Review

A review of soluble transition-metal nanoclusters as arene hydrogenation catalysts[☆]

Jason A. Widegren, Richard G. Finke[*]

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, USA

Abstract

A critical review of the use of soluble transition-metal nanoclusters for the hydrogenation of monocyclic aromatic compounds is presented. The review begins with a brief introduction to arene hydrogenation and to nanocluster science. The introductory material is followed by a detailed discussion of the approximately 20 papers in the literature that deal with the use of soluble transition-metal nanoclusters for the hydrogenation of monocyclic aromatic compounds. Metal particle catalysts on solid supports are not reviewed herein, and are considered only as far as they serve to compare and contrast with soluble transition-metal nanoclusters. The major findings of this review are: (i) soluble nanocluster catalysts are implicated as the true catalysts in many putatively "homogeneous" arene hydrogenations; (ii) with few exceptions, nanocluster catalysts used for arene hydrogenation are poorly characterized; (iii) soluble nanocluster catalysts for arene hydrogenation have modest activity and lifetime; (iv) Rh and Ru are used almost exclusively as the active metals; (v) two catalyst systems, one developed by Roucoux and co-workers and the other by our own research group, stand out from the rest in terms of activity and lifetime; (vi) selective arene hydrogenation, especially for the synthesis of the all-*cis* diastereomer of substituted cyclohexanes, has received considerable attention and is a promising area for future study and, perhaps, fine chemical applications (selectivities >90% for the all-*cis* diastereomer have been achieved by several groups).
© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanoclusters; Arene hydrogenation catalysts; Diastereomers; Monocyclic aromatic compounds

1. Introduction

1.1. Arene hydrogenation

Sabatier and Senderens [1,2] hydrogenated benzene for the first time a century ago using finely divided nickel as the catalyst. For his studies of the hydrogenation of organic compounds in the presence of metallic catalysts, Sabatier shared the Nobel Prize in Chemistry with Victor Grignard in 1912. To this day, the hydrogenation of monocyclic arenes is an active area of research [3–11]. The production of substituted cyclohexanes from the corresponding substituted arenes is a goal of much of this research [12–15]. The hydrogenation of benzene to cyclohexane is probably the most important industrially practiced arene hydrogenation reaction, the cyclohexane being used primarily in the production of adipic acid, a precursor to nylon [16,17]. Partial arene hydrogenation to cyclohex*enes* is also an active area of research [3,18–20]. An example of this chemistry is the partial hydrogenation of benzene to cyclohexene (Eq. (1)), which is practiced industrially by Asahi Chemical Industry in Japan using a

heterogeneous Ru catalyst [21].

$$(1)$$
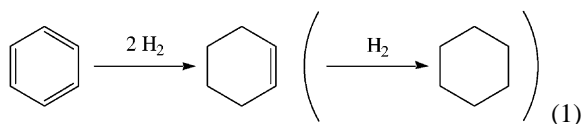
Arene hydrogenation has also garnered interest because of the demand for cleaner-burning, low-aromatic-content diesel fuels [6], which has been stimulated in part by the discovery that diesel exhaust particles contain powerful carcinogens [22], particles which also contribute to the prevalence of asthma and nasal allergies [23,24]. Hydrogenating aromatic polymers is also of current interest because the resultant polymers can have dramatically improved thermal and oxidative stability as well as improved optical properties [25]. For example, hydrogenation of polystyrene to poly(cyclohexylethylene) [25] (Eq. (2)), converts benzylic C–H bonds into more stable aliphatic C–H bonds. Dow Plastics is developing a commercial polystyrene hydrogenation process, and intends to use the poly(cyclohexylethylene) in optical media applications such as digital versatile discs (DVDs) [26]. As a second example, hydrogenation of aromatic rings in lignin, a biopolymer, has been suggested as a way to inhibit the oxidative yellowing (from quinone formation) of paper made from mechanical pulps [27–30]. In short, monocyclic arene hydrogenation is still a very important research area in catalysis.

$$(2)$$
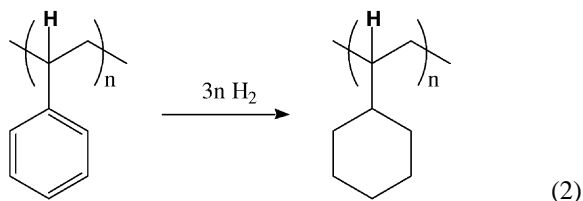
The hydrogenation of arenes is more difficult to catalyze than the hydrogenation of simple olefins [31]. This is as expected because at least some fraction of the resonance stabilization energy that is lost during arene hydrogenation appears in the transition state of the rate-determining step. Herein a distinction is made between monocyclic arenes (e.g., benzene and toluene) and polycyclic arenes (e.g., naphthalene and

anthracene [32–34])[1] because, at least under mild conditions, monocyclic arenes are more difficult to hydrogenate [6,35].[2]

Monocyclic arene hydrogenation is typically performed with heterogeneous catalysts of Group VIII metals, such as Rh/Al_2O_3 and Raney nickel [36]. The catalytic activity of such metals for the hydrogenation of benzene and alkylbenzenes decreases in the order Rh > Ru > Pt > Ni > Pd > Co [36,37]. Metal sulfides, including MoS_2 and WS_2, are another important class of heterogeneous arene hydrogenation catalysts, especially for petroleum refining [38–41]. In general, and as Gates [41] has noted, "the most active metal sulfides are typically several orders of magnitude less active than the most active metal catalysts", but metal sulfide catalysts are useful because sulfur compounds do not (further) poison them.

There have also been several claims of homogeneous, single-metal-complex catalysts capable of *monocyclic arene* hydrogenation [4,42] (see footnote 1). Unfortunately, these catalysts typically have poor catalytic activity [42], there is usually little evidence to support the hypothesis that the true catalyst in these systems is homogeneous,[3] and several such claimed

---

[1] The hydrogenation of *polycyclic* arenes such as naphthalene and anthracene with homogeneous, mononuclear catalysts is well established. For example, Halpern and co-workers [32–34] present compelling kinetic plus other evidence that certain *mononuclear* Ru and Rh hydrido complexes are homogeneous catalysts for polycyclic arene hydrogenation.

[2] The hydrogenation of a monocyclic arene results in a greater loss of resonance stabilization energy than the hydrogenation of one of the rings in a polycyclic arene. Consider the following comparison as an illustration of this point. The resonance stabilization energies of benzene and naphthalene can be estimated as 36 and 61 kcal/mol, respectively [35]. Upon hydrogenation, benzene loses all 36 kcal/mol of resonance stabilization energy. In comparison, when naphthalene is hydrogenated to tetralin (i.e., 1,2,3,4-tetrahydronaphthalene) it retains ~36 kcal/mol of resonance stabilization energy in the remaining aromatic ring, so only ~25 kcal/mol is lost.

[3] The monocyclic arene hydrogenation catalysts developed by Rothwell [4], such as $[Ta\{OC_6H_3(C_6H_{11})_2-2,6\}_2(H)_3(PMe_2Ph)_2]$, are an exception to this statement. These Nb^V or Ta^V hydrido aryloxide complexes are almost surely true homogeneous catalysts based on the following evidence: (i) the reduction of Nb^V or Ta^V by hydrogen is implausible under the reaction conditions, so the formation of Nb(0) or Ta(0) metal particles is extremely unlikely; (ii) the observed selectivity of the catalyst for the intramolecular hydrogenation of the aryloxide ligands is consistent with a homogeneous mononuclear catalyst, but difficult to explain if the true catalyst is heterogeneous (*ortho*-phenyl substituents on the

mononuclear "homogeneous" catalysts have more recently been shown to be heterogeneous, soluble nanocluster catalysts [43–45], a point we will return to in a moment. The use of soluble nanoclusters as catalysts for monocyclic arene hydrogenation has received increased attention in recent years, and is the focus of this review.

1.2. Background information on transition-metal nanoclusters

For the purposes of this review, transition-metal nanoclusters [46–61] are defined as metal particles with a diameter in the 1–10 nm range [49]. Such particles have generated intense interest in recent years because of the fundamental interest in these "strange morsels of matter" [62], and because of their many potential uses [48,50,58]. Modern transition-metal nanoclusters differ from classical colloids in several important respects [46,49]. Modern transition-metal nanoclusters are generally: (i) smaller (1–10 nm in diameter) than classical colloids (typically >10 nm in diameter); (ii) isolable and redissolvable ("bottleable"), unlike classical colloids; (iii) soluble in organic solvents (classical colloid chemistry is typically aqueous); and (iv) well defined compositionally, unlike classical colloids. Additionally, modern transition-metal nanoclusters typically have: (v) narrower size dispersions than classical colloids; (vi) clean surfaces (less to none of the X^-, O^{2-}, OH^-, H_2O or polymers that are prevalent in classical colloid chemistry); (vii) reproducible syntheses; (viii) reproducible ($\leq \pm15$–20%) catalytic activities (unlike the irreproducible, often $\geq \pm500\%$, catalytic activities of classically prepared colloids [46,63]). Catalysis is an especially important area of nanocluster science in that processes already exist that could potentially use nanoclusters as "soluble analogs of heterogeneous catalysts" [49] to improve catalytic rates, selectivities or possibly even lifetimes.

1.2.1. Synthesis

The synthesis of soluble transition-metal nanoclusters has been accomplished using five general methods

aryloxide ligand are hydrogenated, while hydrogenation of phenyl rings *meta* or *para* to the aryloxide oxygen is not observed nor is hydrogenation of the phenoxide nucleus itself ever observed) [4].

[48,58]: (i) the chemical reduction of transition-metal salts; (ii) the electrochemical reduction of transition-metal salts; (iii) thermal or photochemical decomposition of transition-metal precursors; (iv) ligand reduction and displacement from organometallic compounds; and (v) metal vapor synthesis. Some synthetic techniques use a combination of these five methods; e.g., sonochemical [64] preparations of nanoclusters involve either (i) or (iii) or a combination of (i) and (iii) [64–69]. Of the five methods, the chemical reduction of transition-metal salts is by far the most common. For example, all but one [159] of the nanocluster arene hydrogenation catalysts in Table 1 were prepared by the chemical reduction of a transition-metal salt. Solubility is often an advantage in nanocluster syntheses, and has even allowed the use of powerful HPLC separation methodologies [70–74].[4]

1.2.2. Stabilization

Transition-metal nanoclusters are only kinetically stable because the formation of bulk metal is the thermodynamic minimum [49,75].[5] Therefore, nanoclusters that are freely dissolved in solution must be stabilized in a way that prevents the nanoclusters from diffusing together and coalescing—any such agglomeration would eventually lead to the formation of the thermodynamically favored bulk metal [49]. Nanocluster stabilization is usually discussed in terms of two general categories of stabilization, electrostatic and steric [76,77]. Electrostatic stabilization is achieved by the coordination of anionic species, such as halides, carboxylates or polyoxoanions, to the coordinatively unsaturated surface metal atoms of the metal particles [76]. This results in the formation of an electrical double-layer (really a diffuse electrical multi-layer) [78], which causes coloumbic

[4] The use of chromatographic techniques, such as HPLC, for the purification of transition-metal nanoclusters is still rare, however, with the work to date focusing on gold nanoclusters. Hence, it is not yet clear how widely applicable chromatographic techniques will be in nanocluster science.

