_1) followed by a pseudo-elementary autocatalytic surface-growth step ($A + B \rightarrow 2B$, rate constant k_2). (A pseudo-elementary step is just the sum of multiple elementary steps which, however, can be treated kinetically as an elementary step [30,31]. Pseudo-elementary steps are, therefore, exceedingly powerful for treating the kinetics of more

¹ Transmission electron microscopy (TEM) is an illustrative example. TEM does not provide any kinetic information and, therefore, cannot identify the nature of the true catalyst in any compelling way. In contrast, some of the other experiments described in this section, notably catalyst formation kinetic studies and the quantitative catalyst poisoning experiment with CS₂ (or other ligands), do provide kinetic information and, hence, do provide compelling evidence for the nature of the true catalyst.

² For example, consider the quote provided elsewhere [27]: “note also that a true homogeneous catalyst usually demonstrates a notably better reproducibility in the values of reaction rate than a catalyst whose activity arises from its decomposition into a colloidal metal. This difference in reproducibility can also be used to distinguish between the two types of catalysis”. As noted in the text, this statement is not true, having been disproved in 1994 [10].

³ Sigmoidal kinetic curves are of course known for other processes, for example, simple acid-catalyzed ester hydrolysis, $\text{RCO}_2\text{R}' + 2\text{H}_2\text{O} + \text{H}_3\text{O}^+ \rightarrow \text{RCO}_2^- + \text{R}'\text{OH} + 2\text{H}_3\text{O}^+$ (see the references summarized elsewhere [30]). Hence, both sigmoidal kinetics and the TEM or visual observation of metal nanoparticles or bulk metal, respectively, are needed to have *prima facie* evidence for the formation of a heterogeneous catalyst from a homogeneous precatalyst.

⁴ The high energy and unknown temperature of the electron beam of TEM is well known to cause crystallizations of metal particles and sometimes more drastic changes, especially for the lighter metals [14]. Hence, control experiments for changes due to the TEM beam, such as those performed elsewhere [10,32], are recommended.

⁵ This mechanism for transition-metal nanocluster formation under H₂ has been observed for at least nine different nanocluster systems and three different transition metals (Ir [10,30–32,34,35], Rh [21,33] and Ru [24,31]). This mechanism has also been shown to hold under conditions where heterogeneous nucleation and direct deposit of a metal film are occurring [24]. In addition, autocatalytic kinetics are common in growth processes (see the references cited elsewhere [30]).

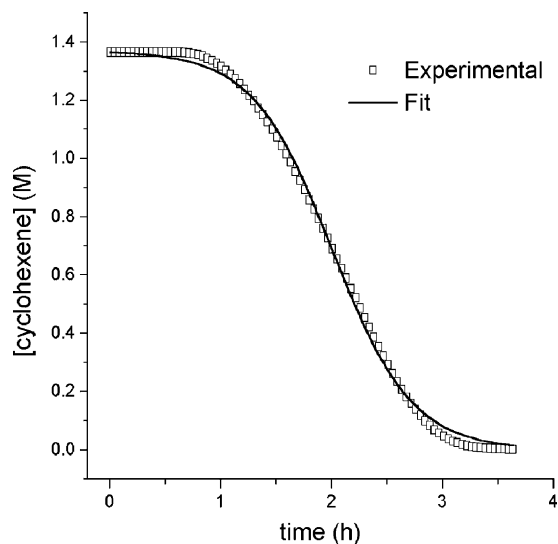


Fig. 1. Typical cyclohexene concentration vs. time curve for a cyclohexene hydrogenation reaction starting with the precatalyst $[\text{Bu}_4\text{N}]_5\text{Na}_3[(1,5\text{-COD})\text{Ir}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$. Note the distinctive, sigmoidal, “autocatalytic” shape of the curve. The true catalyst in this system is a distribution of soluble $\text{Ir}(0)_{\sim 300}$ nanoclusters that forms in situ from the reduction of the $\text{Ir}(\text{I})$ precatalyst by H_2 . The $\text{Ir}(0)_{\sim 300}$ nanoclusters form via a nucleation pseudo-elementary [30,31] step ($\text{A} \rightarrow \text{B}$, rate constant k_1) followed by an autocatalytic surface-growth pseudo-elementary step ($\text{A} + \text{B} \rightarrow 2\text{B}$, rate constant k_2). The kinetics of nanocluster formation is responsible for the observed sigmoidal kinetics of the cyclohexene hydrogenation reaction. In general, the observation of sigmoidal kinetics, at least for a catalytic hydrogenation reaction starting with a monometallic precatalyst, is excellent evidence for the in situ formation of a metal-particle catalyst.

complicated reactions such as those in catalysis or materials chemistry.) Such a kinetic scheme results in a characteristic sigmoidal curve for the nanocluster formation reaction. Fig. 1 shows an example of these kinetics for an $\text{Ir}(0)_{\sim 300}$ nanocluster that forms in situ from an $\text{Ir}(\text{I})$ precatalyst [10,30–32] while concomitant cyclohexene hydrogenation is employed as the monitoring reaction. The experimental data in Fig. 1 are closely fit by the kinetic scheme $\text{A} \rightarrow \text{B}$ (rate constant k_1) and $\text{A} + \text{B} \rightarrow 2\text{B}$ (rate constant k_2) [30,31]. Given the prior literature [10,21,24,30–35] and if the metal product has been shown to be a nanocluster [10,30–32] or bulk metal precipitate or film [24], such a kinetic curve and curve-fit are as compelling a single piece of evidence as exists for the formation of a heterogeneous catalyst, at least for hydrogenation

catalysis. Note, however, that the absence of sigmoidal reaction kinetics does not rule out heterogeneous catalysis: in order for the sigmoidal kinetics to be obvious, k_1 must be relatively small and k_2 must be relatively large; this results in a long induction period followed by a rapid increase in catalytic activity, that is, a sigmoidal curve. Sigmoidal kinetics are not expected if formation of the heterogeneous catalyst is complete before a significant amount of the substrate has been hydrogenated (i.e., if catalyst formation is fast relative to catalysis, or if the precatalyst is pretreated with reductant in the absence of substrate). No induction period is observed in such a case. A second scenario obscuring sigmoidal kinetics is if the heterogeneous catalyst deactivates to a significant extent in comparison to its in situ rate of formation during the catalytic hydrogenation reaction. In this case, an induction period is still observed, but the reaction does not “turn on” in such a dramatic fashion due to the continual loss of activity. The important case of the addition, to the $\text{A} \rightarrow \text{B}$, $\text{A} + \text{B} \rightarrow 2\text{B}$ mechanism, of an nanocluster agglomeration step, $\text{B} + \text{B} \rightarrow \text{C}$ (agglomerated, deactivated catalyst; rate constant k_3), has recently been reported [39].

If one can show that the precatalyst is decomposing to form metal particles, then it is very useful to follow the kinetics of precatalyst decomposition [30,31,33,40–42]. If precatalyst decomposition and catalytic hydrogenation both occur with sigmoidal kinetics and identical induction periods to a product established to be a nanocluster or bulk-metal precipitate, then this is typically compelling evidence for a heterogeneous catalyst. In such a case, it is also useful to measure the catalytic activity after the precatalyst has been completely reduced to $\text{metal}(0)_n$ since the activity should be near its maximum at this point, if agglomeration or other catalyst deactivation processes are minimal.

Despite the central importance of reaction kinetics in determining the true nature of the catalyst (and for catalysis in general), the literature shows that it is quite common to ignore kinetics in catalytic studies. A common scenario involves introducing the precatalyst and substrate into a reactor, waiting for a given length of time, stopping the reaction, and analyzing the final reaction products. Clearly, the observation of an induction period or of sigmoidal kinetics is impossible in such an experiment.

Furthermore, in cases where the catalytic reactions go to completion before any analysis, it is impossible to judge the kinetic reproducibility. Hence, it is crucial to follow the reaction progress versus time whenever possible.

2.2. Transmission electron microscopy (TEM)

Transmission electron microscopy is a sensitive technique for detecting the presence of nanoclusters deposited from reaction solutions [8,10]. A back-of-the-envelope calculation shows that TEM can detect nanoclusters in solutions where the concentration of colloidal metal is $\geq 10^{-12}$ M.⁶ However, such sensitivity is potentially deceiving since TEM does not provide evidence for the kinetic competence of the nanoclusters as catalysts. Put another way, TEM can show the presence of very low levels of nanocluster formation, but cannot show if the nanoclusters are responsible for the observed catalysis. Another problem with TEM is that small (<1 nm) nanoclusters and nanoclusters of lighter, first-row transition metals are difficult to image by TEM due to the inherently lower contrast of such species. Also, because of the nature of negative results, TEM cannot rule out the presence of a nanocluster catalyst—if nanoclusters are not seen by TEM, one cannot safely conclude that the catalyst is truly homogeneous. The problems of routine TEM nearly always missing Au nanoclusters under 1 nm is a case in point [43,44]. These limitations require that TEM be used in combination with other techniques in order to convincingly determine the nature of the true catalyst. However, if one understands its limitations, TEM is an excellent, if not first-choice, technique for scouting cases where a nanocluster catalyst is suspected. Up-front use of TEM is emphasized in a more general approach to distin-

⁶ TEM samples are commonly prepared by simply depositing a drop of the reaction solution onto a carbon-coated TEM grid; the solvent evaporates, leaving the nanoclusters (and any other non-volatile material) on the support film of the TEM grid. Let us assume that the drop size is 10 μ l (which is reasonable, given the size of normal TEM grids), that the drop contains 10,000 nanoclusters (which should be sufficient for finding and imaging the nanoclusters on the grid), and that the average nanocluster has 1000 metal atoms (which corresponds to a nanocluster with a diameter of a few nanometers). The concentration of colloidal metal in such a solution is 1.7×10^{-12} M.

guishing homogeneous versus heterogeneous catalysis [10].