[5] From the enthalpies of vaporization (i.e., ignoring solvation effects), one finds that the bulk metal is 133, 155 and 160 kcal/mol more stable than single Rh(0), Ru(0) and Ir(0) atoms, respectively [75]. 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 every metal atom has the maximum possible number of metal–metal bonds.

repulsion between the nanoclusters. Steric stabilization is achieved by the presence of bulky, typically organic materials that, due to their bulk, impede the nanoclusters from diffusing together [76]. Polymers, dendrimers and large alkylammonium cations are examples of organic steric stabilizers. Some types of stabilizers provide both steric and electrostatic stabilization—the 15×12 Å, highly charged $P_2W_{15}Nb_3O_{62}{}^{9-}$ polyoxoanion is presently the premier example of such a "Gold Standard" [79] nanocluster stabilizing anion [48,49,79]. The choice of stabilizer also allows one to tune the solubility of the nanoclusters [80,81]. For example, the transfer of nanoclusters from organic solvents to water (and vice versa) has been demonstrated using phosphine [80] or pyridine [82] stabilizers.[6]

1.2.3. Advantages of nanoclusters as soluble metal particle catalysts

The use of soluble nanocluster catalysts for arene hydrogenation provides some advantages over traditional metal particle heterogeneous catalysts on solid supports (Fig. 1). To begin with, nanoclusters are often more active under mild conditions than corresponding supported metal particle catalysts [13,162]. This must be due to the number and type (degree of coordinative unsaturation) of the active sites present, which is a function of the conditions under which the catalysts are prepared. Traditional heterogeneous catalysts are typically prepared at high-temperatures, which causes annealing to the most stable (but probably not the most active) surface structure [83]. On the other hand, soluble nanoclusters are typically synthesized under mild conditions, resulting in a tendency towards kinetically controlled surface structures [84]. Based on studies of CO adsorption on nanocluster surfaces, de Caro and Bradley [83] conclude that "surface irregularity is probably to be found for colloidal metal particles in most, if not all, cases where the preparation conditions do not lead to annealing of the as-prepared surface".

A second advantage of soluble nanocluster catalysts is that they have been found to be more selective than corresponding traditional heterogeneous cata-

lysts for some reactions [48,85]. Relevant here is Schmid's [85] study of the ligand-modified selectivity of nanocluster catalysts for the hydrogenation of 2-hexyne, an important precedent that *presages a new area of ligand-modified, highly selective, nanocluster catalysts*.

Perhaps the most important, albeit still under-exploited, advantage of soluble nanocluster catalysts is that they are easier to study and, therefore, to optimize than traditional heterogeneous catalysts. Their solubility allows the use of analytical techniques in solution such as high resolution NMR [86–90], solution-phase IR [83,91–96], and *homogeneous* solution-phase kinetic and mechanistic studies [97]. The absence of support material generally simplifies characterization of soluble nanoclusters by eliminating the heterogeneity and other effects of the solid support [98].

1.2.4. Disadvantages of nanoclusters as soluble metal particle catalysts

Soluble nanocluster catalysts also have disadvantages compared to traditional heterogeneous catalysts (Fig. 1). The greatest disadvantage of at least the presently known soluble nanocluster catalysts is their poorer stability towards agglomeration in comparison to metal particle catalysts on solid supports. Reports of nanoclusters that are thermally stable in *solution* at $\geq 100\,°C$ are rare [99–106]. Of these, the solvent (and chloride [48]) stabilized Pd nanoclusters prepared by Reetz and Lohmer [104] have the highest demonstrated thermal stability; a propylene carbonate solution of the Pd nanoclusters shows no visually observable formation of bulk metal even after several days at $140–155\,°C$; unfortunately, the apparent absence of agglomeration was not verified by transmission electron microscopy (TEM) in that study. Reetz's [104] nanoclusters were also shown to catalyze Heck coupling reactions at temperatures as high as $160\,°C$, a record reaction temperature for a soluble nanocluster catalyst. Two other thermally stable nanocluster systems of note are the polymer-stabilized Pd nanoclusters developed by Bradley and co-workers [102] and Antonietti and co-workers [103], both of which were used to catalyze Heck coupling reactions. These two nanocluster systems show excellent stability and catalytic lifetime at $140\,°C$; Bradley's poly(vinylpyrrolidone)-stabilized nanoclusters are capable of $100\,000$ total turnovers (TTO) [102], and

---

[6] As a third example, with the use of appropriate thiolates the solubility of thiolate-stabilized nanoclusters can be changed easily, ranging from water to nonpolar solvents [81]. Of course such nanoclusters are of little interest for catalysis because they are thiolate-poisoned (vide infra).

Nanoclusters as Soluble Analogs
of Heterogeneous Catalysts

Advantages:

- *Ease of study (and optimization) due to solubility and lack of support material*

- Relatively good activity under mild conditions

- High, ligand-modified selectivity possible

Disadvantages:

- *Relatively poor thermal stability*

- Problematic separation of the catalyst from the reaction mixture (*except for biphasic systems; see the discussion in the text*)

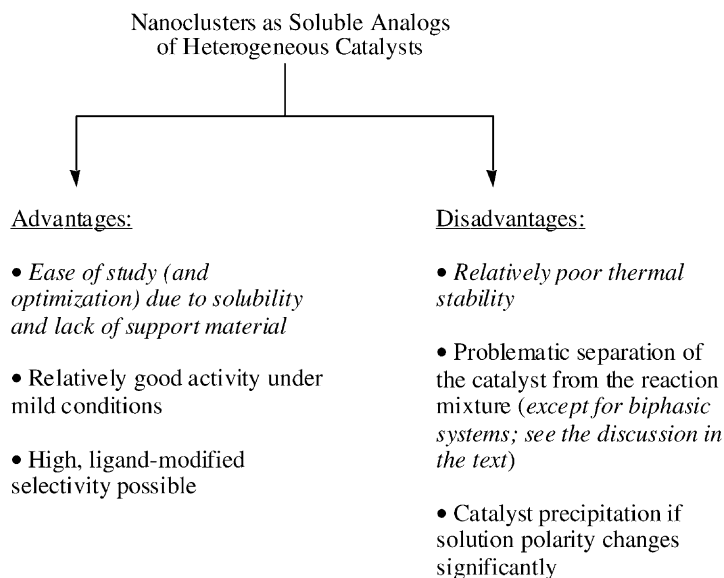- Catalyst precipitation if solution polarity changes significantly

Fig. 1. Some advantages and disadvantages of using nanoclusters as soluble analogs of heterogeneous catalysts.

Antonietti's [103] polystyrene-*b*-poly-4-vinylpyridine-stabilized (i.e., block copolymer-stabilized) nanoclusters are capable of at least 50 000 TTO. In contrast to these soluble nanocluster catalysts, metal particle catalysts on solid supports are routinely used at several hundred degrees Celsius; e.g., naphtha reforming with Pt/Al$_2$O$_3$ is performed industrially at 500 °C [98]. An added difficulty in the stabilization of soluble nanoclusters for catalysis is that the substrate must have some access to the nanocluster surface. Some types of stabilizers, such as thiols[7] [81,107–112] and silica[8] [113–120], effectively poison the nanoclusters.

Another disadvantage of soluble nanocluster catalysts is the problem of separating the catalyst from the reaction products; in this respect soluble nanocluster catalysts are similar to traditional homogeneous catalysts. Nevertheless, this separations problem is probably surmountable with the use of aqueous/organic biphasic systems (vide infra) or other modern immobilization systems for soluble catalysts. Two such modern immobilization systems are Horvath's [121–124] fluorous phase methods and Davis's [125,126] immobilization of homogeneous hydrophilic catalysts in thin films of hydrophilic liquids on a porous hydrophilic support (the reactants and products form a hydrophobic phase). Nanoclusters in biphasic organic substrate/ionic liquids are another possible solution to the problem of separat-

---

[7] Thiol-stabilized nanoclusters, often referred to as "monolayer-protected" clusters [81], can be repeatedly isolated and redissolved without agglomeration or decomposition, they can be chromatographed, and they are generally air- and solvent-stable [81]. Of course, the nanocluster surface is poisoned by the thiols, and so is of little interest for catalytic studies. However, there are reports describing the use of thiol ligands to tether homogeneous catalysts to nanoclusters, thereby making catalysis with such nanoclusters possible [110,111]. There is also a report of thiols anchoring nanoclusters to a silica support (i.e., Si–SH groups on the silica particles tether the nanoclusters to the silica surface), resulting in an alkene hydrogenation catalyst, presumably because it is not possible to achieve a full monolayer of thiol on the nanocluster under these conditions [112].

[8] The interesting silica-coated nanoclusters developed by Mulvaney and co-workers [113–117] have good thermal stability. It is

reported, for example, that gold nanoclusters coated with a 5 nm layer of silica show excellent stability against agglomeration at 70 °C (higher temperatures were not tested) [115]. More work is needed to determine if these nanoclusters will be of any use for catalysis, however. The silica layer appears to smoothly coat the entire surface of the nanocluster (see the electron micrographs in reference [116]), which would effectively poison it by limiting access of the substrate to the metal. However, the silica-coated metal core can be etched by cyanide or I$_2$ [118–120], demonstrating that at least small molecules can penetrate the silica layer.

ing the product from soluble nanocluster catalysts [127–129].[9]

A final disadvantage of soluble nanocluster catalysts is that they must remain in solution to be effective. This can be problematic, e.g., if the polarity of the solution changes during the course of the reaction, causing the nanoclusters to precipitate from solution (a phenomenon observed when using a batch reactor for the hydrogenation of cyclohexene with a record-lifetime Rh(0) nanocluster catalyst which showed 190 000 TTOs of cyclohexene hydrogenation [130]).

1.3. The historically perplexing problem of distinguishing soluble nanocluster catalysts from homogeneous, single-metal-complex catalysts

A problem that has caused considerable consternation in the study of arene hydrogenation catalysis is the difficult task of distinguishing homogeneous, single-metal-complex catalysts from soluble nanocluster or colloid (vide supra) catalysts. The literature in this area dates back to about 1980 and includes contributions from Maitlis [131], Whitesides [132,133], Crabtree [134–136], Collman [42,137], Lewis [138,139] and our group [140,141]. A more general approach for distinguishing the two was developed only recently [140,141], and involves the four-pronged approach outlined in Fig. 2. This method emphasizes: (1) the early use of TEM as a simple, powerful (but before the 1994 study [140], underutilized) way to detect soluble nanoclusters; (2) kinetic studies (because catalysis is a wholly kinetic phenomenon [142,143]); (3) catalyst poisoning experiments using mercury or added ligand (PPh$_3$, CS$_2$, H$_2$S, etc.),[10] especially if performed quantitatively

(the mercury test is easy to perform and is perhaps the best single test for metal particle catalysis, but it is not definitive by itself because mercury can react with single-metal-complexes [133]); and (4) the important concept that *the identity of the true catalyst will be consistent with all the data.*

There are now several examples in the literature of arene hydrogenation catalysts that were initially believed to be homogeneous, but later evidence suggests that a soluble nanocluster is the true catalyst. Perhaps the best example is the important arene hydrogenation catalyst based on RhCl$_3$ and [(C$_8$H$_{17}$)$_3$NCH$_3$]Cl [144,145]. Initially, it was believed that the [(C$_8$H$_{17}$)$_3$NCH$_3$]$^+$[RhCl$_4$]$^-$ ion-pair was the true arene hydrogenation catalyst [144]. Later work using the more general approach to the "is it homogeneous or heterogeneous catalysis problem" [140] mentioned above, including TEM plus powerful solution-phase kinetic studies, convincingly shows that the true catalyst is actually a distribution of Rh(0) nanoclusters stabilized by Cl$^-$ and [(C$_8$H$_{17}$)$_3$NCH$_3$]$^+$ [43].

A second example involves the use of [Rh(η^5-C$_5$Me$_5$)Cl$_2$]$_2$ for arene hydrogenation [146,147]. The catalyst in this system was originally claimed to be homogeneous on the basis of light scattering experiments. However, later work suggests that the true catalyst may be heterogeneous, though the evidence is not definitive [44]. 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 nanoparticle formation [140,141]; (iii) the deposition of Rh metal on the reactor walls, an observation which virtually demands the formation of Rh$_n$ nanoparticles since the precatalyst is monometallic [140,141]; 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 [44].

A third example involves Ru$_2$Cl$_2$(μ-H)$_2$(μ-Cl)(η^6-C$_6$Me$_6$)$_2$ as a precatalyst for arene hydrogenation

---

[9] It is unclear if the true catalyst in Reference [127] employing [H$_4$Ru$_4$(η^6-C$_6$H$_6$)$_4$][BF$_4$]$_2$ as the precatalyst, is a nanocluster or not.