2.3. Mercury poisoning

The ability of Hg(0) to poison metal-particle heterogeneous catalysts, by amalgamating the metal or adsorbing on the metal surface, has been known for more than 80 years [3,45] and is a widely used test [3,4,8,10,21,23,24,46–48]. This experiment is performed by adding Hg(0) to the reaction solution.^{7,8} The suppression of catalysis by Hg(0) is evidence for a heterogeneous catalyst; if Hg(0) does not suppress catalysis, that is (negative) evidence for a homogeneous catalyst. The Hg(0)-poisoning experiment is easy to perform, *but is not definitive by itself and is not universally applicable*. Hg(0) can cause complicating side reactions [3] and is known to react with some single-metal complexes [3,23,49,50]. To avoid incomplete poisoning and erroneous conclusions, one must be able to ensure intimate contact of the Hg(0) bead with the entire reactor; hence, using a large excess of Hg(0) in a well stirred solution is key [10,21]. Hg(0) is probably most effective in poisoning metals that form an amalgam, such as Pt, Pd and Ni; metals that do not form amalgams with Hg(0), such as Ir, Rh and Ru are probably more difficult to poison with

⁷ The Hg(0)-poisoning experiment is occasionally performed improperly. In one literature example a solution of *precatalyst* was stirred with Hg(0) for 1 h, the solution was *then filtered*, and a catalytic hydrogenation reaction was then started [47]. The hydrogenation proceeded with the same catalytic activity as an experiment in which Hg(0) was never present; this was then used (erroneously) to rule out the presence of a nanocluster catalyst. The problem with this experiment is perhaps obvious, the Hg(0) was removed *before the catalytic reaction was allowed to start* (i.e., before a heterogeneous catalyst could have formed). As performed, the experiment only shows that the precatalyst does not react with Hg(0), which is not what the authors involved believed they were testing. The Hg(0) should have remained in the reaction solution for the duration of the catalytic reaction or, better, added after the catalytic reaction had already begun (i.e., after the true catalyst was proven to be present), as done elsewhere [10,21,24].

⁸ For a hydrogenation reaction, the following protocol developed elsewhere is recommended [10,21]: allow the catalytic hydrogenation reaction to proceed to $\sim 50\%$ completion, release the H₂ pressure, add the (excess of) Hg(0) to the reaction solution, let the reaction solution stir so that the Hg(0) has a chance to contact any metal particles that may be present, re-pressurize the reactor with H₂, and check for catalytic activity [21].

Hg(0) [3]⁹—although a detailed study of Hg(0) poisoning of well established nanoclusters of different metals as a function of different temperatures and other conditions would be a welcome addition to the literature. Hence, if the addition of Hg(0) to the reaction solution suppresses the catalytic activity, one should perform a control experiment showing that the precatalyst complex does not react with Hg(0); if Hg(0) does react with the precatalyst, then this test becomes ambiguous. Similarly, if the addition of Hg(0) to the reaction solution has no effect on the catalytic activity, it is crucial to perform a control experiment showing that an authentic heterogeneous catalyst of the same metal *is* poisoned under identical conditions. Such a control experiment would have caught the error in the Hg(0) poisoning experiment in a recent report of a claimed Ru homogeneous catalyst [47] that, so far, appears to be a clear case of nanocluster catalysis by our reinvestigation of this catalyst [101].

2.4. Quantitative CS₂ (or other ligand) poisoning

Though underutilized, poisoning experiments using added ligands, such as CS₂, PPh₃, and thiophene can be powerful if performed quantitatively [10,11,23,24,51–53]. These poisons bind strongly to metal centers, thereby blocking access of the substrate to the active site. If a catalyst can be poisoned completely with $\ll 1.0$ eq. of the added ligand (per metal atom), that is highly suggestive (kinetic-based) evidence for a heterogeneous catalyst. The logic here is that in a heterogeneous catalyst only a fraction of the metal atoms are on the surface (e.g., about 50% of the Ir is on the surface of a 2 nm, Ir(0)_{~300} nanocluster [10,30,32]); hence, even if every surface atom is active, $\ll 1.0$ eq. of ligand will be sufficient to poison the catalyst.¹⁰ On the other hand, typically ≥ 1.0 eq. of ligand is required to completely poison

homogeneous, monometallic catalysts.¹¹ See elsewhere [10,11,51] for prototypical examples of this powerful, but underutilized, “fractional poisoning” experiment.

One limitation of this experiment is that it must be performed at approximately $< 50^\circ\text{C}$ because ligands such as CS₂ will begin to dissociate from a heterogeneous catalyst at higher temperatures [24,54–56]. For example, in a cyclohexene hydrogenation experiment 5 mol% CS₂ completely poisons an authentic Rh(0)_n nanocluster at 25 °C; however, simply raising the reaction temperature *of that same, poisoned solution* to 100 °C results in rapid and complete hydrogenation of the substrate [24]. The development of poisons that bind irreversibly at higher temperatures is an important, but presently unfulfilled, goal in this area.

2.5. Crabtree’s test (homogeneous catalyst poisoning)

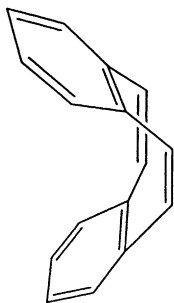
Crabtree and co-workers discovered that dibenzo [*a,e*]cyclooctatetraene (DCT) poisons at least some homogeneous catalysts [4] by binding strongly to them. They found that 1.0 eq. of DCT completely poisons homogeneous catalysts such as RhCl(PPh₃)₃. On the other hand, DCT has little or no effect on at least Rh colloids, Pd colloids and Pd/C heterogeneous catalysts [4]. Poisoning with DCT is in principle a nice complement to the mercury-poisoning experiment described earlier. If 1 eq. of DCT completely inhibits catalysis, but a properly performed Hg(0) experiment has little effect on catalysis, then one has strong evidence for a homogeneous catalyst. Conversely, if DCT has little effect on catalysis, but Hg(0) acts as a poison, that is strong (kinetic-based) evidence for a heterogeneous catalyst. One potential problem with using DCT is that the inhibition of homogeneous catalysis develops slowly in some

⁹ As evidence for this statement, experiments show that a large excess of Hg(0) plus good stirring are necessary to poison completely an authentic Rh(0)_x nanocluster [21]. Hence, an improperly performed poisoning experiment can lead to incorrect conclusions about the nature of the catalyst.

¹⁰ Experimentally, 1–3 mol% CS₂ poisons >90% of the catalytic activity of ~ 4 nm, Rh(0)_{~2400} nanoclusters, which have about 30% of the Rh on the surface [51]. In that study it was also found that 3.5 mol% CS₂ completely poisons a commercial Rh/Al₂O₃ catalyst with an average metal-particle diameter of ~ 3.6 nm [51].

¹¹ This argument assumes a large equilibrium constant for the binding of the poison to the metal. Because of this assumption, we recommend using well-established poisons (such as CS₂) and performing appropriate control experiments with authentic homogeneous and heterogeneous catalysts. One such control experiment is to show that the added ligand is unable to disassemble authentic nanoclusters *of the same metal* into monometallic complexes: $M_n + (x \cdot n)L \rightarrow nML_x$. Metals with weaker M–M bonding (such as first row metals), or other cases for reasons that are less clear (e.g., Pd), appear to be most prone to such a process.

cases, so DCT must be stirred with the active catalyst species for hours [4]. Consequently, the active catalyst must be stable on that longer time scale in order to obtain meaningful results. Another potential limitation is that DCT is unlikely to bind to (and poison) all homogeneous catalysts [4] and, to date, has been tested with only a few complexes of Group VIII metals. A final difficulty is that DCT is not commercially available and its synthesis is unreliable [57]; hence, the development of a better synthesis for DCT or of a generally applicable DCT replacement is needed.



dibenzo[*a,e*]cyclooctatetraene (DCT)

2.6. Maitlis' test (filtration)

The filtration test relies on a comparison of catalytic activity before and after filtering the active catalyst solution [2,4,23,28,58,59]. In one version of this test, a high-surface-area filter aid such as powdered cellulose [2], Celite [4] or powdered graphite [59] is added to the active catalyst solution. The reaction solution is then filtered through a glass frit. The filter aid, along with any adhering metal particles, is washed with solvent and then returned to the (rinsed) reaction vessel. After adding fresh solvent and substrate, the catalytic activity of the filter aid (plus any adhering metal particles) is tested; any observed catalytic activity is attributed to heterogeneous catalysis. Ideally, the filtrate is also tested for catalytic activity, as this allows one to determine the relative amount of homogeneous versus heterogeneous catalysis (it also functions as a control experiment since the total catalytic activity of the filter aid and the filtrate should be approximately the same as the catalytic activity of the original reaction solution). This test is probably most useful for

determining if *bulk metal* is responsible for the catalysis. As pointed out in the original paper [2], it is not clear if this method will be capable of reliably testing for the presence of a nanocluster catalyst. One report in the literature indicates that this filtration method (using Celite) is unsuccessful at detecting a colloidal Rh catalyst [4], but another report (using powdered graphite) apparently detects a colloidal Rh catalyst [59].

A second version of the filtration test involves filtering the active catalyst solution through a small-pore membrane filter [23,28,58]. If filtration does not change the observed catalytic activity, the catalyst is assumed to be homogeneous. Unfortunately, membrane filters with pores small enough to exclude nanoclusters are slow and difficult to use [28], so this version of the filtration test is again best for determining if *bulk metal* is responsible for the catalysis.

Both versions of the filtration test share some drawbacks. In order for either filtration test to be convincing, control experiments with authentic homogeneous catalysts and authentic nanocluster catalysts are needed.¹² Also, the filtration tests do not address the problem of continued generation of heterogeneous species following the filtration [28]. Additionally, the physical manipulations involved in the filtration could lead the decomposition of a truly homogeneous catalyst, thereby leading to the erroneous conclusion that a heterogeneous catalyst is involved, and in the absence of additional, suitable control experiments [28]. Finally, in one well-documented case where *bulk metal* is the true catalyst in a Ru-catalyzed benzene hydrogenation [24], simply showing *quantitatively* that all the catalytic activity resided with the bulk metal, and none with the filtrate, proved to be sufficient (kinetic-based) evidence to provide a compelling case for bulk-metal catalysis (along with the observation of sigmoidal kinetics, Hg(0)-poisoning of the catalyst and TEM evidence showing that nanoclusters were not detected under experimental conditions where nanoclusters were detected previously hundreds of times).

¹² Note how the use of (often-ignored) controls with, for example, authentic nanoclusters is a recurring key to reliably distinguishing homogeneous from heterogeneous catalysts, a point first made elsewhere [10].

2.7. Collman's test (hydrogenation of polymer-bound substrates)

Collman et al. described the use of polymer-bound substrates to distinguish homogeneous catalysts from heterogeneous catalysts that are >8 nm in diameter [1,7]. Homogeneous catalysts are believed to be more active for the hydrogenation of polymer-bound substrates, apparently due to the lack of mobility of the heterogeneous catalysts in the polymer matrix; however, the heterogeneous¹³ Ziegler-type polymer hydrogenation catalyst based on nickel(II)octanoate and triethyl aluminum [53] appears to be a counterexample to the belief that heterogeneous catalysts are relatively inactive for polymer hydrogenation. The difference in activity between homogeneous and heterogeneous catalysts is then used to suggest the nature of the true catalyst. A nice feature of this method is that it is based on the reactivity of the active catalytic species and is not influenced by inactive components in the reaction solution. As pointed out in the original paper [7], though, only large (>8 nm in diameter) metal particles were used to verify this method, so it is not clear if it will work for smaller nanoclusters. It would be instructive to check this method with small, well-characterized, modern nanocluster catalysts as well as with soluble, heterogeneous, Ziegler-type catalysts [53].

2.8. Light scattering

Light scattering has been used to test for the presence of metal particles in catalyst solutions [4,8,22,28,48,60,61]. The detection limits are quite good for this technique, although not as good as TEM; Crabtree found that a solution of iridium colloids with 3×10^{11} particles/cm³ (25 nm average radius) could easily be detected [5]. Light scattering can detect particles >1 nm in diameter [48]. An advantage of light scattering (compared to TEM) is that the analysis is done in solution (i.e., in situ). Like

¹³ The Ziegler-type catalyst based on nickel(II)octanoate and triethyl aluminum is believed to be "a colloidal suspension of small Ni clusters embedded in an amorphous organo-alumina soap" [53]. The evidence for heterogeneity includes complete inhibition of catalysis by $\ll 1$ eq. of sulfur-containing poisons and EXAFS spectra showing intense Ni–Ni signals at distances comparable to bulk Ni [53].

TEM, however, light scattering can detect nanoclusters, but cannot determine their kinetic competence as catalysts; hence, light scattering must be used in combination with other experiments to convincingly determine the nature of the true catalyst. One problem with light scattering is that the presence of dust or particles from abrasion of the reactor can lead to "false positives" [28]; another problem is that larger particles scatter light more effectively than do smaller particles. Again, suitable control experiments are imperative. Note the distinction here between light scattering and light *absorption* (Mie theory calculated, UV-visible "plasmon resonance" absorption spectra for 10 nm colloids of 52 different metals can be found in a seminal paper by Creighton and Eadon [62]).

2.9. Centrifugation

The centrifugation of nanoclusters has been known for many years [63–67], but is rarely used to test for nanocluster catalysts [68–70]. Metal particles have a high molecular weight and are relatively dense, so they are relatively easy to sediment from solution by centrifugation (i.e., compared to common transition-metal complexes). In principle, this powerful, non-invasive, solution technique allows the separation of soluble nanoclusters from lighter, soluble, transition-metal complexes.¹⁴ To test for a soluble nanocluster catalyst, one would first spin a solution containing the active catalyst. Then, if sediment forms, it is separated from the supernatant and both are tested for catalytic activity. Catalytically active sediment and catalytically inactive supernatant are consistent with a nanocluster catalyst. One problem with this experiment is that it is very difficult to achieve a quantitative separation of the sediment and the supernatant without using specialized, viscous gels; therefore, both will probably have some residual catalytic activity. Another problem is that this experiment will not work if the reaction is catalyzed by a low concentration of highly active nanoclusters since no visible sediment

¹⁴ See elsewhere for an example of this type of experiment [10]. In that study, Ir(0)_{~300} nanoclusters were separated from P₂W₁₅Nb₃O₆₂⁹⁻ by spinning at 20,000 rpm for less than 10 min. Under these conditions, the Ir(0)_{~300} nanoclusters form a dark brown precipitate while (most of) the polyoxoanion remains in the colorless supernatant.

will form. Given these problems, centrifugation alone cannot be used to rule out a nanocluster catalyst. A final difficulty with this experiment is that small nanoclusters and nanoclusters of lighter elements are more difficult to sediment from solution, which leaves some question about the appropriate conditions for the experiment. In addition, control experiments with authentic samples of the nanoclusters, the homogeneous precatalyst, and the nanoclusters plus homogeneous precatalyst should be done when using this technique. The experimental problem here, of course and as the topmost part of Fig. 5 elsewhere emphasizes [10], is that authentic samples of each type of potential catalyst for the metal, ligands and other experimental conditions under consideration simply do not exist—a “chicken versus egg” problem of sorts.

2.10. Reactivity patterns

The ability of a catalyst to promote certain reactions is occasionally used as an indication of the catalyst's identity. The idea is to choose a reaction that a heterogeneous catalyst will catalyze, but that a homogeneous catalyst will not (or vice versa). The problem with using reactivity patterns is that it is difficult to find a reaction that only works with heterogeneous catalysts (or only homogeneous catalysts). In practice, only two reactions have been widely used, hydrogenation of monocyclic arenes [7,21] and hydrogenation of aromatic nitro groups [4,22,23,48]. The lore of catalysis once held the belief that benzene hydrogenation could be used as a test for heterogeneous catalysis because only heterogeneous catalysts were capable of promoting the reaction [21]. This test is close to being the truth, but is not definitive since there are now a few well-established examples of monometallic catalysts capable of benzene hydrogenation [71,72].^{15,16}

¹⁵ There are actually many claims of homogeneous arene hydrogenation catalysis in the literature [1,71,72]. However, few of these claims are based on solid evidence, and there is now compelling evidence that several of these systems are actually heterogeneous [72]. This is certainly an area of catalysis that would benefit from further efforts to distinguish homogeneous from heterogeneous catalysis. So far, true homogeneous catalysts for monocyclic arene hydrogenation are rare (see footnote 16).

¹⁶ The Nb^V and Ta^V hydrido aryloxy complexes, such as [Ta{OC₆H₃(C₆H₁₁)_{2-2,6}}₂(H)₃(PMe₂Ph)₂], developed by Rothwell are premier examples of monometallic catalysts capable of

monocyclic arene hydrogenation based on the following evidence [71]: (i) the reduction of Nb^V or Ta^V to Nb(0) or Ta(0) metal particles by hydrogen is thermodynamically significantly uphill under the reaction conditions; and (ii) the observed selectivity of the catalyst for the intramolecular hydrogenation of the aryloxy ligands is consistent with a homogeneous mononuclear catalyst, but difficult to explain if the true catalyst is heterogeneous (*ortho*-phenyl substituents on the aryloxy ligand are hydrogenated, while hydrogenation of phenyl rings *meta* or *para* to the aryloxy oxygen is not observed nor is hydrogenation of the phenoxide nucleus itself ever observed).

3. A more general approach to distinguishing homogeneous catalysis from heterogeneous catalysis

As mentioned earlier (and also emphasized elsewhere [4,10]), no single experiment is capable of answering the “homogeneous or heterogeneous” question for all systems. It should be clear from the discussion above that it is desirable to perform a series of experiments if one wants to convincingly determine the nature of the catalyst. Along these lines, a more general approach has been developed for distinguishing homogeneous and heterogeneous catalysts [10]. This approach, which has been used successfully on several catalytic systems [10,21,24], is diagrammed in Fig. 2. This more general approach emphasizes: (1) catalyst isolation and characterization, especially by initial TEM studies; (2) kinetic studies; (3) quantitative catalyst poisoning experiments; and (4) the perhaps obvious, but still important, concept that the identity of the true catalyst must be consistent with *all* the data.

3.1. Catalyst isolation and at least initial characterization

The first step in the general method for answering the “homogeneous or heterogeneous” question

monocyclic arene hydrogenation based on the following evidence [71]: (i) the reduction of Nb^V or Ta^V to Nb(0) or Ta(0) metal particles by hydrogen is thermodynamically significantly uphill under the reaction conditions; and (ii) the observed selectivity of the catalyst for the intramolecular hydrogenation of the aryloxy ligands is consistent with a homogeneous mononuclear catalyst, but difficult to explain if the true catalyst is heterogeneous (*ortho*-phenyl substituents on the aryloxy ligand are hydrogenated, while hydrogenation of phenyl rings *meta* or *para* to the aryloxy oxygen is not observed nor is hydrogenation of the phenoxide nucleus itself ever observed).