[10] Though underutilized, poisoning experiments using added ligands, such as PPh$_3$, CS$_2$ and H$_2$S, can be powerful if performed quantitatively [140]. If a catalyst can be completely poisoned with $\ll 1.0$ equivalent of the added ligand (per metal atom), then this is excellent evidence for a heterogeneous, metal particle catalyst. The logic here is that in a metal particle catalyst only a fraction of the metal atoms are on the surface; hence, even if every surface atom is active, $\ll 1.0$ equivalent of ligand will be sufficient to poison the catalyst. On the other hand, if ≥ 1.0 equivalent of ligand is required to completely poison the catalyst that is com-

pelling evidence that the catalyst is a homogeneous, probably even monometallic, catalyst (and if control experiments show that the added ligand is unable to dissociate authentic nanoclusters of the same metal). See elsewhere [140,141] for a prototypical example of how this "fractional poisoning" experiment can be used to identify a nanocluster catalyst.
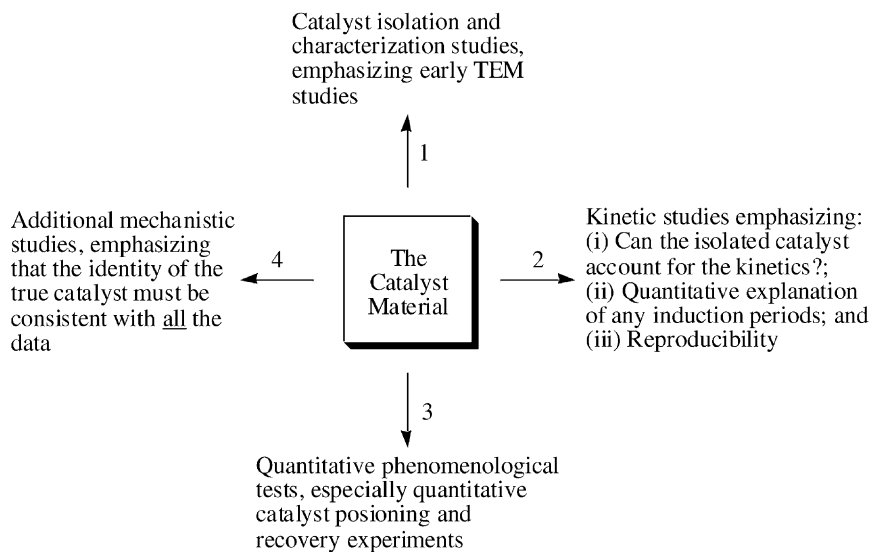
Fig. 2. A more general approach to distinguishing between a "heterogeneous" nanocluster (colloid) catalyst and a discrete, "homogeneous" catalyst.

[148,149]. This catalyst was originally thought to be homogeneous; however, a later study shows that the catalyst is inactive in the presence of elemental mercury [45], implying that the catalyst is colloidal in nature [140,150].[11] A fourth example involves the use of $Ru(\eta^6-C_6Me_6)(O_2CMe)_2$ for benzene hydrogenation [151–154]. Early catalytic studies [151,152] were unable to determine the nature of the true catalyst [151], but recent work, including TEM and kinetic studies, shows that the true catalyst is colloidal Ru [154]. These examples show that soluble nanoclusters are fairly pervasive in known ("homogeneous") arene hydrogenation. On this basis alone nanocluster arene hydrogenation catalysts merit further study.

The problem of distinguishing homogeneous vs heterogeneous catalysis is not limited to arene hydrogenation catalysis. The pervasiveness of this problem in

catalytic science is illustrated by the identification of *homogeneous species* as the true catalysts for initially *heterogeneous* oxidation catalysts based on molecular sieves [155,156], and for carbonylation and Heck coupling catalysts where Pd/C and Pd/Al₂O₃ are the *precatalysts* [157].

2. The use of soluble transition-metal nanoclusters as arene hydrogenation catalysts

2.1. Introduction and description of the nanocluster catalysts

Most arene hydrogenation to date has been done with traditional heterogeneous catalysts [3,6]. However, the use of soluble transition-metal nanoclusters for arene hydrogenation has increased dramatically in recent years [12–14,27,28,43,45,158–168]. To the best of our knowledge, Table 1 shows a complete list of the papers (including brief descriptions) in chronological order dealing with monocyclic arene hydrogenation with soluble nanocluster catalysts.

Much of the work using soluble nanocluster arene hydrogenation catalysts follows a seminal paper by Januszkiewicz and Alper [158]. The colloidal nature of the catalyst was not known at the time of this 1983

---

[11] Additionally, and in hindsight, poisoning experiments reported in the original study [149] are more consistent with the hypothesis that the catalyst is colloidal than with the hypothesis that it is homogeneous. For example, the presence of only 0.05 equiv. 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 equiv. of thiophene) [149]. Such a result is difficult to explain for a homogeneous catalyst, but makes perfect sense for a nanocluster catalyst where only a fraction of the total metal atoms are on the surface and active (see footnote 10).

Table 1
Summary of monocyclic arene hydrogenation with soluble nanocluster catalysts

	Authors (publication date)	System	Results	Reference
1	K.R. Januszkiewicz, H. Alper (1983)	This is an important paper because much of the other work in the area is based directly upon it. The precatalyst is [RhCl(1,5-hexadiene)]$_2$ and a tetraalkylammonium halide. Several substrates were tried, including benzene, o-xylene, p-methylanisole and phenol. The conditions are room temperature and 1 atm H$_2$; biphasic benzene/water or hexane/water is the reaction medium. The authors do not probe whether or not the catalyst is homogeneous or heterogeneous, but in a 1984 paper by the same authors they suggest that the actual catalyst is "a highly active form of colloidal rhodium", and reference "unpublished results". Use of variations of this catalyst system (see below) by later groups, who recognize its colloidal nature, makes it fairly certain that the catalyst described in this paper is indeed colloidal.	Up to 100 TTO are demonstrated for some substrates; pH is shown to be an important variable. No activity is given (i.e., the authors do not say how long their hydrogenation experiments last) so the catalytic results cannot be compared to later work. Only the *cis* product is observed in the hydrogenation of 2-methylanisole (at 92% yield).	[158]
2	J. Foise, R. Kershaw, K. Dwight, A. Wold (1985)	In this study the electrochemical reduction of benzene is combined with direct catalytic hydrogenation of benzene. Platinum and ruthenium colloids are used as the hydrogenation catalysts in solution and are prepared from the decomposition of Pt and Ru sulfite acid solutions. The conditions are room temperature and 1.7 atm H$_2$. The solvent is ethanol mixed with HMPA.	Only the ruthenium colloids are active. However, the colloids are poorly characterized by today's standards and it is not possible to calculate an activity or lifetime for the hydrogenation.	[159]
3	Z. Duan, M.J. Hampden-Smith, A.P. Sylwester (1992)	[(1,5-COD)RhH]$_4$ is synthesized from [(1,5-COD)RhCl]$_2$ and used as a precursor for 2 nm sized colloids. NMR monitoring of the loss of [(1,5-COD)RhH]$_4$ and the evolution of cyclooctane shows that hydrogenation activity is still seen after all of the [(1,5-COD)RhH]$_4$ is gone, leading the authors to conclude that the nanoclusters are the (primary) active species. Cyclohexane-d$_{12}$ is sometimes used as a solvent. Toluene is the primary substrate, but benzene and pyridine are also used. The conditions are room temperature and 1 atm H$_2$.	A lifetime of at least 127 TTO is demonstrated, though this seems to be based on substrate/[(1,5-COD)RhH]$_4$, not on substrate/Rh atom. The authors calculate an activity of 1.83×10^{-3} molecules of toluene/(Rh atom·s), which is compared to a literature value of benzene hydrogenation with Rh/Al$_2$O$_3$ of 9.6×10^{-4} molecules of benzene/(Rh atom·s). Assuming a crystallite size of 2 nm, the authors calculate an activity of 2.3×10^{-3} molecules of toluene/(Rh surface atom·s). TEM shows the presence of agglomerated 2 nm sized nanoclusters.	[160]
4	P. Drognat Landré, M. Lemaire, D. Richard, P. Gallezot (1993)	The precatalyst is RhCl$_3$·3H$_2$O in the presence of Aliquat 336 (tricaprylylmethyammonium chloride) and/or trioctylamine. Dibenzo-18-crown-6 ether is the only substrate. The conditions are room temperature and 1–50 atm H$_2$; biphasic CH$_2$Cl$_2$/water is the solvent.	The authors demonstrate the hydrogenation of about 20 mol of crown ether per mole of Rh in <1 h. TEM shows the presence of nanoclusters in the 2–3 nm size range. At higher pressure, the stereoselectivity increases to a 95/5 ratio of the *syn/anti* isomers of the dicyclohexyl-18-crown-6 ether.	[161]

5	K. Nasar, F. Fache, M. Lemaire, J.C. Beziat, M. Besson, P. Gallezot (1994)	The precatalyst is $RhCl_3 \cdot 3H_2O$ in the presence of Aliquat 336 (tricaprylylmethyammonium chloride), trioctylamine or dioctylcyclohexylethylamine. The substrates are 2-methylanisole (for which the *cis/trans* hydrogenation selectivity is investigated) and *o*-cresol derivatives (for which the enantioselective hydrogenation is investigated). The conditions are room temperature and 1–50 atm H_2; biphasic CH_2Cl_2/water is the solvent.	The authors demonstrate 40 TTO in 24 h for the hydrogenation of 2-methylanisole. About 10% hydrogenolysis of the methoxy group of 2-methylanisole is observed. No activity is observed in the absence of water, but this may be due to the low solubility of $RhCl_3 \cdot 3H_2O$ in the organic phase. About 5% ee is observed in the enantioselective reductions using a chiral amine as the nanocluster stabilizer. TEM shows the presence of nanoclusters in the 2–3 nm size range.	[14]
6	P. Drognat Landré, D. Richard, M. Draye, P. Gallezot, M. Lemaire (1994)	The authors survey colloidal catalysts based on various metal chlorides ($RhCl_3$, $RuCl_3$, $NiCl_2$, $PdCl_2$, $IrCl_3$, K_2PtCl_6) with tertiary amines or Aliquat-336 (tricaprylylmethylammonium chloride) as the stabilizer. They also survey several supported heterogeneous catalysts (e.g., Ru/Al_2O_3, Rh/C, $Rh/SrTiO_3$). Dibenzo-18-crown-6 ether is the only substrate. The reaction conditions are varied from 25 to 60 °C and 1–50 atm H_2; the solvent is biphasic CH_2Cl_2/water.	The Rh colloids are by far the most active, exhibiting the hydrogenation of 20 mol of crown ether per mol of Rh in 42 min at 5 MPa H_2. The authors observe hydrogenolysis of the crown ether, the main reaction pathway under certain conditions. An increase of the hydrogen pressure to 5 MPa leads to a *cis–syn–cis/cis–anti–cis* isomer ratio of 95/5. TEM shows the presence of colloids. Also, a modified "Maitlis test" (a reaction rate comparison before and after filtration through a graphite powder) points to nanoclusters as the true catalyst.	[162]
7	F. Fache, S. Lehuede, M. Lemaire (1995)	The authors use $RuCl_3 \cdot 3H_2O$ (and $RhCl_3 \cdot 3H_2O$) in the presence of trioctylamine as the precursor to their colloidal catalyst. Several mono- and di-substituted benzene derivatives are hydrogenated (containing a variety of different functional groups), including 2-methylanisole and 2-methylbenzoate. The conditions are room temperature and 50 atm H_2; the solvent is methanol/water.	The authors appear to demonstrate about 40 TTO in 1 h for the most easily hydrogenated substrates (the data are not completely clear). The authors say that no hydrogenolysis is observed. The authors show that the activity of Ru/Al_2O_3 is 5- or 10-fold lower (on a per-metal-atom basis) than the colloidal catalyst. *Cis/trans* selectivities up to 60 are observed in the hydrogenation of di-substituted arenes. No attempt is made to characterize the putative nanocluster catalyst. It is noted that the rate is slower without water.	[13]
8	B.R. James, Y. Wang, T.Q. Hu (1996)	Much of this work is based on the catalyst system developed by Januszkiewicz and Alper (entry 1 in this table). $[RhCl(\eta^4\text{-}1,5\text{-hexadiene})]_2$, $[RhCl(\eta^4\text{-}1,5\text{-cyclooctadiene})]_2$, $RhCl_3 \cdot 3H_2O$, $Rh_6(CO)_{16}$ and $[Rh(OC_6H_5)(\eta^4\text{-}1,5\text{-cyclooctadiene})]_2$ are used as nanocluster precursors; tetrabutylammonium hydrogen sulfate is the nanocluster stabilizer. The substrates are 4-propylphenol, 2-methoxy-4-propylphenol and 2,6-dimethoxy-4-propylphenol. The reaction is performed in a biphasic (aqueous/organic) medium at 20 °C and 1 atm H_2.	The initial red or yellow solutions darken within 0.5 h to give the catalytically active solutions; over longer periods, bulk Rh metal precipitates with a resulting loss of activity. The formation of Rh metal, and a comparison to literature colloids (noting the necessity of the tetrabutylammonium hydrogen sulfate), are given as evidence that nanoclusters are the real catalyst. The TTO and TOF cannot be determined from the information given, but appear to be in the same range as later papers published by these researchers.	[163]