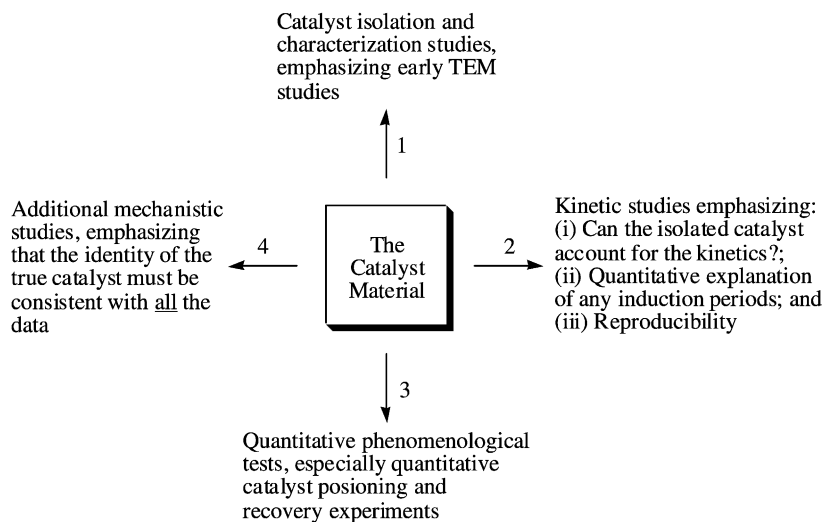


Fig. 2. A more general approach to distinguishing between a metal-particle “heterogeneous” catalyst and a metal-complex “homogeneous” catalyst [10]. See Fig. 5 elsewhere [10] for the expanded version of this figure.

involves attempted isolation and characterization of the catalyst material. These experiments are not intended to unequivocally identify the true catalyst; rather, they are intended as scouting experiments to give one a better idea what the possibilities are. Ideally, the first thing one would like to know is if metal particles form under catalytic conditions. The in situ formation of bulk metal is typically evidenced by the visible formation of a dark powder or metallic mirror; verification that such a precipitate is indeed bulk metal can be readily accomplished using XPS or XRD [24,40]. The formation of soluble nanoclusters is easier to miss because nanocluster solutions may appear homogeneous to the naked eye. Indeed, highly catalytic solutions of well-stabilized nanoclusters will remain completely soluble and apparently “homogeneous” [10,32,33,73]. For this reason, the use of TEM is suggested as the single most powerful and broadly applicable method for the detection of nanoclusters. Other techniques, such as light scattering and centrifugation, can also be used to detect soluble nanoclusters. If bulk metal or metal nanoclusters are detected in the isolated catalyst material, then one needs to turn to kinetic methods to determine if they are the true catalyst.

Two points of note here: first, the ability to isolate a large percentage of the precatalyst complex (or some other soluble metal complex) following cataly-

sis has been used as evidence of homogeneous catalysis [47,74–77]. *This is incorrect!* Such a result does not rule out the possibility that a small percentage of highly active colloids or bulk metal is responsible for the observed catalysis. See elsewhere for further discussion of this point [2,10]. Second, the possibility that what one identifies as the bulk of the material is *not* the catalyst is of course a common problem in catalysis. Hence, kinetic studies are of central importance as discussed next.

3.2. Kinetic studies

The second step in the general method for answering the “homogeneous or heterogeneous” question involves kinetic studies. If an induction period is observed then the “catalyst” added to the reaction must actually be a *precatalyst*, which has to convert into the true catalyst before any catalysis occurs. Any time an induction period is observed in reductive catalysis, one should suspect the in situ formation of a heterogeneous catalyst. If the overall kinetics of a hydrogenation reaction making nanoclusters or bulk metal is sigmoidal, that is by itself excellent and typically compelling evidence—*indeed, the to-date kinetic signature* [10,21,24,30–35]—for the in situ formation of a heterogeneous catalyst (*vide supra*). Of course, pre-treatment of the “catalyst” with reductant may

eliminate the induction period by allowing the true catalyst to form in the absence of substrate. If one is able to isolate the putative catalyst from a reaction solution, then one should check to see if the isolated material can account for the observed kinetics. Basically, one must show that the isolated catalyst, after adding fresh solvent and substrate, can catalyze the reaction at a kinetically competent rate without an induction period.

3.3. Catalyst poisoning experiments

The third step in the general method for answering the “homogeneous or heterogeneous” question emphasizes quantitative poisoning studies. Of the three poisoning methods discussed above (mercury, CS₂ and DCT), mercury poisoning is by far the most commonly used method, one that is, however, less than perfect since an excess of mercury must be used, thereby ruling out the possibility of obtaining quantitative results (*vide supra*). On the other hand, quantitative experiments are possible with CS₂ and other ligand-based poisons. As mentioned earlier, if one can show that $\ll 1$ eq. of CS₂ completely poisons catalysis, that is compelling evidence for a heterogeneous catalyst because such a result is consistent with the geometric features of metal-particle catalysis,¹⁰ but difficult to explain for homogeneous catalysis. It is advisable to try more than one type of poisoning experiment on each catalyst system. For example, the Hg(0)- and CS₂-poisoning experiments form a nice complement.

3.4. The identity of the true catalyst will be consistent with all the data

The fourth step in the general method for answering the “homogeneous or heterogeneous” question emphasizes the important concept that the identity of the true catalyst must be consistent with *all* the data—a well known principle of mechanistic chemistry and careful science in general. After performing multiple experiments a consistent picture should emerge regarding the true nature of the catalyst. However, a situation may arise in which some experimental results indicate a heterogeneous catalyst and others indicate a homogeneous catalyst. In such a circumstance, one should first make sure that the reaction conditions have not

changed significantly from one experiment to the next since this can cause the nature of the catalyst to change [7,23,48]. Also, one should consider performing additional control experiments with authentic nanoclusters and other relevant catalysts of that same metal to ensure that the experiments are functioning as expected and that the interpretation of the data is not complicated in some unseen way.

4. An overview of when to suspect soluble-metal-particle heterogeneous catalysis

The formation of a soluble-metal-particle heterogeneous catalyst from a monometallic precatalyst is more likely under certain circumstances. It is important to be familiar with those circumstances so that one can be on the lookout for the telltale signs of heterogeneous catalysis. Conditions under which a heterogeneous catalyst is likely to form include: (i) when easily reduced transition-metal complexes are used as precatalysts; (ii) when forcing reaction conditions are employed; (iii) when nanocluster stabilizers are present (anions such as halides or carboxylates, polar solvents, R₄N⁺ counterions, etc. [34]); and (iv) when monocyclic arene hydrogenation is observed. The telltale signs of heterogeneous catalysis include (v) the formation of dark reaction solutions and metallic precipitates; and (vi) the observation of induction periods and sigmoidal kinetics. A key point regarding the observation of a metallic precipitate when starting with a single-metal precatalyst: this demands that either nanoclusters were formed en route to the metallic precipitate or that heterogeneous nucleation to directly form the bulk metal film or particles [24] has occurred (*i.e.*, there are no other known ways to go from monometallic species to bulk metal [10,24]). Hence, in such cases nanoclusters as the true catalyst must be considered and supported or ruled out.

4.1. The use of easily reduced transition-metal complexes

The reduction of many late-transition-metal salts with H₂ is thermodynamically favorable under routine reaction conditions. Hence, whether or not metal particles form in such systems is simply a question of kinetics. To complicate matters, such metal

particles are good catalysts for a variety of reactions, including hydrogenation. Consequently, the in situ formation of heterogeneous hydrogenation catalysts from late-transition-metal precatalysts is probably quite common (see Section 4.4. for some examples). However, in some cases the oxidative-addition activation of H_2 by a M^{n+} precatalyst is not viable because it would require the formation of an energetically prohibitive $n + 2$ oxidation state, $[M^{n+2}(H)_2]^{n+}$. In such cases, reduction of the precatalyst can still occur via *heterolytic hydrogen activation* [1,78] if the needed base [31] is present, since the $M^{n+} + H_2 + B: \rightarrow [M^{n+} - H]^{(n-1)+} + B - H^+$ reaction causes no increase in the M^{n+} oxidation state. The literature reveals (i) that the key requirements for heterolytic hydrogen activation are a metal whose oxidation state is high enough that further oxidation is unfavorable, an available coordination site, and a way to stabilize the released proton (i.e., the presence of a base), especially in non-aqueous solvents; (ii) that amines, carboxylates, alkoxides and hydroxide are commonly used bases (the base can also be an internal M–R which undergoes a four-centered reaction with H_2 , a second version of heterolytic hydrogen activation); and (iii) that the metals for which heterolytic hydrogen activation is to be expected (i.e., when a base is also present) include Pd(II), Pt(IV), Ru(II), Ru(III), Rh(III), Ir(III), Ag(I), Au(III), Cu(I), and Cu(II) [31].

4.2. The use of forcing reaction conditions

The use of forcing reaction conditions (high temperature, high H_2 pressure, strong reducing agents) increases the probability that a heterogeneous catalyst will form. For example, hydrogenations with the precatalyst $[Rh(C_5Me_5)Cl_2]_2$ appear to be homogeneously catalyzed at ~ 5 atm H_2 and $50^\circ C$, but develop a heterogeneous component [101] at 50 atm H_2 and $50^\circ C$ [7]. As a second example, Wilkinson's catalyst, a well-know homogeneous catalyst under mild reaction conditions, develops a heterogeneous component after several hours at $130^\circ C$ and ~ 3.5 atm of H_2 [48]. Even subtle changes in reaction conditions can cause the nature of the catalyst to change. Homogeneous catalysis was observed with (*N,N'*-diaryl-diiminoacene)naphthene)Pd⁰(alkene) as the precatalyst, THF as the solvent, and electron defi-

cient alkenes as the substrate [23]. However, switching either the solvent to benzene or the substrate to cyclohexene caused a significant heterogeneous component to develop [23]. The lesson is that the nature of the true catalyst can change with the reaction conditions. An important point here is that the reaction $M_n + (x \cdot n)L \rightleftharpoons nML_x$ appears to be exothermic in many cases (i.e., shifted to the left at higher reaction temperatures). Further studies of such equilibria are needed to verify or refute this point, however.

4.3. The presence of nanocluster stabilizers

Transition-metal nanoclusters, $M(0)_n$, possess only kinetically stability since the formation of bulk metal is the thermodynamic minimum [12,79].¹⁷ Therefore, nanoclusters that are freely dissolved in solution must be stabilized in a way that prevents the nanoclusters from diffusing together and coalescing [12], ultimately to bulk metal. Nanocluster stabilization is usually discussed in terms of two general categories of stabilization, electrostatic stabilization (treated by DLVO theory [80,81]) and steric stabilization [80,81]. Electrostatic stabilization is achieved by the coordination of anionic ligands, such as halides, carboxylates or polyoxoanions, to the coordinatively unsaturated metal atoms on the surface of the metal particles [80]. This results in coulombic repulsion between individual nanoclusters with their coordinated anions due to the formation of an electrical double-layer (really a diffuse electrical multi-layer) [82]; this coulombic repulsion is opposed by van der Waals attractive forces, these two opposing effects being the essence of DLVO theory. Steric stabilization is achieved by the presence of bulky, typically organic materials that, due to their steric bulk, impede the nanocluster surfaces from touching and thereby agglomerating [80]. Polymers (particularly polyvinylpyrrolidone), dendrimers and large alkylammonium cations are examples of

¹⁷ From the enthalpies of vaporization (i.e., ignoring solvation effects), one finds that the bulk, $M(0)_n$ metal is 133, 155 and 160 kcal/mol more stable than *n* single Rh(0), Ru(0) and Ir(0) atoms, respectively [79]. Obviously, nanoclusters are more stable than isolated metal atoms because they have many metal–metal bonds, but they are still less stable than the thermodynamic sink of bulk metal, in which essentially every metal atom has the maximum possible number of metal–metal bonds.

common organic steric stabilizers of nanoclusters and colloids.