Table 1 (*Continued*)

	Authors (publication date)	System	Results	Reference
9	T.Q. Hu, B.R. James, S.J. Rettig, C.-L. Lee (1997)	This catalyst system is based on that of Januszkiewicz and Alper (entry 1 in this table). [RhCl(η^4-1,5-hexadiene)]$_2$ is the nanocluster precursor. A tetrabutylammonium salt is the nanocluster-stabilizing agent. The substrates are lignin model compounds: 4-propylphenol, 2-methoxy-4-propylphenol, and 2,6-dimethoxy-4-propylphenol. The reaction conditions include room temperature and 1–13.6 atm H$_2$; the solvent is biphasic hexane/water.	The authors demonstrate about 50 TTO in about 50 h at 1 atm H$_2$. The reaction time decreases to about 6 h at 13.6 atm H$_2$. No nanocluster characterization is done. The authors simply say, probably correctly, that "the active Rh catalyst is probably present in a colloidal form: as the hydrogenation proceeds, metal particles accumulate and these are not active for subsequent hydrogenation reactions". The all-*cis* diastereomer is obtained selectively when the phenolic hydroxyl group is protected as a methyl ether or when a model compound possessing two methoxy substituents adjacent to the phenolic hydroxyl group is used.	[164]
10	T.Q. Hu, B.R. James, C.-L. Lee (1997)	A water-soluble, polymer-stabilized, colloidal Rh catalyst is prepared by reducing RhCl$_3$·3H$_2$O with ethanol in the presence of polyvinylpyrrolidone and triethylamine. The substrates are benzyl acetone, 4-propylphenol, 2-methoxy-4-propylphenol, and 1,2-dimethoxy-4-propylbenzene. The reaction conditions include 25 °C and 1 atm H$_2$; monophasic, aqueous ethanol is the solvent.	The authors demonstrate about 50 TTO for the hydrogenation of benzyl acetone in <43 h. About 20% hydrogenolysis is observed for compounds with methoxy groups. The authors attempt to use small, *neutral* organic molecules to stabilize their colloids, but with little success. The polymer-stabilized nanoclusters are prepared using a literature method, and no further characterization of the catalyst is done.	[27]
11	T.Q. Hu, B.R. James, C.-L. Lee (1997)	This work is based on that of Januszkiewicz and Alper (entry 1 in this table). [RhCl(η^4-1,5-hexadiene)]$_2$ is the primary catalyst precursor. A tetrabutylammonium salt is used as the nanocluster-stabilizing agent. The authors describe the hydrogenation of benzyl acetone, 4-propylphenol, eugenol, 1,2-dimethoxy-4-propylbenzene, and 2,6-dimethoxy-4-propylphenol under mild conditions (25 °C, 1 atm H$_2$) in a biphasic (water/hexane) medium at pH 7.5.	The authors demonstrate about 50 TTO in <24 h for the hydrogenation of benzyl acetone. Moderate to high diastereoselectivities are observed for the hydrogenated products; only the all-*cis* diastereomer is obtained for substrates where the phenolic hydroxyl group is protected as a methyl ether or where the substrate possesses two methoxy substituents adjacent to the phenolic hydroxyl group. [RhCl(η^4-1,5-cyclooctadiene)]$_2$, RhCl$_3$·3H$_2$O and RuCl$_3$·3H$_2$O are found to be less active precatalysts.	[28]
12	K.S. Weddle, J.D. Aiken III, R.G. Finke (1998)	This paper re-examines a putative "homogeneous" arene hydrogenation catalyst developed by others (J. Org. Chem. 52 (1987) 2804). Several experiments (TEM, reaction kinetics, Hg poisoning, H/D exchange) provide definitive evidence for Rh(0) nanoclusters being the true catalyst when using RhCl$_3$·3H$_2$O and trioctylamine and Aliquat 336 as the catalyst precursor. Benzene is the only substrate used in this paper (benzene and anisole were the primary substrates in the 1987 J. Org. Chem. paper). Reaction conditions include 30 °C and 0.9 atm H$_2$; the reactions are done in biphasic dichloroethane/water or in monophasic THF.	A total of 40 TTO are demonstrated in an experiment where the catalyst is re-used once (i.e., after doing 20 TTO in about 2 h, more benzene is added and another 20 TTO are demonstrated in an additional 4 h). Additional notes from the 1987 J. Org. Chem. paper: those authors say that, "In general, hydrogenation of benzenes did not give partially hydrogenated products . . . . Cyclohexene derivatives were, however, isolated when sterically hindered compounds were reduced". The J. Org. Chem. authors see a big water effect on the catalytic activity and say that a minimum of 2 equiv. of water (in addition to the waters of hydration on the RhCl$_3$·3H$_2$O) are necessary for activity; H/D exchange between water and substrate occurs under catalytic conditions.	[43]

13	B.R. James, Y. Wang, C.S. Alexander, T.Q. Hu (1998)	The nanoclusters are synthesized from $RhCl_3 \cdot 3H_2O$, $[RhCl(diene)]_2$ or $RuCl_3/(n\text{-}C_8H_{17})_3N$. A Ziegler-Natta catalyst and a Bennett-type Ru catalyst are also tried. The nanocluster stabilizers are tetraalkylammonium salts, R_4NX (R = alkyl, X = Cl, Br or HSO_4). The substrates are 4-propylphenols (used as lignin model compounds) and "milled wood lignin". Reaction conditions include 1–50 atm H_2 and 20–100 °C; biphasic (aqueous/organic) solvent systems are used.	This paper discusses the effects of water in detail. D-labeling studies show that some of the H in the product comes from water. Hydrogenolysis of the methoxy group is observed. The authors demonstrate up to 300 TTO in 24 h for the hydrogenation of 2-methoxy-4-propylphenol with $RuCl_3/(n\text{-}C_8H_{17})_3N$ as the catalyst. Some *cis/trans* selectivity is observed.	[45]
14	J. Schulz, A. Roucoux, H. Patin (1999)	What separates this system from several of the others is the use of *hydroxy*alkylammonium bromide salts (which are highly water soluble) as the nanocluster stabilizer. The nanoclusters are synthesized by reducing $RhCl_3 \cdot 3H_2O$ with $NaBH_4$ in dilute aqueous solutions of the hydroxyalkylammonium salts. The organic phase apparently consists of just the substrate and products. Various mono- and di-substituted arenes are hydrogenated including benzene, toluene, anisole and xylene. The conditions include 20 °C and 1 atm H_2; the reaction solutions are biphasic (aqueous/organic).	The nanoclusters have an average diameter of 3.6 nm by TEM. The authors demonstrate 1000 TTO for anisole hydrogenation in 47 h. Some *cis/trans* selectivity is observed for the hydrogenation of multiply substituted arenes. No hydrogenolysis products are seen.	[165]
15	R.-W. Albach, M. Jautelat (1999)	In this patent nanoclusters are synthesized from a number of different precursors [$RuCl_3$, $RhCl_3$, $PdCl_2$, $NiBr_2$, $Pd(OAc)_2$]. The sulfobetaine 3-(dodecyldimethylammonium)propanesulfonate was used as a nanocluster stabilizer. Substrates include isopropylbenzene and benzene. The reaction conditions include 50–180 °C and 10–400 atm H_2; the reaction solutions are biphasic (aqueous/organic).	The authors appear to demonstrate 200 TTO for the hydrogenation of benzene and isopropyl benzene.	[12]
16	J. Schulz, A. Roucoux, H. Patin (2000)	This is the follow-up full paper to these authors' 1999 Chem. Commun. paper (see entry 14 in this table). The nanoclusters are synthesized by reducing $RhCl_3 \cdot 3H_2O$ with $NaBH_4$ in dilute aqueous solutions of the hydroxyalkylammonium salts. Various mono- and di-substituted arenes are hydrogenated including benzene, toluene, anisole and xylene. The conditions include 20 °C and 1 atm H_2; the reaction solutions are biphasic (aqueous/organic).	The nanoclusters are 2–2.5 nm in diameter by TEM. The metal particle nature of the catalyst is confirmed with a Hg(0) poisoning experiment. No hydrogenolysis products are formed. The activity of the nanocluster catalyst for anisole hydrogenation is compared with the activity of Hirai's polymer-stabilized Rh nanoclusters and with 5% Rh/C, all under identical conditions. The authors observe a TOF of $20\,h^{-1}$ for Rh/C, of $47\,h^{-1}$ for the PVP stabilized nanoclusters, and of $60\,h^{-1}$ for the nanoclusters. The Rh nanoclusters give 2000 TTO for anisole hydrogenation in 37 h. The maximum TOF for the same experiment is 188 mol H_2/(mol Rh·h). *Cis/trans* selectivities up to 99:1 are observed for the hydrogenation of di-substituted benzenes.	[166]

Table 1 (*Continued*)

	Authors (publication date)	System	Results	Reference
17	R.J. Bonilla, P.G. Jessop, B.R. James (2000)	$[RhCl(1,5\text{-}COD)]_2$ is the nanocluster precursor and tetrabutylammonium hydrogen sulfate is the surfactant and nanocluster stabilizer. Several arenes are used as substrates, including lignin model compounds, anisole, phenol and *p*-xylene. The reaction conditions include 36 °C and 10 atm H_2. The reactions are performed in a biphasic aqueous/supercritical ethane reaction medium.	The authors demonstrate as many as 110 TTO in 62 h for the hydrogenation of benzyl alcohol. Some *cis/trans* selectivity is observed for the hydrogenation of multiply substituted arenes. The nanoclusters are not characterized.	[167]
18	J.A. Widegren, R.G. Finke	The nanocluster catalyst is formed in situ by reducing $[Bu_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$ with H_2 in a monophasic propylene carbonate solution, which gives polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters. Anisole is the only substrate. The reaction conditions include 22 °C and 3.7 atm H_2; propylene carbonate is the solvent.	With 10 equiv. (vs Rh) of $HBF_4 \cdot Et_2O$ added, the authors demonstrate 2600 TTO for anisole hydrogenation in 144 h. The Rh(0) nanoclusters are shown by TEM to have an average diameter of between ∼4 and 6 nm, depending on the nanocluster formation conditions. A combination of hydrogenation kinetics and the kinetics and stoichiometry of nanocluster formation provide excellent evidence that the nanoclusters are the true catalyst. These nanoclusters also display an unprecedented selectivity for the partial hydrogenation of anisole to 1-methoxycyclohexene, with initial selectivities of ∼30% and overall yields up to 8%.	[168]

paper, but these authors insightfully suggest in 1984 paper that the true catalyst is "a highly active form of colloidal rhodium" [169]. (Additional study by others on very similar systems, and where colloidal Rh is also identified [28,45,163,164], leaves little doubt that Rh(0) nanoclusters are the true arene hydrogenation catalyst.) Januszkiewicz and Alper performed hydrogenations under biphasic, aqueous/organic reaction conditions using [RhCl(1,5-hexadiene)]$_2$ as the precatalyst, and tetraalkylammonium hydrogen sulfate or tetraalkylammonium bromide as the phase transfer agent and nanocluster stabilizer. Note here: (i) that halide and tetraalkylammonium salts are well-known, widely used nanocluster stabilizers [48,49]; and (ii) there is a close correspondence of this system to established Rh(0) nanocluster systems [28,45,163,164]. Using mild reaction conditions (room temperature, 1 atm H$_2$) Januszkiewicz and Alper [158] demonstrated up to 100 TTO for a variety of arenes. Unfortunately, no reaction times were given, so the catalytic activity or turnover frequency (TOF, i.e., turnovers divided by time) is unknown.