The formation of highly active nanocluster catalysts is more likely if nanocluster stabilizers are present in the reaction solution. To illustrate this point, 2100 catalytic turnovers for cyclohexene hydrogenation are observed with $[(1,5\text{-COD})\text{Rh}^{\text{I}}(\text{CH}_3\text{CN})_2][\text{BF}_4]$ as the precatalyst; however, due to the absence of nanocluster stabilizers, the catalyst quickly deactivates by forming low-surface-area bulk Rh metal [73]. On the other hand, cyclohexene hydrogenation with $[\text{Bu}_4\text{N}]_5\text{Na}_3[(1,5\text{-COD})\text{Rh}^{\text{I}}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ as the precatalyst at low (ca. 10^{-7} M) concentrations yields an active and long-lived nanocluster catalyst capable of >190,000 catalytic turnovers in part due to the effects of the polyoxoanion and tetrabutylammonium stabilizers [33,40,73]. The use of low concentrations [73] of nanoclusters has a significant stabilizing effect because it slows down the kinetics of the bimolecular aggregation [39]. Note here the insidious nature of this effect in regards to determining the true catalyst: low concentrations of small, highly active nanoclusters can easily be the true, longer-lived, harder-to-detect catalyst!

The solvent also plays a role in nanocluster stability. DLVO theory [80,81] of colloid stabilization predicts that the thickness of the stabilizer double layer will increase as the dielectric constant (ϵ) of the solvent increases; hence, theory predicts that colloid stability will be enhanced in high dielectric solvents. This prediction has not been carefully tested [34], but some data are available. Notably, Reetz and Lohmer found [83] that Pd nanoclusters are especially stable in propylene carbonate, for which $\epsilon = 69$ (for comparison $\epsilon = 20$ for acetone and $\epsilon = 39$ for acetonitrile). These solvent-stabilized (and chloride-stabilized [14]) nanoclusters have the highest demonstrated thermal stability of any known soluble nanocluster, showing no visually observable formation of bulk metal even after several days at 140–155 °C [83]. Reetz and Lohmer's nanoclusters were also shown to catalyze Heck coupling reactions at temperatures as high as 160 °C [83], a record reaction temperature for a soluble nanocluster catalyst. A recent report shows that nanoclusters might also be especially stable in ionic liquids [84]. In that work, chloride-stabilized Ir nanoclusters were found to be capable of >8400 catalytic turnovers for olefin hydrogenation at 70 °C and 4 atm of H_2 in the ionic

liquid 1-butyl-3-methylimidazolium hexafluorophosphate [84].¹⁸ A scrutiny of the literature reveals several probable, but unrecognized, cases of nanocluster catalysis in ionic liquids [85–89]. These are systems where more evidence is needed for or against nanoclusters as the true catalyst.

4.4. The hydrogenation of monocyclic arenes

The hydrogenation of monocyclic arenes is a difficult reaction to catalyze [90–92]. Typically, it is accomplished with heterogeneous catalysts of Group VIII metals, such as Rh/ Al_2O_3 or Raney nickel [93]. There are several claims of metal-complex homogeneous catalysts capable of monocyclic arene hydrogenation [1,71,72]. However, (i) there is usually little evidence to support the hypothesis that the true catalyst in these systems is homogeneous;¹⁶ (ii) two such catalysts have now been shown to be heterogeneous, as the following examples and references illustrate; and (iii) there is at least some evidence that other systems are heterogeneous as well.

Perhaps the best example of an arene hydrogenation catalyst that was initially believed to be homogeneous, but where later evidence definitely shows that it is heterogeneous, is the important arene hydrogenation catalyst based on RhCl_3 and $[(\text{C}_8\text{H}_{17})_3\text{NCH}_3]\text{Cl}$ [94,95]. Initially, it was claimed that the $[(\text{C}_8\text{H}_{17})_3\text{NCH}_3]^+[\text{RhCl}_4]^-$ ion-pair was the true catalyst [94]. Later work using the more general approach to the “homogeneous or heterogeneous catalysis problem” [10] mentioned above, including TEM, Hg(0)-poisoning, and solution-phase kinetic studies demonstrating sigmoidal, $\text{A} \rightarrow \text{B}$, $\text{A} + \text{B} \rightarrow 2\text{B}$ kinetics, convincingly shows that the true catalyst is actually a distribution of Rh(0) colloids stabilized by Cl^- and $[(\text{C}_8\text{H}_{17})_3\text{NCH}_3]^+$ [21]. It remains unclear as to whether a sol–gel entrapped version of this same Rh ion-pair precatalyst is homogeneous or heterogeneous [96].

The second example involves the use of $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{O}_2\text{CMe})_2$ for benzene hydrogenation [24,97–99]. Early catalytic studies [97,98] were unable to determine the nature of the true catalyst

¹⁸ Autocatalytic kinetics, a mercury-poisoning experiment, TEM data, and catalyst isolation experiments leave little doubt that Ir nanoclusters are the true catalyst in this system.

[97]; however, recent work including TEM, Hg(0)-poisoning, and kinetic studies showing characteristic sigmoidal kinetics, convincingly shows that the true catalyst is in fact a bulk metal particle plus metal thin-film heterogeneous catalyst [24]. An important finding of that work is it is the first quantitative demonstration that the $A \rightarrow B$, then $A + B \rightarrow 2B$ mechanism of formation *also applies to heterogeneous nucleation of metal thin-film and bulk metal formation* (see the discussion and references therein for a further discussion of such heterogeneous nucleation [24]).

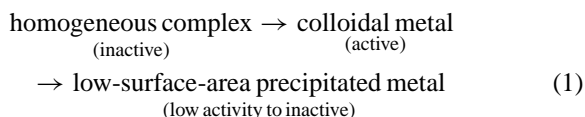
There is evidence for the in situ formation of a heterogeneous catalyst in other arene hydrogenation systems that employ homogeneous precatalysts. One example involves the use of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ for arene hydrogenation [60,100]. The catalyst in this system was originally claimed to be homogeneous on the basis of light scattering experiments. However, later work [7] suggested that the true catalyst may be heterogeneous, although the evidence from that study is not definitive—note here the problem caused in the initial study by relying solely on light scattering without, for example, kinetic studies. Briefly, the evidence for heterogeneity includes: (i) the observation of dark colored reaction solutions, (ii) the routine observation of 1–2 h induction periods, an observation characteristic of metal-particle formation [10,30,31], (iii) the deposition of Rh metal on the reactor walls, and (iv) the observation that the catalyst is much more active for the hydrogenation of benzene and cumene than it is for the hydrogenation of polystyrene [7]. Very recently, this system has been reinvestigated by the methods in Fig. 2. Sigmoidal kinetics, TEM observation of nanoclusters, Hg(0)-poisoning and other evidence is unequivocal in identifying soluble Rh nanoclusters as the true benzene hydrogenation catalyst [101]. An interesting point here is that the presence of the nanocluster-stabilizing Cl^- anion leads to a nanocluster catalyst in this case. In the seemingly closely similar case of benzene hydrogenation beginning with $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{O}_2\text{CMe})_2$, the inefficient anionic stabilizer OAc^- yields an insoluble, bulk-metal plus thin-metal film catalyst [24].

Yet another example involves $\text{Ru}_2\text{Cl}_2(\mu\text{-H})_2(\mu\text{-Cl})(\eta^6\text{-C}_6\text{Me}_6)_2$ as a precatalyst for arene hydrogenation [102,103]. This catalyst was originally thought to be homogeneous; however, a later study shows

that the catalyst is inactive in the presence of Hg(0) [104], implying that the true catalyst is heterogeneous [3,10].¹⁹ These examples show that soluble nanoclusters are fairly pervasive in claimed “homogeneous” arene hydrogenations, especially benzene hydrogenations since benzene is more difficult to reduce.

4.5. The formation of metallic precipitates and dark reaction solutions

Certain experimental observables can indicate the in situ formation of a heterogeneous catalyst. The most obvious of these is the formation of metallic precipitates during the course of the reaction in the form of a metal powder or mirror. Verification that a precipitate is indeed bulk metal can be accomplished with XPS or XRD [24,40] as mentioned earlier. Since metal surfaces are good catalysts for a variety of reactions, one must strongly suspect heterogeneous catalysis in such systems. As pointed out elsewhere [5], one cannot rule out heterogeneous catalysis by showing that the metallic precipitate is inactive, because the process in Eq. (1) may be occurring:



The in situ formation of a soluble nanocluster catalyst is difficult if not impossible to detect visually because the reaction solutions typically appear homogeneous and may not precipitate bulk metal. Nevertheless, nanocluster solutions of transition metals are often dark brown or black, so a darkening reaction solution suggests the possibility that a nanocluster catalyst is forming.

¹⁹ Additionally, poisoning experiments reported in the original study [103] are, in hindsight, more consistent with the hypothesis that the catalyst is heterogeneous than with the hypothesis that it is homogeneous. For example, the presence of only 0.05 eq. of thiophene (per Ru atom) dramatically slows the turnover frequency (from 4.1 min^{-1} in an unpoisoned experiment to 0.3 min^{-1} with 0.05 eq. of thiophene) [103]. Such a result is difficult to explain for a homogeneous catalyst, but makes perfect sense for a heterogeneous catalyst where only a fraction of the total metal atoms are on the surface and active (see footnote 10).