A perusal of the literature studies of soluble nanocluster arene hydrogenation catalysis in Table 1 demonstrates the following points: (i) most studies use Rh(0), which is not surprising because the literature of heterogeneous arene hydrogenation generally shows Rh to be the most active metal [36,37,170]; (ii) Ru(0) nanoclusters are the second most common catalyst in this literature, paralleling the extensive use of Ru in the heterogeneous catalysis of arene hydrogenation; (iii) the three most commonly used nanocluster precursor compounds are [RhCl(diene)]$_2$, RhCl$_3$·3H$_2$O and RuCl$_3$·3H$_2$O; and (iv) most soluble nanocluster arene hydrogenation catalysts use tetraalkylammonium salts to stabilize the nanoclusters against agglomeration. In addition: (v) the reaction conditions are typically mild (approximately room temperature and 1 atm H$_2$) and often biphasic (aqueous/organic); and (vi) there is scant (often nonexistent), characterization of the nanocluster catalyst in most studies.

Additionally, there is often little to no compelling evidence that nanoclusters are indeed the active catalyst—recall the earlier discussion and (Fig. 2) concerning the problem of distinguishing homogeneous, single-metal-complex catalysts from soluble nanocluster catalysts. We recommend the following minimum criteria for any work that claims the use of nanoclusters for catalysis. First, there must be evidence that nanoclusters are present during catalysis; TEM is the single most powerful technique for this purpose. Second, there must be kinetic evidence that the nanoclusters are the actual catalyst. If properly performed [43,140,150], poisoning studies can be used for this purpose (the underutilized fractional poisoning experiment described in footnote 10 is particularly powerful). It is instructive to re-examine Table 1 with these criteria in mind. Only five [43,160,162,166,168] of the 18 papers in Table 1 satisfy both criteria.

A final issue is the general lack of information regarding reproducibility for these nanocluster catalysts. Are reproducible results obtained from different laboratories on the same system? To date, only one of the nanocluster catalysts described herein has been studied by two different laboratories under the exact same conditions [43,144]. In that case the catalytic results were reproducible [43,144]. Nevertheless, more information about the repeatability of these nanocluster catalysts is needed.

2.2. Catalytic lifetime and activity of the nanocluster catalysts for the hydrogenation of monocyclic arenes

Practical catalytic applications as well as mechanistic studies of meaningful catalysts both require a reasonable catalyst lifetime. Table 1 documents that, to date, most of the literature systems using soluble nanoclusters as arene hydrogenation catalysts have modest lifetimes at best, generally in the range of ≤100 TTO. Two nanocluster systems in Table 1 are exceptional in that they are capable of ≥2000 TTO. The first of these longer-lived nanocluster catalysts was developed by Roucoux and co-workers [165,166] (Eq. (3)), and the second was developed in our own labs [168] (Eq. (4)). These two catalyst systems are discussed in detail next.

The nanocluster catalyst developed by Roucoux and co-workers [165,166] is formed by the reduction of RhCl$_3$·3H$_2$O with NaBH$_4$ in an aqueous solution of N-alkyl-N-(2-hydroxyethyl)ammonium bromide. TEM shows the presence of nanoclusters with a diameter of 2–2.5 nm [166]. Adding a large excess of Hg(0) to a catalytically active solution after 50% conversion completely deactivates the catalyst [166], a single piece of good evidence that the Rh

nanoclusters are the true catalyst [43]. Compelling kinetic or fractional poisoning evidence for nanocluster catalysis is not available, however, and would be of interest for this important catalyst. The arene hydrogenations were performed as biphasic (aqueous/organic) reactions simply by adding the substrate to an aqueous solution of the nanoclusters. The nanoclusters remain in the aqueous phase because of the water-solubility of the nanocluster stabilizing agent, *N*-alkyl-*N*-(2-hydroxyethyl)ammonium bromide; the organic substrate and products form the second phase in the reaction. Because of the biphasic reaction solution, the nanocluster catalyst can be separated from the reaction products by simple decantation. This experimental design is a possibly general way to overcome the problematic catalyst/product separation discussed earlier (Fig. 1). Roucoux and co-workers [166] demonstrate 2000 TTO for anisole (methoxybenzene) hydrogenation in 37 h at 20 °C and 1 atm H_2, with a reported selectivity to methoxycyclohexane of 100% (determined by GC analysis) (Eq. (3)). It is not stated if the catalyst is still active after 2000 TTO, although it appears that it probably is. For the lifetime experiment the average TOF is 54 mol anisole converted/(mol of Rh·h), the highest known TOF for monocyclic arene hydrogenation with a soluble nanocluster catalyst.


$$(3)$$
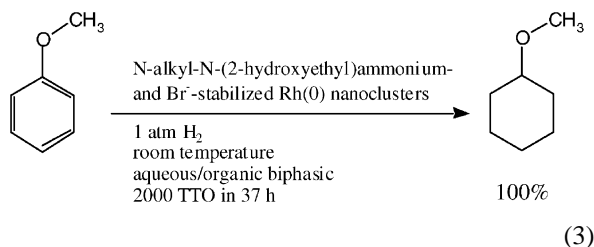
The other best soluble nanocluster arene hydrogenation catalyst in terms of catalytic lifetime was developed in our own labs [168] (Eq. (4)). The nanocluster catalyst is formed in situ by reducing $[Bu_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$ with H_2 in a monophasic propylene carbonate solution. The resulting polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters are shown by TEM to have an average diameter between ∼4 and 6 nm, depending on the nanocluster formation conditions [168]. A combination of TEM, hydrogenation kinetics, and the kinetics and stoichiometry of nanocluster formation provide compelling evidence that

nanoclusters are the true catalyst.[12] Polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters [130,171] were previously known to have a record catalytic lifetime in solution for olefin hydrogenation [130]. Consequently, it is not surprising that they also have a relatively long lifetime for arene hydrogenation in solution. With 10 equiv. (vs Rh) of $HBF_4 \cdot Et_2O$ added, 2600 TTO are demonstrated for anisole hydrogenation in 144 h at 22 °C and 3.7 atm of H_2 [168], which corresponds to an average TOF of 18 mol anisole converted/(mol of Rh·h). Although this anisole hydrogenation reaction went to completion (2600 TTO), preliminary experiments with larger amounts of substrate have failed to give more than this modest 2600 TTO [172].

The development of soluble nanocluster catalysts with better lifetime and activity for arene hydrogenation remains an important goal. In this respect, state-of-the-art soluble nanocluster catalysts lag behind some types of supported catalysts. For example, Angelici and co-workers [173] recently reported the use Rh complexes tethered to the SiO_2 of Pd/SiO_2 for the hydrogenation of anisole. They demonstrate 14 500 TTO in 6 h at 70 °C and 4 atm of H_2, which corresponds to an average TOF of 2400 mol anisole converted/(mol of Rh·h). Although more forcing reaction conditions are used, the absolute performance of Angelici's catalyst is clearly better than the best soluble nanocluster catalysts known for the hydrogenation of anisole. A second example is Ahn and Marks' [174] heterogeneous arene hydrogenation catalyst consisting of an organozirconium complex chemisorbed on sulfated

---

[12] Briefly, the evidence for nanocluster catalysis includes: (i) a quantitative curve fit of the precatalyst concentration vs time to the nucleation (A → B, rate constant k_1) and autocatalytic surface-growth (A + B → 2B, rate constant k_2) mechanism that is the *kinetic signature for nanocluster formation from a monometallic precatalyst* ("A") *when using H_2 as the reductant* [43]; (ii) direct confirmation of the expected stoichiometry of reduction of the precatalyst $[Bu_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$ with H_2 using GC analysis for cyclooctane formation and H_2 gas-uptake experiments; (iii) TEM confirmation that nanoclusters are indeed product "B" formed from the reduction of the precatalyst; (iv) the observation of induction periods that are identical within experimental error for the nanocluster formation reaction and the arene hydrogenation reaction; and (v) catalytic arene hydrogenation activity long after the precatalyst, $[Bu_4N]_5Na_3[(1,5\text{-}COD)Rh \cdot P_2W_{15}Nb_3O_{62}]$, has been completely consumed by reduction.

(4)
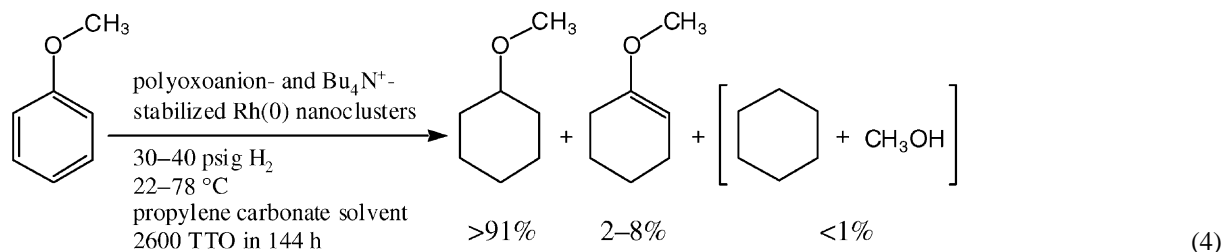
zirconia. They demonstrate an initial TOF of 970 mol benzene converted/(mol of Zr·h) at 25 °C and 1 atm of H_2 (no TTO was reported for this catalyst). Even under these mild, directly comparable conditions, the activity of Ahn and Marks' catalyst is more than an order of magnitude better than the most active nanocluster catalyst.

2.3. Selectivity studies

Much of the effort in monocyclic arene hydrogenation with soluble nanocluster catalysts has been towards selective hydrogenation. Several types of selectivity have been studied: (i) the hydrogenation of arenes with two or more substituents on the benzene ring allows for selectivity to *cis* or *trans* diastereomers in the hydrogenated products; (ii) multi-substituted arenes can also contain prochiral carbons on the benzene ring, so enantioselective hydrogenation is possible; (iii) side reactions such as the hydrogenolysis of substituents can compete with the arene hydrogenation, so that there is a selectivity issue there; (iv) selectivity for the partial hydrogenation of arenes (to form cyclic olefins) is also possible. Each of these types of selectivity will be considered in the following sections.
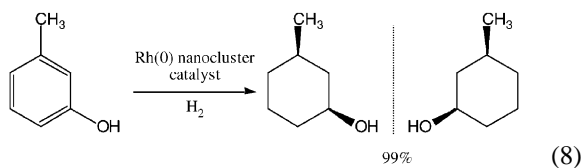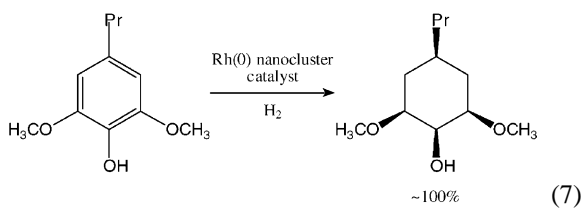
2.3.1. Cis/trans diastereomers

The most widely studied type of selectivity in the hydrogenation of monocyclic arenes with soluble nanocluster catalysts is the selectivity for the formation of *cis* diastereomers in the hydrogenation of di- or multi-substituted benzenes (Table 1). Arenes hydrogenated with metal particles are known to favor formation of the thermodynamically less favorable all-*cis* diastereomer [162]. This selectivity is rationalized by a continuous coordination of the substrate to the catalyst during hydrogenation, leading to the addition of hydrogen to only one "face" of the arene [164]. The studies of nanocluster catalysis have typically used

di-substituted benzenes such as 2-methylanisole or xylenes. Without exception, the all-*cis* diastereomer is the major product; *trans* diastereomers, commonly observed as minor products, are formed when a partially hydrogenated intermediate dissociates from the catalyst surface and then re-associates with the opposite "face" before further hydrogenation [36].