4.6. The observation of induction periods and sigmoidal kinetics

The presence of an induction period is one consequence of the in situ formation of a heterogeneous catalyst from a monometallic precatalyst [30,31]. If the end of the induction period is followed by an “autocatalytic burst” of activity and an accompanying darkening of the reaction solution or the formation of a metallic precipitate, that is excellent and often compelling evidence for the in situ formation of a heterogeneous catalyst. However, an induction period may be too short to observe in some cases of heterogeneous catalysis. Additionally, if the precatalyst is pretreated with reductant in the absence of substrate [21,94], then no induction period is expected. However, overall and at least for hydrogenation reactions, the prior literature shows that sigmoidal, “autocatalytic” kinetics are the kinetic signature of in situ nanocluster formation [10,21,24,30–35].

4.7. The issue of the $M_n + (x \cdot n)L \rightleftharpoons nML_x$ equilibrium

One key, presently poorly understood, issue is the position of the $M_n + (x \cdot n)L \rightleftharpoons nML_x$ equilibrium as a function of metal, ligand type, amount of ligand, and temperature. The position of this equilibrium determines what species are present as potential catalysts. Relevant literature includes the fact that CO treatment of $Rh(0)_n$ rafts yields discrete $Rh(CO)_x^{0/+}$ species, a process that can be reversed [105,106]. Also, Union Carbide’s study of $CO + H_2 \rightarrow CH_3OH + HOCH_2CH_2OH + \text{other products}$, using Rh carbonyl cluster precatalysts, showed that these precatalysts are unstable because the Rh–Rh and Rh–CO bond energies are of similar strengths, with the Rh–CO bond being a bit stronger [107]. That makes the $M_n + (x \cdot n)L \rightleftharpoons nML_x$ equilibrium exothermic, meaning that nanocluster formation is thermodynamically favored at higher temperatures in at least this system [107].

In other cases, it appears that the presence of strongly binding or chelating ligands may inhibit, perhaps completely, reduction to a $M(0)_n$ state. An example under investigation [108] that is probably a true homogeneous catalyst is the interesting $[Ir(1,5-COD)Cl]_2$ /bidentate chiral phosphine cata-

lyst system for imine asymmetric hydrogenation at ~ 70 atm of H_2 [109,110]. In the absence of phosphine, $[Ir(1,5-COD)Cl]_2$ is readily reduced to $Ir(0)_n$ at only ~ 4 atm of H_2 [34]; however, presence of the bidentate phosphine ligand appears to inhibit reduction of the $Ir^I(\text{phosphine})$ complex to $Ir(0)$ even at ~ 70 atm of H_2 , although this has not yet been conclusively demonstrated [108]. One piece of evidence for the homogeneity of this system is that its high enantioselectivities are without precedent in heterogeneous catalysis.

The case of Pd(0) complexes and nanoclusters provides another important example, making clear that the type of ligands, and the ligand to metal ratio, are important in determining the form of Pd(0) present. First, the commercially available complex $Pd(0)(PPh_3)_4$ reminds us that mononuclear, 18-electron complexes of Pd(0) are well-known and isolable. Second, in the absence of phosphine ligands $Pd(0)_n$ colloids are known to form in Pd-catalyzed C–C coupling reactions with $Pd(OAc)_2$ as the precatalyst [111,112]; however, the addition of 4 eq. of PPh_3 (versus Pd) to this system completely inhibits colloid formation [111]. Third, the existence of Pd nanoclusters of average formulas such as $Pd_{\sim 560}phen_{\sim 60}(OAc)_{\sim 180}$ ($phen = 1,10\text{-phenanthroline}$), $Pd_{\sim 1400}phen_{\sim 60}O_{\sim 1100}$ and $Pd_{\sim 2000}phen_{\sim 80}O_{\sim 1600}$ [113] shows that the number and type of ligands are factors in determining the average size of the resultant distribution of nanoclusters.

Another important paper in this general regard is a very recent one showing $Au(0)_n + (m \cdot x)L \rightleftharpoons Au(0)_{n-m} + mAuL_x$ [114], that is, the formation of smaller $Au(0)_{n-m}$ particles from larger ones in the presence of added ligands such as $RSH \geq RNH_2 \geq R_3P \geq RSiH_3$ (the ordering indicates the ligands qualitative ability to effect breakup of the $Au(0)_n$ nanoclusters). In short, not nearly enough is known about how the metal, ligand type, amount of ligand, temperature, and other variables influence the $M_n + (x \cdot n)L \rightleftharpoons nML_x$ equilibrium. Understanding these factors will be important to a better understanding of when to expect homogeneous versus heterogeneous catalysis.

A study that is quite important if not unique in showing the conditions where a single-metal, homogeneous catalyst results, even though one starts with a nanocluster heterogeneous catalyst, is that using a PVP (i.e., poly(vinylpyrrolidone)) stabilized Rh colloid to

try to catalyze $\text{CH}_3\text{OH} + \text{CO}$ to $\text{CH}_3\text{CO}_2\text{H}$ in the presence of I^- —that is, an attempt to catalyze Monsanto's famous acetic acid process using a Rh nanocluster [115]. Not unexpectedly, the true catalyst in this system is the well established Rh(I) homogeneous catalyst, $\text{Rh}^{\text{I}}(\text{CO})_2\text{I}_2^-$, produced by MeI oxidation of the Rh(0) nanoclusters under CO pressure. As expected, kinetic plus spectroscopic data are again a key to the identification of the catalyst: the PVP-stabilized Rh(0) nanoclusters are considerably less reactive than is $\text{Rh}^{\text{I}}(\text{CO})_2\text{I}_2^-$; the rate upon recycling the Rh(0) nanocluster precatalyst increases concomitant with the increase in the concentration of $\text{Rh}^{\text{I}}(\text{CO})_2\text{I}_2^-$ which builds to $\sim 29\%$ of the total Rh, and the activation energy, E_a , for the reaction beginning with the Rh(0) nanoclusters is the same within experimental error as the E_a for $\text{Rh}^{\text{I}}(\text{CO})_2\text{I}_2^-$ (another piece of kinetics-based evidence). Note also the value of literature precedent²⁰ here: $\text{Rh}^{\text{I}}(\text{CO})_2\text{I}_2^-$, but not Rh(0) nanoclusters, are the precedented catalyst in this case.

Although we focus on hydrogenation catalysis in this review, the problem of distinguishing homogeneous and heterogeneous catalysis is not limited to hydrogenation reactions. In situ formation of heterogeneous catalyst has also been identified as an issue in hydrosilylation reactions [8,9,50,116], ring-opening polymerization catalysis [117], alkane activation [118], and C–C coupling reactions [111]. The pervasiveness of the “homogeneous or heterogeneous” problem in catalytic science is further illustrated by the identification of *homogeneous species* as the true catalysts for initially *heterogeneous* oxidation catalysts based on molecular sieves [119,120], and for carbonylation and Heck coupling catalysts where Pd/C and Pd/Al₂O₃ are the *precatalysts* [121].

5. Examples of catalyst systems of interest for further study

One of the aims of this review is to enable researchers to determine for themselves probable cases

of heterogeneous catalysis. Since most catalyst systems in the literature have not been examined carefully in light of the “homogeneous or heterogeneous” question, a large number of systems are of interest for further study. To guide the reader, we reference a few such systems here. See Table A.1 for detailed information about each of these catalyst systems. Systems that employ easily reduced transition-metal complexes as precatalysts can be found in references [70,85,86,111,112,122–127]. Systems employing forcing reaction conditions can be found in references [47,68,69,77,86–88,109,111,112,122,124,125,128–136]. Systems in which known nanocluster stabilizers are present can be found in references [68–70,77,86,87,109,111,112,122,123,125,126,130,134–136]. Systems in which monocyclic arene hydrogenation is observed can be found in references [1,47,68,70,88,111,122–124,132–137]. Systems that form dark reaction solutions or metallic precipitates can be found in references [7,68–70,77,86,89,111,112,122,123,125,126,131,133,137]. Systems that exhibit induction periods or sigmoidal kinetics can be found in references [7,69,111,126,130,131,137]. Systems that meet at least four of the six criteria, that is, systems that very likely involve metal-particle catalysts, are found in references [68–70,86,111,112,122,123,125,126].

The probable cases of nanoclusters in ionic liquids mentioned earlier also merit closer scrutiny [85–89]. The SiO₂-tethered Rh organometallic plus SiO₂-supported Pd(0) precatalyst complex that leads to interesting arene hydrogenation and other catalysis is another case meriting close scrutiny for the possibility of heterogeneous catalysis [138–142]. Is the tethered Rh organometallic serving not as the claimed homogeneous catalyst, but rather as a slow-release of Rh route to small, highly active, SiO₂-supported Rh(0) nanoclusters, a rather different concept? It is also important to determine unequivocally whether or not sol–gel entrapment of a $[\text{R}_3\text{NH}^+][\text{RhCl}_4^-]$ ion-pair precatalyst can remain as a monometallic homogeneous catalyst as implied elsewhere [96]. Alternatively, is the documented formation of Cl⁻ stabilized Rh(0) nanoclusters from this precatalyst in solution [21] really also the true catalyst in this sol–gel case as well as one now must suspect? The needed kinetic and other studies as outlined herein remain to be accomplished for these systems—it is crucial

²⁰ The use of literature precedent was also a key in the benzene hydrogenation catalysts examples cited earlier: Rh or Ru metal particle heterogeneous catalysts, but not soluble, 18-electron single metal Rh or Ru complexes, were—and still are [21,24,101]—the precedented benzene hydrogenation catalysts.

that workers stop making pronouncements about the nature of their catalysts without doing kinetic studies! Note that supporting or refuting the *concepts* behind these systems depends upon correctly identifying the true catalyst.

Finally, it is noteworthy that we continue to find systems in the literature which merit examination by the methods detailed herein. This observation suggests that there are probably many more systems than those listed in this review for which the “is it homogeneous or heterogeneous catalysis?” question is important, even though we have tried to be comprehensive and have been working and gathering references in this area for more than a decade now [10]. A recent case of some conceptual interest concerns whether or not a monometallic Ni homogeneous hydrogenation catalyst has ever been conclusively demonstrated.²¹ Or, are trace amounts of highly active nanoclusters really the true catalysts in recent claims of homogeneous Ni hydrogenation catalysis [143–145]? This question²¹ is not just of academic interest. Inexpensive, highly active Ni hydrogenation catalysts are commercially quite important. Hence, understanding them at a level that allows their rational improvement is a topic of continuing interest.