Several nanocluster catalysts display high selectivity for the *cis* diastereomer, as the following examples demonstrate. Januszkiewicz and Alper [158] obtained *cis*-4-methylcyclohexyl methyl ether as the only product (in 92% yield) from the hydrogenation of 4-methylanisole (Eq. (5)). Lemaire and co-workers [14] found that the *cis* diastereomer was formed with selectivities of >97% for the hydrogenation of 2-methylanisole (Eq. (6)). James and co-workers [164] found that the all-*cis* diastereomer was formed exclusively in the hydrogenation of 2,6-dimethoxy-4-proplyphenol (Eq. (7)). Roucoux and co-workers [166] observed a *cis/trans* ratio of 99:1 in the hydrogenation of *m*-cresol (Eq. (9)). Note that the lack of a mirror plane in the reactant of Eqs. (6) and (8) leads to the formation of both enantiomers of the *cis* diastereomer.

92%   (5)

>97%

(6)

$$\sim 100\% \qquad (7)$$

$$99\% \qquad (8)$$
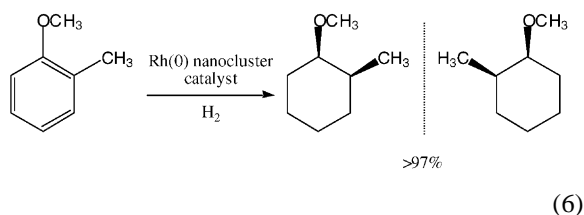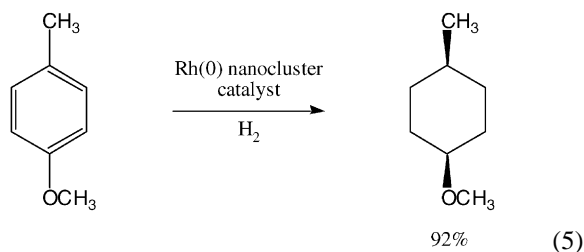
Traditional heterogeneous metal particle catalysts are also known to favor the formation of the *cis* diastereomer [162,175]. Using heterogeneous catalysts it was found that the ratio of *cis–trans* diastereomers was affected by: (i) the identity of the metal; (ii) the nature and position of the substituents; and (iii) the reaction temperature (lower temperatures favored the *cis* diastereomer) [162,175]. It is not clear if all the same trends will hold for soluble nanocluster catalysts. It is also not clear how the selectivities of the traditional heterogeneous metal particle catalysts compare to the selectivities of soluble nanocluster catalysts. Although three of the studies using nanocluster catalysts also use heterogeneous catalysts, either the reaction conditions are different for the two kinds of catalysts [162], or no selectivities are reported for the heterogeneous catalysts [13,166]; hence, more comparisons of selectivity between the same metal nanocluster and supported metal heterogeneous catalysts, under otherwise identical conditions, would be useful. Overall, the high diastereoselectivities commonly observed for nanocluster arene hydrogenation catalysts makes them promising as a way to produce the kinetically controlled *cis* isomers of a variety of cyclohexanes in smaller scale, fine chemical applications.

2.3.2. Enantioselectivity

The enantioselective hydrogenation of arenes with soluble nanoclusters has apparently only been attempted once [14].[13] In that study *o*-cresol deriva-

tives were enantioselectively reduced using Rh(0) nanoclusters. Enantioselectivity was induced either by covalently binding a chiral auxiliary, menthoxyacetic acid, to the substrate or by using a chiral amine, R-(−)-dioctylcyclohexyl-1-ethylamine, as the nanocluster stabilizer. When the chiral auxiliary was added, a very modest enantiomeric excess of 10% was observed. Smaller enantiomeric excesses were observed in experiments using the chiral amine stabilizer. Obviously, these enantiomeric excesses are too small for useful preparative chemistry. However, future work in this area will very likely yield better nanocluster asymmetric arene hydrogenation catalysts, an interesting topic for further research and perhaps one of the best opportunities for fine chemical synthesis from nanocluster catalyzed arene hydrogenation.
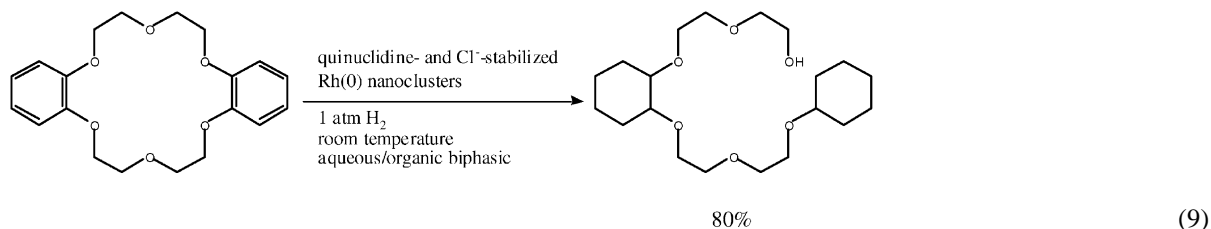
2.3.3. Hydrogenolysis vs hydrogenation

Hydrogenolysis is commonly observed as a side reaction in the hydrogenation of some types of substituted arenes (e.g., aryl ethers). Generally, hydrogenolysis is slow compared to the hydrogenation reaction. There is, however, one noteworthy exception to this rule in the literature of arene hydrogenation with soluble nanoclusters. For the hydrogenation of dibenzo-18-crown-6 ether with Rh(0) nanoclusters, Lemaire and co-workers [162] found that under certain conditions the main product is a hydrogenolysis product (Eq. (9)). The uses or value of such compounds were not stated or studied, however [162].

2.3.4. Partial hydrogenation

As mentioned in Section 1, the partial hydrogenation of monocyclic arenes is an important goal in arene hydrogenation [3,18,19]. Unfortunately, the valuable partial hydrogenation products are rarely observed when using soluble nanocluster catalysts. There are only two reports in the literature of soluble nanocluster catalysts that yield observable amounts of partial hydrogenation products [144,168]. In the first report Blum et al. [144] simply note that cyclohexene derivatives are observed only when very sterically hindered substrates like durene (1,2,4,5-tetramethylbenzene) are hydrogenated—sterically bulky substrates dissociate more readily from the catalyst surface and,

---

[13] In a related case, bovine serum albumin was used as an additive in an attempt to induce chirality in the hydrogenation of acetophenone [158]. Unfortunately, the hydrogenation afforded only racemic products. In addition, the prochiral carbon in acetophe-

none is not in the benzene ring, so this reduction is not an enantioselective *arene* hydrogenation.

quinuclidine- and Cl⁻-stabilized
Rh(0) nanoclusters

1 atm H₂
room temperature
aqueous/organic biphasic

80%   (9)

therefore, favor partial hydrogenation. Recall that the true arene hydrogenation catalyst in this system was later found to be a nanocluster catalyst [43]. In the other available report, the partial hydrogenation of anisole was observed when polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters were used as the catalyst [168], an unprecedented selectivity among known soluble nanocluster catalysts [176].[14] The partial hydrogenation product, 1-methoxycyclohexene, was formed with an initial selectivity of ~30% and overall yields up to 8% [168]. Although the selectivity and yield are modest, this system is of interest as a model for the study of the many important variables that increase selectivity to the monoene in the partial hydrogenation of monocyclic arenes with heterogeneous catalysts (e.g., higher temperatures, added H_2O or glycol solvents, added salts, H_2 mass-transfer (i.e., H_2-starved) conditions, or pH [3,18,19]). Temperature is an especially important variable, with a ~70% selectivity

for benzene to cyclohexene being observed at 200 °C vs a ~5% selectivity at 50 °C when using a heterogeneous Ru catalyst [19]. Hence, the development of high-temperature stable nanocluster arene hydrogenation catalysts for monoene production is another important goal, as is further study of polyoxoanion and other ligand-modified nanoclusters as high selectivity catalysts (see footnote 14).

3. Summary and future outlook

The major findings of this review of arene hydrogenation with soluble nanocluster catalysts are: (i) soluble nanocluster catalysts have been identified as the true catalysts in several putatively "homogeneous" arene hydrogenation systems, suggesting that they are considerably more common than realized at present; (ii) with only a few exceptions [43,160,162,166,168], nanocluster catalysts used for arene hydrogenation are poorly characterized; (iii) Rh and Ru are used almost exclusively as the active metals; (iv) it would be of interest, however, to study in more detail nanoclusters composed of Pd [173,177], Pt [25,178], Ni [179,180] as well as bimetallics [181,182] for arene hydrogenation; (v) soluble nanocluster catalysts for arene hydrogenation have modest activity and lifetime, with current records being an activity of 54 mol product/(mol metal·h) [166] and a lifetime of 2600 TTO [168]. Other major findings are: (vi) two catalyst systems, one developed by Roucoux and co-workers and one developed in our group, stand out from the rest in terms of activity and lifetime (the values cited just above); (vii) much attention has been given to selective arene hydrogenation, especially for the synthesis of the all-*cis* diastereomer of substituted cyclohexanes, where selectivities of >90% are often observed [13,14,28,45,158,163–166], so that the application of nanocluster catalysts to produce all-*cis* substituted cyclohexanes is a promising

---

[14] Of course, it is possible that other researchers using soluble nanocluster catalysts for arene hydrogenation simply missed the alkene intermediate because of low yields or the eventual complete hydrogenation to alkane. However, some researchers specifically mention that no partial hydrogenation intermediates are observed [163,166]. For example, Roucoux and co-workers state, "Unfortunately, we did not observe any cyclohexene or cyclohexadiene derivatives as intermediates which ideally would have been desirable" [166]. Additionally, many of the reports in this area include careful product studies and most of the reports mention GLC as a means of product quantitation. Therefore, it seems likely that, among known soluble nanocluster catalysts, the polyoxoanion- and tetrabutylammonium-stabilized Rh(0) nanoclusters display a unique selectivity for the partial hydrogenation of arenes. The reason for this unique selectivity is not completely clear, but the available evidence suggests that the polyoxoanion stabilizer is involved [168]. In this regard, a recent report describes the use of a $Pd(0)_n/C$ catalyst, prepared from the precursor $K_5PPd(H_2O)W_{11}O_{39}\cdot12H_2O$, for the selective hydrogenation of arenes in the presence of distal ketone moieties; the $PW_{11}O_{39}{}^{7-}$ polyoxoanion is implicated as the key to the selectivity in that case as well [176]. *These examples again point to a relatively unexplored area of ligand-modified nanoclusters as higher-selectivity*, *metal-particle catalysts* [85].

area of future research and, perhaps, fine chemical synthesis.