6. Summary and future outlook

The major findings of this review are as follows:

- Catalysis under reducing conditions is often performed with a transition-metal complex as the precatalyst. In situ reduction of such a precatalyst to form a metal-particle heterogeneous catalyst is common.
- A variety of experiments can be used to help distinguish homogeneous catalysis from heterogeneous catalysis; however, there is no single definitive experiment for making this distinction.
- Distinguishing homogeneous catalysis from heterogeneous catalysis is most difficult when a nanocluster catalyst is involved, partly because nanocluster solutions appear homogeneous to the eye. Addition-

ally, nanoclusters can be as small as ~ 1 nm in diameter, which makes them difficult to detect by some methods.

- Kinetic information is crucial to the determination of the true catalyst, catalysis being a “wholly kinetic phenomenon” [25,26].
- A general approach for distinguishing homogeneous catalysis from heterogeneous catalysis is available and involves the four components shown back in Fig. 2.
- Conditions under which a heterogeneous catalyst is likely to form include: (i) when easily reduced transition-metal complexes are used as precatalysts; (ii) when forcing reaction conditions are employed; (iii) when nanocluster stabilizers are present [34]; and (iv) when monocyclic arene hydrogenation is observed.
- The telltale signs of heterogeneous catalysis include the formation of dark reaction solutions and metallic precipitates, plus the observation of induction periods and sigmoidal kinetics.
- Under conditions that favor nanocluster formation, the primary hypothesis to be disproven [146] is that nanoclusters are the true catalyst.
- The very low concentrations sometimes used for a homogeneous precatalyst, and thus low concentrations of nanoclusters, can make detecting soluble heterogeneous nanocluster catalysts more difficult. However, the high sensitivity of TEM, and the kinetic information possible due to the *amplification* provided by fast catalytic reactions [10,30,31], are two key tools to use both in general and in difficult cases. One can, of course, also always do controls raising the precatalyst concentrations to levels that allow the other physical methods described herein to be used with confidence.

An obvious area for future research is to investigate more catalytic systems in terms of the “homogeneous or heterogeneous” question. Table A.1 of the Appendix A lists about 30 catalytic systems for which the in situ formation of a heterogeneous catalyst is worth investigating. Related to this, a few areas of catalysis warrant closer inspection:

- Further study of Pd-catalyzed C–C coupling reactions is of interest. It appears that Pd nanoclusters are commonly formed in such systems

²¹ We thank Prof. George Stanley at Louisiana State University for bringing this question, as well as the cited Ni references, to our attention.

- [86,111,112,125,147]. The role of such nanoclusters in catalysis needs to be clarified.
- The role of nanoclusters in Pt-catalyzed hydrosilylation reactions is much debated [8,9,50,116,126]. However, the central importance of kinetics in determining the nature of the true catalyst(s) in these systems has been largely ignored. Kinetic studies, including quantitative CS₂-poisoning experiments, are of interest for these systems.
 - Precatalysts composed of transition-metal complexes with polymeric ligands are quite common [77,122,123,134,135,137]. Under reducing conditions, how common is the formation of a polymer-stabilized nanocluster catalyst?
 - The in situ generation of a heterogeneous catalyst appears to be common for systems that are capable of monocyclic arene hydrogenation [72]. Hence, studying more of these systems by the more general method [10] for answering the “homogeneous or heterogeneous” question would be of interest.
 - And, as far as developing *monometallic homogeneous* arene hydrogenation catalysts goes, rare systems that merit further investigation are Rothwell’s Nb^V and Ta^V [71,72] systems and soluble analogs, if possible, of Mark’s active, supported Th [180] or other actinide systems.

Another general area for future research is the further development of methods for distinguishing homogeneous and heterogeneous catalysts. Some worthwhile problems include:

- A systematic study of the poisoning of transition-metal catalysts with mercury would be useful. For example, it would be valuable to know the poisoning properties of mercury versus temperature. It would also be useful to know which metals require a large excess of mercury, or other specialized conditions, for complete poisoning.
- Developing ligand-based poisons similar to CS₂, but which work at higher temperatures, would be quite valuable. Currently, the powerful, quantitative, ligand-based poisoning experiment can only be performed for systems that operate near room temperature [51]. Many systems of interest, including many monocyclic arene hydrogenation catalysts, are active only at higher temperatures.

- An improved synthesis of DCT, further study of DCT, and DCT analogs or replacements are all of interest.
- Further investigation of Maitlis’ filtration test using proven nanocluster catalysts is of interest. Can this test be used, perhaps under modified conditions, to detect nanocluster catalysts, or is it limited to the detection of catalysis by bulk metal precipitates?
- It would be instructive to check Collman’s test with smaller, well-characterized, modern nanocluster catalysts, as well as with soluble, heterogeneous, Ziegler-type, polymer hydrogenation catalysts [53].
- Developing methods to detect ionic species formed from nanocluster catalysts by, perhaps, ion-exchange or dialysis of catalyst solutions (i.e., down to very low conductivities), is another area meriting attention. (We thank a referee for this suggestion.) We would add that this may prove most important for nanoclusters undergoing oxidative chemistries, a relatively little investigated area at present [14]. The Rh colloid tested for Monsanto acetic acid synthesis conditions mention earlier, and where an ionic Rh^I(CO)₂I₂⁻ is formed as the true catalyst [115], would seem to be an excellent system in which to do the needed up-front methods development and controls.
- And finally, more information is needed about the $M_n + (x \cdot m)L \rightleftharpoons M_{n-m} + mML_x$ equilibrium as a function of the specific L, bidentate L–L, and temperature to understand its impact on the “is it homogeneous or heterogeneous catalysis” problem.

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Appendix A

See Table A.1 for detailed information about each of the catalyst system.

Table A.1

A partial list of catalyst systems which merit testing for the in situ formation of a metal-particle catalyst

	Authors (publication date)	Catalyst system	Why in situ metal-particle formation as the true catalyst merits consideration	Reference
1	Süss-Fink et al. (2002)	Triruthenium clusters are used as precatalysts for benzene hydrogenation at 60 atm of H ₂ and 110 °C	Forcing reaction conditions are used and monocyclic arene hydrogenation is observed. A mercury poisoning experiment was performed, but the mercury was (inappropriately) removed before the hydrogenation reaction was started	[148]
2	Xiao and Zhang (2001)	The precatalyst is formed in situ from [Ir(COD)Cl] ₂ and a chelating phosphine ligand. This precatalyst is used for imine hydrogenation at room temperature and ~70 atm of H ₂	Forcing reaction conditions are used and a known nanocluster stabilizer is present (chloride). However, the presence of a chelating phosphine ligand perhaps keeps this catalyst homogeneous	[149]
3	Hartwig and co-workers (2000)	Cp* <i>Rh</i> (η ⁴ -C ₆ Me ₆) is used as a precatalyst for alkane activation at 150 °C	Forcing reaction conditions are used	[150]
4	Reetz and Westermann (2000)	Palladium-catalyzed coupling reactions (Heck and Suzuki) are investigated using several different precatalysts	In this important paper, using phosphine-free catalyst systems, the authors observe induction periods and sigmoidal kinetics (see Figs. 1 and 2). They also observe the presence of nanoclusters by TEM. These systems contain nanocluster stabilizers (acetate and tetrabutylammonium halide). Forcing conditions and easily reduced precatalysts like Pd(OAc) ₂ are used. The lack of sufficient kinetic data in this study make it unclear if the Pd nanoclusters are directly involved in the catalytic cycle, or if they only serve as a reservoir for Pd in these systems	[151]
5	Sasson and co-workers (2000)	Palladium-catalyzed coupling reactions are investigated using a precatalyst of PdCl ₂ /tetrahexylammonium chloride/AcOH/AcONa. The reactions were performed at 80–105 °C	The formation of metallic precipitates is observed. This system contains nanocluster stabilizers (acetate and tetrahexylammonium chloride). Forcing conditions and an easily reduced precatalyst are employed	[152]
6	Arai and co-workers (2000)	Palladium-catalyzed Heck reactions are investigated using a precatalyst of Pd(OAc) ₂ /triethylamine/NaCO ₃ . The reactions were performed at 80–110 °C	They observe the presence of nanoclusters by TEM, along with the formation of metallic precipitates. This system contains nanocluster stabilizers (acetate and carbonate). Forcing conditions and an easily reduced precatalyst are employed	[153]
7	Dyson and et al. (1999)	[H ₄ Ru ₄ (η ⁶ -C ₆ H ₆) ₄][BF ₄] ₂ is used as the precatalyst for arene hydrogenation at 60 atm of H ₂ and 90 °C	Forcing reaction conditions are used and monocyclic arene hydrogenation is observed	[154]
8	Süss-Fink and co-workers (1998)	(η ⁶ -C ₆ H ₆) ₂ Ru ₂ Cl ₄ is used as a precatalyst for the hydrogenation of benzene derivatives at 60 atm of H ₂ and 90 °C	Forcing reaction conditions are used and monocyclic arene hydrogenation is observed. This system contains a nanocluster stabilizer (chloride)	[155]
9	Trzeciak et al. (1998)	HRh[P(NC ₄ H ₉) ₃] ₄ and HRh(CO)[P(NC ₄ H ₉) ₃] ₃ are used as the precatalysts for alkene and arene hydrogenation at 5 atm of H ₂ and 80 °C	Forcing reaction conditions are used and monocyclic arene hydrogenation is observed	[156]

Table A.1 (Continued)