Reasonable lifetime, activity and good selectivity have all been demonstrated for the hydrogenation of monocyclic arenes, so that the following additional studies of soluble nanocluster catalysts, leading to further improvements in arene hydrogenation, are warranted:

- Further examination of the many claimed "homogeneous" arene hydrogenation catalysts is of interest, since it is likely that many of these catalysts are soluble nanoclusters.
- *Development of nanoclusters that will withstand more forcing conditions (e.g., higher temperatures and pressures) is a key goal, one important not only to arene hydrogenation, but also to nanocluster catalysis in general.*
- Synthesis of the all-*cis* diastereomer of substituted cyclohexanes is probably the most promising practical application for nanocluster catalysts that has been demonstrated to date, an area that warrants further study as noted above.
- Nanocluster catalysis of enantioselective hydrogenations of substituted arenes is an interesting, but largely unexplored, area.
- The study of partial arene hydrogenation with nanocluster catalysts is an intriguing line of future inquiry.
- The hydrogenation of aromatic polymers with nanocluster catalysts is little studied, yet deserves a careful investigation with one or two prototype systems and in comparison to supported catalysts of the same metal(s).
- More information is needed regarding the repeatability of nanocluster catalyzed arene hydrogenations when the exact same system is used in different laboratories; the examination of supported heterogeneous catalysts of the same metal should also be part of these studies.
- Studies of the kinetics and mechanism of nanocluster arene hydrogenation reactions by powerful solution-phase spectroscopic techniques and homogeneous kinetic studies are needed and should provide insights to help optimize these reactions.
- The use of polyoxoanion and other ligands to change and improve the selectivity of nanoclus-

ter catalysts [85,168,176] is quite promising and, therefore, deserves further study.
- Methods to immobilize soluble arene hydrogenation catalysts hold promise [121–126], e.g., taking advantage of two-phase, aqueous/organic or organic/ionic liquid [127] (see footnote 9) systems in synthetically driven studies.
- The direct comparison of the arene hydrogenation selectivity of soluble nanocluster catalysts to their same metal heterogeneous (supported) analogs under identical reaction conditions is rarely done [168], but is, of course, essential if one is to understand the strengths and weaknesses of nanocluster catalysts in comparison to their heterogeneous counterparts.
- The use of nanocluster catalysts in systems with confined spaces (such as inside mesoporous solids) is a conceivable application that takes advantage of the solubility and small size of the nanoclusters. In this regard, it would be especially interesting to make small, narrow size-distribution, clean surface nanoclusters for placement within ultra-wide-pore silica, and test them as polystyrene hydrogenation catalysts [25].

In short, nanocluster arene hydrogenation research is an area still wide open for additional, creative developments and practical applications.

Acknowledgements

References

[1] P. Sabatier, Ind. Eng. Chem. 18 (1926) 1004.
[2] P. Sabatier, J.-B. Senderens, C.R. Hebd, Sciences Acad. Sci. 132 (1901) 210.
[3] S.-C. Hu, Y.-W. Chen, J. Chin. Inst. Chem. Eng. 29 (1998) 387.
[4] I.P. Rothwell, Chem. Commun. (1997) 1331.
[5] W.D. Harman, Chem. Rev. 97 (1997) 1953.
[6] A. Stanislaus, B.H. Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75.
[7] M. Bennett, Chemtech 10 (1980) 444.
[8] E.L. Muetterties, J.R. Bleeke, Acc. Chem. Res. 12 (1979) 324.

[9] P.M. Maitlis, Acc. Chem. Res. 11 (1978) 301.

[10] R.B. Moyes, P.B. Wells, Adv. Catal. 23 (1973) 121.

[11] J.L. Garnett, Catal. Rev. 5 (1971) 229.

[12] R.-W. Albach, M. Jautelat, Two-phase hydrogenation method and colloidal catalysts for the preparation of cyclohexanes from benzenes, Bayer, A.G. (Ed.), German Patent, DE 19 807 995 (1999).

[13] F. Fache, S. Lehuede, M. Lemaire, Tetrahedron Lett. 36 (1995) 885.

[14] K. Nasar, F. Fache, M. Lemaire, J.C. Beziat, M. Besson, P. Gallezot, J. Mol. Catal. 87 (1994) 107.

[15] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1979.

[16] K. Weissermel, H.-J. Arpe, Industrial Organic Chemistry, VCH, New York, 1993.

[17] G.W. Parshall, S.D. Ittel, The applications and chemistry of catalysis by soluble transition metal complexes, in: Homogeneous Catalysis, 2nd Edition, Wiley, New York, 1992.

[18] J. Struijk, R. Moene, T. Van der Kamp, J.J.F. Scholten, Appl. Catal. A 89 (1992) 77.

[19] J. Struijk, M. D'Angremond, W.J.M. Lucas-De Regt, J.J.F. Scholten, Appl. Catal. A 83 (1992) 263.

[20] H. Arnold, F. Döbert, J. Gaube, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 5, VCH, Weinheim, 1997, pp. 2181–2182.

[21] A more efficient route for making cyclohexanol, Chem. Eng. 97 (1990) 25.

[22] T. Enya, H. Suzuki, T. Watanabe, Y. Hirayama, Y. Hisamatsu, Environ. Sci. Technol. 31 (1997) 2772.

[23] A.M. Casillas, T. Hiura, N. Li, A.E. Nel, Ann. Allergy Asthma Immunol. 83 (1999) 624.

[24] A.E. Nel, D. Diaz-Sanchez, D. Ng, T. Hiura, A. Saxon, J. Allergy Clin. Immunol. 102 (1998) 539.

[25] D.A. Hucul, S.F. Hahn, Adv. Mater. 12 (2000) 1855.

[26] A. Tullo, New DVDs Provide Opportunities for Polymers, Chemical and Engineering News 77 (1999) 14.

[27] T.Q. Hu, B.R. James, C.-L. Lee, J. Pulp Pap. Sci. 23 (1997) J200.

[28] T.Q. Hu, B.R. James, C.-L. Lee, J. Pulp Pap. Sci. 23 (1997) J153.

[29] T.Q. Hu, B.R. James, Y. Wang, J. Pulp Pap. Sci. 25 (1999) 312.

[30] T.Q. Hu, B.R. James, J. Pulp Pap. Sci. 26 (2000) 173.

[31] J. March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 4th Edition, Wiley–Interscience, New York, 1992, p. 780.

[32] D.E. Linn Jr., J. Halpern, J. Am. Chem. Soc. 109 (1987) 2969.

[33] C.R. Landis, J. Halpern, Organometallics 2 (1983) 840.

[34] R. Wilczynski, W.A. Fordyce, J. Halpern, J. Am. Chem. Soc. 105 (1983) 2066.

[35] R.J. Fessenden, J.S. Fessenden, Organic Chemistry, 5th Edition, Brooks/Cole Publishing Company, Pacific Grove, 1993 (Chapter 11).

[36] R.L. Augustine, Heterogeneous Catalysis for the Synthetic Chemist, Marcel Dekker, New York, 1996 (Chapter 17).

[37] H. Greenfield, Ann. NY Acad. Sci. 214 (1973) 233.

[38] A.N. Startsev, G.I. Aleshina, D.G. Aksenov, V.N. Rodin, Kinet. Catal. 39 (1998) 363.

[39] A.N. Startsev, I.I. Zakharov, V.N. Rodin, G.I. Aleshina, D.G. Aksenov, Kinet. Catal. 39 (1998) 507.

[40] A.N. Startsev, V.N. Rodin, G.I. Aleshina, D.G. Aksenov, Kinet. Catal. 39 (1998) 221.

[41] B.C. Gates, Catalytic Chemistry, Wiley, New York, 1992 (Chapter 6).

[42] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Book, Mill Valley, 1987 (Chapter 10).

[43] K.S. Weddle, J.D. Aiken III, R.G. Finke, J. Am. Chem. Soc. 120 (1998) 5653.

[44] J.P. Collman, K.M. Kosydar, M. Bressan, W. Lamanna, T. Garrett, J. Am. Chem. Soc. 106 (1984) 2569.

[45] B.R. James, Y. Wang, C.S. Alexander, T.Q. Hu, Chem. Ind. 75 (1998) 233.

[46] R.G. Finke, in: D.L. Feldheim, C.A. Foss Jr. (Eds.), Metal Nanoparticles: Synthesis, Characterization, and Applications, Marcel Dekker, New York, 2001 (Chapter 2).

[47] R.J. Puddephatt, Met. Clusters Chem. 2 (1999) 605.

[48] J.D. Aiken III, R.G. Finke, J. Mol. Catal. A 145 (1999) 1.

[49] J.D. Aiken III, Y. Lin, R.G. Finke, J. Mol. Catal. A 114 (1996) 29.

[50] G. Schmid, M. Baumle, M. Geerkens, I. Heim, C. Osemann, T. Sawitowski, Chem. Soc. Rev. 28 (1999) 179.

[51] M.N. Vargaftik, N.Y. Kozitsyna, N.V. Cherkashina, R.I. Rudyi, D.I. Kochubei, B.N. Novgorodov, I.I. Moiseev, Kinet. Catal. 39 (1998) 740.

[52] N. Herron, D.L. Thorn, Adv. Mater. 10 (1998) 1173.

[53] J.S. Bradley, Schr. Forschungszent. Juelich Mater. Mater. 1 (1998) D6.1.

[54] H. Bönnemann, W. Brijoux, A.S. Tilling, K. Siepen, Top. Catal. 4 (1998) 217.

[55] H. Bönnemann, W. Brijoux, Adv. Catal. Nanostruct. Mater. (1996) 165.

[56] H. Bönnemann, G. Braun, G.B. Brijoux, R. Brinkman, A.S. Tilling, K. Seevogel, K. Siepen, J. Organomet. Chem. 520 (1996) 143.

[57] G. Schmid, V. Maihack, F. Lantermann, S. Peschel, J. Chem. Soc., Dalton Trans. (1996) 589.

[58] J.S. Bradley, in: G. Schmid (Ed.), Clusters and Colloids: From Theory to Applications, VCH, New York, 1994, pp. 459–544.

[59] L.N. Lewis, Chem. Rev. 93 (1993) 2693.

[60] G. Schmid, Chem. Rev. 92 (1992) 1709.

[61] G. Schmid, Endeavour 14 (1990) 172.

[62] R. Pool, Clusters: strange morsels of matter, Science 248 (1990) 1186.

[63] I. Willner, D. Mandler, J. Am. Chem. Soc. 111 (1989) 1330.

[64] K.S. Suslick, G.J. Price, Ann. Rev. Mater. Sci. 29 (1999) 295.

[65] T. Fujimoto, Y. Mizukoshi, Y. Nagata, Y. Maeda, R. Oshima, Scr. Mater. 44 (2001) 2183.

[66] E. Tagaki, Y. Mizukoshi, R. Oshima, Y. Nagata, H. Bandow, Y. Maeda, Stud. Surf. Sci. Catal. 132 (2001) 335.

[67] Y. Mizukoshi, E. Takagi, H. Okuno, R. Oshima, Y. Maeda, Y. Nagata, Ultrason. Sonochem. 8 (2001) 1.

[68] R.A. Caruso, M. Ashokkumar, F. Grieser, Colloids Surf. A 169 (2000) 219.

[69] T. Fujimoto, S. Terauchi, H. Umehara, I. Kojima, W. Henderson, Chem. Mater. 13 (2001) 1057.

[70] J.P. Wilcoxon, J.E. Martin, P. Provencio, Langmuir 16 (2000) 9912.

[71] J.P. Wilcoxon, G.A. Samara, P.N. Provencio, Phys. Rev. B 60 (1999) 2704.

[72] J.G.C. Veinot, J. Galloro, L. Pugliese, R. Pestrin, W.J. Pietro, Chem. Mater. 11 (1999) 642.

[73] J.P. Wilcoxon, S.A. Craft, Nanostruct. Mater. 9 (1997) 85.

[74] T. Siebrands, M. Giersig, P. Mulvaney, C.H. Fischer, Langmuir 9 (1993) 2297.

[75] D.F. Shriver, P. Atkins, C.H. Langford, Inorganic Chemistry, 2nd Edition, Freeman, New York, 1994, p. 317.

[76] R.J. Hunter, Foundations of Colloid Science, Vol. 1, Oxford University Press, New York, 1986.

[77] C.S. Hirtzel, R. Rajagopalan, Colloidal Phenomena: Advanced Topics, Noyes Publications, Park Ridge, NJ, 1985.

[78] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiley, New York, 1980.

[79] S. Özkar, R.G. Finke, Nanocluster formation and stabilization fundamental studies: ranking commonly employed anionic stabilizers via the development, then application, of five comparative criteria, in press.

[80] H. Liu, N. Toshima, J. Chem. Soc., Chem. Commun. (1992) 1095.

[81] A.C. Templeton, W.P. Wuelfing, R.W. Murray, Acc. Chem. Res. 33 (2000) 27.

[82] D.I. Gittins, F. Caruso, Angew. Chem. Int. Ed. 40 (2001) 3001.

[83] D. de Caro, J.S. Bradley, New J. Chem. 22 (1998) 1267.

[84] R.G. Finke, unpublished observations.

[85] G. Schmid, V. Maihack, F. Lantermann, S. Peschel, J. Chem. Soc., Dalton Trans. (1996) 589.

[86] J.J. van der Klink, H.B. Brom, Prog. Nucl. Magn. Reson. Spectrosc. 36 (2000) 89.

[87] K. Kimura, Mesosc. Mater. Clusters (1999) 153.

[88] J.S. Bradley, J.M. Millar, E.W. Hill, J. Am. Chem. Soc. 113 (1991) 4016.

[89] G. Schmid, Struct. Bonding 62 (1985) 51.

[90] J.P. Yesinowski, J. Am. Chem. Soc. 103 (1981) 6266.

[91] D. de Caro, J.S. Bradley, Langmuir 14 (1998) 245.

[92] D. de Caro, J.S. Bradley, Langmuir 13 (1997) 3067.

[93] A. Rodriguez, C. Amiens, B. Chaudret, M.-J. Casanove, P. Lecante, J.S. Bradley, Chem. Mater. 8 (1996) 1978.

[94] J.S. Bradley, E.W. Hill, B. Chaudret, A. Duteil, Langmuir 11 (1995) 693.

[95] C. Amiens, D. de Caro, B. Chaudret, J.S. Bradley, R. Mazel, C. Roucau, J. Am. Chem. Soc. 115 (1993) 11638.

[96] J.S. Bradley, J.M. Millar, E.W. Hill, S. Behal, J. Catal. 129 (1991) 530.

[97] M.A. Watzky, R.G. Finke, J. Am. Chem. Soc. 119 (1997) 10382.

[98] B.C. Gates, Catalytic Chemistry, Wiley, New York, 1992, pp. 396–403.

[99] J.P. Wilcoxon, R.L. Williamson, R. Baughman, J. Chem. Phys. 98 (1993) 9933.

[100] M.T. Reetz, R. Breinbauer, P. Wedemann, P. Binger, Tetrahedron 54 (1998) 1233.

[101] M.T. Reetz, E. Westermann, Angew. Chem. Int. Ed. 39 (2000) 165.

[102] J. Le Bars, U. Specht, J.S. Bradley, D.G. Blackmond, Langmuir 15 (1999) 7621.

[103] S. Klingelhöfer, W. Heitz, A. Greiner, S. Oestreich, S. Förster, M. Antonietti, J. Am. Chem. Soc. 119 (1997) 10116.

[104] M.T. Reetz, G. Lohmer, Chem. Commun. (1996) 1921.

[105] M.T. Reetz, R. Breinbauer, K. Wanninger, Tetrahedron Lett. 37 (1996) 4499.

[106] M. Beller, H. Fischer, K. Kühlein, C.-P. Reisinger, W.A. Herrmann, J. Organomet. Chem. 520 (1996) 257.

[107] M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, R. Whyman, J. Chem. Soc., Chem. Commun. (1994) 801.

[108] A.C. Templeton, M.J. Hostetler, E.K. Warmoth, S. Chen, C.M. Hartshorn, V.J. Krishnamurthy, M.D.E. Forbes, R.W. Murray, J. Am. Chem. Soc. 120 (1998) 4845.

[109] A.C. Templeton, M.J. Hostetler, C.T. Kraft, R.W. Murray, J. Am. Chem. Soc. 120 (1998) 1906.

[110] M. Bartz, J. Küther, R. Seshadri, W. Tremel, Angew. Chem. Int. Ed. 37 (1998) 2466.

[111] H. Li, Y.-Y. Luk, M. Mrksich, Langmuir 15 (1999) 4957.

[112] Y. Wang, H. Liu, Y. Jiang, J. Chem. Soc., Chem. Commun. (1989) 1878.

[113] P. Mulvaney, L.M. Liz-Marzán, M. Giersig, T. Ung, J. Mater. Chem. 10 (2000) 1259.

[114] L.M. Liz-Marzán, P. Mulvaney, Recent Res. Dev. Phys. Chem. 2 (1998) 1.

[115] L.M. Liz-Marzán, P. Mulvaney, New J. Chem. 22 (1998) 1285.

[116] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, Langmuir 12 (1996) 4329.

[117] L.M. Liz-Marzán, M. Giersig, P. Mulvaney, Chem. Commun. (1996) 731.

[118] T. Ung, L.M. Liz-Marzán, P. Mulvaney, Langmuir 14 (1998) 3740.

[119] M. Giersig, L.M. Liz-Marzán, T. Ung, D. Su, P. Mulvaney, Ber. Bunsen-Ges. 101 (1997) 1617.

[120] M. Giersig, T. Ung, L.M. Liz-Marzán, P. Mulvaney, Adv. Mater. 9 (1997) 570.

[121] I.T. Horvath, Aqueous-phase Organomet. Catal. (1998) 548.

[122] I.T. Horvath, G. Kiss, R.A. Cook, J.E. Bond, P.A. Stevens, J. Rabai, E.J. Mozeleski, J. Am. Chem. Soc. 120 (1998) 3133.

[123] I.T. Horvath, J. Rabai, Science 266 (1994) 72.

[124] J.A. Gladysz, Science 266 (1994) 55.

[125] K.T. Wan, M.E. Davis, Nature 370 (1994) 449.

[126] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature 339 (1989) 454.

[127] P.J. Dyson, D.J. Ellis, D.G. Parker, T. Welton, Chem. Commun. (1999) 25.

[128] J. Dupont, G.S. Fonseca, A.P. Umpierre, P.F.P. Fichtner, S.R. Teixeira, J. Am. Chem. Soc. 124 (2002) 4228–4229.

[129] R.G. Finke, K.R. Seddon, experiments in progress.

[130] J.D. Aiken III, R.G. Finke, J. Am. Chem. Soc. 121 (1999) 8803.

[131] J.E. Hamlin, K. Hirai, A. Millan, P.M. Maitlis, J. Mol. Catal. 7 (1980) 543.

[132] G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.

[133] P. Foley, R. DiCosimo, G.M. Whitesides, J. Am. Chem. Soc. 102 (1980) 6713.

[134] D.R. Anton, R.H. Crabtree, Organometallics 2 (1983) 855.

[135] R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, J.M. Quirk, J. Am. Chem. Soc. 104 (1982) 107.

[136] R.H. Crabtree, J.M. Mihelcic, J.M. Quirk, J. Am. Chem. Soc. 101 (1979) 7738.

[137] J.P. Collman, K.M. Kosydar, M. Bressan, W. Lamanna, T. Garrett, J. Am. Chem. Soc. 106 (1984) 2569.

[138] L.N. Lewis, N. Lewis, J. Am. Chem. Soc. 108 (1986) 7228.

[139] L.N. Lewis, J. Am. Chem. Soc. 112 (1990) 5998.

[140] Y. Lin, R.G. Finke, Inorg. Chem. 33 (1994) 4891.

[141] Y. Lin, Ph.D. Dissertation, Department of Chemistry, University of Oregon, March 1994.

[142] J. Halpern, Inorg. Chim. Acta 50 (1981) 11.

[143] J. Halpern, T. Okamoto, A. Zakhariev, J. Mol. Catal. 2 (1977) 65.

[144] J. Blum, I. Amer, K.P.C. Vollhardt, H. Schwarz, G. Hoehne, J. Org. Chem. 52 (1987) 2804.

[145] J. Blum, I. Amer, A. Zoran, Y. Sasson, Tetrahedron Lett. 24 (1983) 4139.

[146] P.M. Maitlis, Acc. Chem. Res. 11 (1978) 301.

[147] M.J. Russell, C. White, P.M. Maitlis, J. Chem. Soc., Chem. Commun. (1977) 427.

[148] M. Bennett, Chemtech 10 (1980) 444.

[149] M.A. Bennett, T.-N. Huang, T.W. Turney, J. Chem. Soc., Chem. Commun. (1979) 312.

[150] G.M. Whitesides, M. Hackett, R.L. Brainard, J.P.P.M. Lavalleye, A.F. Sowinski, A.N. Izumi, S.S. Moore, D.W. Brown, E.M. Staudt, Organometallics 4 (1985) 1819.

[151] J.P. Ennett, Ph.D. Dissertation, Department of Chemistry, Australian National University, 1984.

[152] M.A. Bennett, J.P. Ennett, Inorg. Chim. Acta 198–200 (1992) 583.

[153] D.A. Tocher, R.O. Gould, T.A. Stephenson, M.A. Bennett, J.P. Ennett, T.W. Matheson, L. Sawyer, V.K. Shah, J. Chem. Soc., Dalton Trans. (1983) 1571.

[154] J.A. Widegren, M.A. Bennett, R.G. Finke, experiments in progress.

[155] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485.

[156] I.W.C.E. Arends, R.A. Sheldon, Appl. Catal. A 212 (2001) 175.

[157] I.W. Davies, L. Matty, D.L. Hughes, P.J. Reider, J. Am. Chem. Soc. 123 (2001) 10139.

[158] K.R. Januszkiewicz, H. Alper, Organometallics 2 (1983) 1055.

[159] J. Foise, R. Kershaw, K. Dwight, A. Wold, Mater. Res. Bull. 20 (1985) 147.

[160] Z. Duan, M.J. Hampden-Smith, A.P. Sylwester, Chem. Mater. 4 (1992) 1146.

[161] P. Drognat Landré, M. Lemaire, D. Richard, P. Gallezot, J. Mol. Catal. 78 (1993) 257.

[162] P. Drognat Landré, D. Richard, M. Draye, P. Gallezot, M. Lemaire, J. Catal. 147 (1994) 214.

[163] B.R. James, Y. Wang, T.Q. Hu, Chem. Ind. 68 (1996) 423.

[164] T.Q. Hu, B.R. James, S.J. Rettig, C.-L. Lee, Can. J. Chem. 75 (1997) 1234.

[165] J. Schulz, A. Roucoux, H. Patin, Chem. Commun. (1999) 535.

[166] J. Schulz, A. Roucoux, H. Patin, Chem. Eur. J. 6 (2000) 618.

[167] R.J. Bonilla, P.G. Jessop, B.R. James, Chem. Commun. (2000) 941.

[168] J.A. Widegren, R.G. Finke, Inorg. Chem. 41 (2002) 1558–1572.

[169] K.R. Januszkiewicz, H. Alper, Can. J. Chem. 62 (1984) 1031.

[170] G.C. Bond, Catalysis by Metals, Academic Press, New York, 1962.

[171] J.D. Aiken III, R.G. Finke, Chem. Mater. 11 (1999) 1035.

[172] J.A. Widegren, R.G. Finke, unpublished experiments.

[173] H. Yang, H. Gao, R.J. Angelici, Organometallics 19 (2000) 622.

[174] H. Ahn, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 13533.

[175] M. Bartók, Stereochemistry of Heterogeneous Metal Catalysis, Wiley, New York, 1985.

[176] V. Kogan, Z. Aizenshtat, R. Neumann, New J. Chem. 26 (2002) 272.

[177] U.K. Singh, M.A. Vannice, AIChE J. 45 (1999) 1059.

[178] J. Wang, Q. Li, J. Yao, Appl. Catal. A 184 (1999) 181.

[179] D. Franquin, S. Monteverdi, S. Molina, M.M. Bettahar, Y. Fort, J. Mater. Sci. 34 (1999) 4481.

[180] R. Molina, G. Poncelet, J. Catal. 199 (2001) 162.

[181] R. Raja, S. Hermans, D.S. Shephard, B.F.G. Johnson, G. Sankar, S. Bromley, J.M. Thomas, Chem. Commun. (1999) 1571.

[182] R. Raja, G. Sankar, S. Hermans, D.S. Shephard, S. Bromley, J.M. Thomas, B.F.G. Johnson, T. Maschmeyer, Chem. Commun. (1999) 2131.