	Authors (publication date)	Catalyst system	Why in situ metal-particle formation as the true catalyst merits consideration	Reference
10	Plasseraud and Süss-Fink (1997)	$[(\eta^6\text{-C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]\text{Cl}_2$ is used as a precatalyst for the hydrogenation of benzene derivatives at 60 atm of H_2 and 90°C	Forcing reaction conditions are used and monocyclic arene hydrogenation is observed. After complete conversion of benzene, the formation of metallic Ru is observed. This system contains a nanocluster stabilizer (chloride)	[157]
11	De Souza and co-workers (1996)	$[\text{Rh}(\text{COD})_2][\text{BF}_4]$ and other precatalysts are used for alkene hydrogenation at 10 atm of H_2 and 25°C	Somewhat forcing conditions (10 atm of H_2), and an easily reduced precatalyst are used	[158]
12	Kaufmann et al. (1996)	$\text{Pd}(\text{OAc})_2$ and other precatalysts are used for Heck coupling reactions at 100°C	Forcing reaction conditions and easily reduced precatalysts are used. This system contains known nanocluster stabilizers (such as tetraalkylammonium bromide salts). Dark brown reaction solutions and metallic precipitates form	[159]
13	Chauvin et al. (1995)	$[\text{Rh}(\text{norbornadiene})(\text{PPh}_3)_2][\text{PF}_6]$ and other precatalysts are used for alkene hydrogenation at 1 atm of H_2 and 30°C	The reaction solution turns from orange to brown upon exposure to hydrogen	[160]
14	Onishi et al. (1992)	$[\text{Rh}(\text{COD})(\text{Ph}_2\text{PCH}_2\text{COO})]$ and $[\text{Rh}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{COO})]$ are used as precatalysts for arene hydrogenation at 50°C and 5–50 atm of H_2	Forcing reaction conditions and easily reduced precatalysts are used. Plus, monocyclic arene hydrogenation and aromatic nitro group hydrogenation are observed	[161]
15	Tsai and Nicholas (1992)	$[\text{Rh}(\text{norbornadiene})(\text{Pme}_2\text{Ph})_3][\text{BF}_4]$ is used as a precatalyst for the hydrogenation of carbon dioxide to formic acid at about 50 atm of H_2 and 40°C	Forcing reaction conditions are used. An induction period is observed unless the precatalyst is pretreated with H_2 . Dark precipitate forms from the precatalyst under hydrogen	[162]
16	Coqueret and Wegner (1991)	$\text{PtCl}_2(\text{diene})$ is used as the precatalyst for hydrosilylation at $25\text{--}60^\circ\text{C}$	Sigmoidal reaction kinetics are observed (see Fig. 1 of the referenced paper). The reaction solution darkens (though only after the hydrosilylation reaction is complete). An easily reduced precatalyst is used and known nanocluster stabilizers are present (chloride)	[163]
17	Basset and co-workers (1990)	$\text{RuCl}_2[(m\text{-NaSO}_3\text{C}_6\text{H}_4)_3\text{P}]_3$ and related complexes are used in conjunction with salts such as NaI. These precatalysts were used to hydrogenate propionaldehyde at 50 atm of H_2 and 100°C	Forcing reaction conditions are used. Induction periods are observed in the absence of added salt (see Fig. 1 of the referenced paper). Known nanocluster stabilizers (halides) are found to cause a “remarkable” increase in activity	[164]
18	Alvanipour and Kispert (1988)	The catalyst was formed from the combination of triethyl aluminum and $\text{Co}(\text{stearate})_2$. This catalyst was used in for naphthalene (and other bicyclic arene) hydrogenation at about 50 atm of H_2 and 22°C	Forcing reaction conditions and strong reducing agents are used. This system contains known nanocluster stabilizers (long-chain carboxylates). Induction periods are observed, as is the formation of black reaction solutions	[165]
19	Collman et al. (1987)	A number of “homogeneous” arene hydrogenation catalysts from the earlier literature are tabulated in Table 10.2 of this reference	This reference discusses the possibility that at least some of these systems are heterogeneous	[166]

Table A.1 (Continued)

	Authors (publication date)	Catalyst system	Why in situ metal-particle formation as the true catalyst merits consideration	Reference
20	Bergbreiter and Chandran (1987)	The precatalyst was formed by tethering Rh(I) complexes to functionalized ethylene oligomers via phosphine groups. This precatalyst was then used to hydrogenate alkenes at 1 atm of H ₂ and 100 °C	Forcing reaction conditions are used. Additionally, known nanocluster stabilizers (polymers) are present, and the catalyst solutions darken during the course of the reaction. However, most of the Rh(I) complex remains intact by ³¹ P NMR and Collman's polymer hydrogenation test appears to indicate a homogeneous catalyst (although Collman's test appears to be a poor choice for this system)	[167]
21	Jones and Seeberger (1985)	The precatalyst was formed by tethering Rh(COD) (or other) moieties to polystyrene beads via phosphido linkages. This precatalyst was then used to hydrogenate benzene at 1–3 atm of H ₂ and 25–45 °C	The polystyrene beads darken during the reaction. Additionally, induction periods and monocyclic arene hydrogenation is observed. However, no metal crystallites were observed by X-ray photoelectron spectroscopy or X-ray diffraction analysis	[168]
22	Pertici et al. (1984)	Rh(η ⁶ -arene)(η ⁴ -COD) complexes are used as precatalysts for alkene hydrogenation at room temperature and 1–60 atm of H ₂	Forcing reaction conditions are used in some cases. Catalyst decomposition is observed under some conditions. However, benzene is not hydrogenated under these conditions	[169]
23	Knifton (1981)	Ru(acac) ₃ and other precatalysts are used to synthesize ethylene glycol from synthesis gas at 430 atm of CO/H ₂ (1:1) and 220 °C	Forcing reaction conditions are used and known nanocluster stabilizers (tetraalkylammonium bromide salts) are present. However, no metallic precipitates or higher hydrocarbons are formed	[170]
24	Maitlis and co-workers (1977)	[Rh(η ⁵ -C ₅ Me ₅)Cl ₂] ₂ is the precatalyst for the hydrogenation of alkenes, alkynes, arenes and nitroaromatics at 50 atm of H ₂ and 50 °C	Forcing conditions are used, a known nanocluster stabilizer is present (chloride), and monocyclic arene hydrogenation is observed. However, no metal particles were visible by light scattering. A second paper [171] using the same system reports (i) the observation of dark colored reaction solutions and the formation of metallic precipitates, (ii) the observation of 1–2 h induction periods, and (iv) the observation that the catalyst is much more active for the hydrogenation of benzene and cumene than it is for the hydrogenation of polystyrene	[172]
25	Rasadkina et al. (1976)	The precatalyst was formed from the combination of a polyamide and a palladium or rhodium salt such as RhCl ₃ ·3H ₂ O. This precatalyst was used to hydrogenate alkenes, arenes and nitroaromatics at 1 atm of H ₂ and 25 °C	Easily reduced precatalysts are used and known nanocluster stabilizers (polymers) are present. Dark brown reaction solutions and metallic precipitates form. Monocyclic arene hydrogenation and nitro group hydrogenation are observed	[173]
26	Rasadkina et al. (1975)	The precatalyst was formed from the combination of a polyamide and a platinum salt such as K ₂ PtCl ₄ . This precatalyst was used to hydrogenate alkenes, arenes and nitroaromatics at 1 atm of H ₂ and 30 °C	Easily reduced precatalysts are used and known nanocluster stabilizers (polymers) are present. Brown reaction solutions and metallic precipitates form. Monocyclic arene hydrogenation and nitro group hydrogenation are observed	[174]

Table A.1 (Continued)

	Authors (publication date)	Catalyst system	Why in situ metal-particle formation as the true catalyst merits consideration	Reference
27	Rasadkina et al. (1974)	The precatalyst was formed from the combination of a polyamide and a Group VIII metal salt such as $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$. This precatalyst was dissolved and treated with H_2 at about 150°C . It was then used to hydrogenate benzene at 1 atm of H_2 and 160°C	Forcing reaction conditions and easily reduced precatalysts are used. Known nanocluster stabilizers (polymers) are present and the dark brown reaction solutions form. Monocyclic arene hydrogenation is observed	[175]
28	Dini et al. (1973)	Precatalysts were prepared by stirring a polyamide (such as Nylon-6) with an aqueous solution of a Pt compound (such as H_2PtCl_6), followed by drying in a vacuum oven. The dried material was then activated in a H_2 atmosphere at 160°C for 7 h. These materials were used to hydrogenate benzene at $140\text{--}190^\circ\text{C}$. The authors believe the true catalyst is "a chloride-containing platinum complex where the metal atom is coordinatively bound to two amide groups of the polymeric chain"	Forcing reaction conditions are used and known nanocluster stabilizers (polymers) are present. Monocyclic arene hydrogenation is observed. Additionally, H_2 chemisorption measurements show that only a fraction of the Pt atoms chemisorb H_2 , suggestive evidence for the formation of nanoclusters. However, the authors conclude that no $\text{Pt}(0)_x$ is forming because of the negative evidence that X-ray measurements failed to show characteristic Pt diffraction patterns	[176]
29	Osborn and Schrock (1971)	$[\text{Ir}(\text{COD})_2][\text{PF}_6]$ and similar complexes are used as hydrogenation catalysts at 30°C and 1 atm of hydrogen	Very easily reduced precatalysts are used. However, the selectivities (at least for COD hydrogenation) appear to be at odds with a metal particle catalyst	[177]
30	Harrison and Rase (1967)	Precatalysts were prepared by stirring nylon fibers with an aqueous solution of H_2PtCl_6 at 100°C , followed by drying in an oven at 120°C . The dried material was then activated in a H_2 atmosphere at reaction temperature for >1 h. These materials were used to hydrogenate benzene at $205\text{--}425^\circ\text{C}$	Forcing reaction conditions are used and known nanocluster stabilizers (polymers) are present. Monocyclic arene hydrogenation is observed. However, the authors conclude that no $\text{Pt}(0)_x$ is forming on the basis of X-ray and IR measurements, and on the selectivity of the catalysts for partial benzene hydrogenation	[178]
31	Laporte and Schuett (1963)	The catalyst was formed from the combination of triethyl aluminum and nickel(II) 2-ethylhexanoate. This catalyst was used for arene hydrogenation at about 70 atm of H_2 and 150°C	Forcing reaction conditions and strong reducing agents are used. Known nanocluster stabilizers (long-chain carboxylates) are present. The formation of black reaction solutions and the hydrogenation of monocyclic arenes are observed	[179]

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